Universitat de Girona

SELENIUM CYCLING IN VOLCANIC ENVIRONMENTS: THE ROLE OF SOILS AS REACTIVE INTERFACES

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Doctoral Thesis

Selenium cycling in volcanic environments: the role of soils as reactive interfaces

Geerke Henriette Floor

2011

Universitat de Girona

University of Girona
Department of Chemistry

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Doctoral thesis

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2011

Environmental Analytical Chemistry

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In candicy for the degree of doctor in Chemistry at the University of Girona

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CERTIFIQUEM:

Que aquest treball, titulat ***“Selenium cycling in volcanic environments: the role of soils as reactive interfaces”***, que presenta **Geerke Henriette Floor** per a l´obtenció del titol de doctora, han estat realitzat sota la nostra direcció i que compleix els requiriments per poder optar a Menció Europea.

I perquè així consti, signem la present certificació.

Dra. Gabriela Román-Ross Dr. Romain Millot

Amb el vist-i-plau de la tutora:

Dra. Mònica Iglesias

Girona, 9 de febrer del 2011

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Summary

Selenium (Se) is an element with important health implications that is emitted in significant amounts from volcanoes. Attracted by the fertility of volcanic soils, around 10% of the world population lives within 100 km of an active volcano. Volcanic activity causes strong pH and Eh gradients in time and space, which are parameters that determine Se mobility. Nevertheless, the behaviour of Se in volcanic environments is poorly understood. Therefore, the main aim of this thesis is to investigate the role of soils in the Se cycling in volcanic environments. This is pursued by a combination of field studies and lab controlled experiments with soils from two contrasting European volcanic settings: Mount Etna in Sicily (Italy) and Mount Teide in Tenerife (Spain).

Prior to my geochemical studies, the development of precise and accurate methods for Se quantification in volcanic soils was required. Selenium measurements in geological materials are challenging due to the low Se concentrations within complex matrices. For determinations of total Se in soils two protocols were developed in the present work. On one hand, total concentrations measurements were performed with inductively coupled plasma – mass spectrometry (ICP-MS) after a micro-wave assisted digestion. Monitoring $^{82}Se^+$ without the use of a collision-reaction cell significantly overestimated the Se content due to spectral overlaps of HBr^+ and ZnO^+. Good results (Se=1.31±0.20 mg/kg) were obtained with $^{78}Se^+$ using a hydrogen-pressurized octupole reaction cell (ORS) for the JSAC-0411 volcanic ash soil certified reference material (Se=1.32±0.27 mg/kg) with procedural blanks <0.03 mg/kg. The addition of methanol (2%) is recommended, since counting statistics were improved, but some soil digests without methanol addition should be measured as a quality control to check that interferences are properly resolved. On the other hand, the analytical possibilities of Total Reflection X-ray Fluorescence (TXRF) were also explored for Se determinations. Direct TXRF analyses are fast, simple and need low sample amounts (20 mg or 10 µl). However, the limit of Se detection (LOD) obtained depends significantly on the matrix due to increased background and automatic reduction of the excitation current of the X-ray tube when high contents of matrix elements (e.g. Fe, Zn) are present. Therefore, direct analyses of samples with a complex matrix lack adequate Se LOD for low-level environmental samples. Nevertheless, using a dispersive liquid-liquid micro-extraction (DDLME) with ammonium pyrrolidinedithiocarbamate (APDC) as a complexing agent, a suitable LOD (0.7 µg/L and 0.05 mg/kg for acid leachates and soil samples respectively) and accurate results were obtained for natural samples.

Speciation plays a key role in Se mobility. However, speciation analyses in acid samples can be hampered by the precipitation of Al and Fe compounds, which can cause Se adsorption and redox transformtions. Since APDC only complexes with selenite, the comparison of results with and without a prereduction step prior to the DDLME procedure can be used to quantify inorganic Se species at low pH. Moreover, a new protocol specific for the determination of Se speciation in acidic samples by High Performance Liquid Chromatography (HPLC) coupled to an ICP-MS was developed. A mobile phase containing 20 mM ammonium citrate and 2% methanol at pH=3, allowed selenite and selenate separation within 10 minutes with a LOD of 0.1 µg/L using ORS pressurized with H_2 and $^{78}Se^+$ for detection. Selenium isotopic signatures can be used as source tracers or to monitor processes that cause redox transformtions. In this

thesis, two new approaches were evaluated for Se isotopic measurements by multi-collector ICP-MS: ´pseudo-high´ mass resolution and a methane-mixed plasma. The´pseudo-high´ mass resolution could not resolve the argon polyatomic ions from Se isotopes and is therefore not suitable for Se isotopic measurements. However, the addition of a small amount of methane appears to be beneficial for Se isotope ratio measurements. Since the Se sensitivity increased and the interference signals decreased, the precision was improved three times.

Using the new developed analytical techniques, the mobility of Se could be studied in two contrasting field sites in order to determine the controlling processes in different volcanic settings. At Mount Etna the volcanic activity causes chemical gradients in time and space. At Teide volcano there is a strong gradient in climatic conditions due to altitude differences and trade winds. Previous work at Etna volcano showed Se enrichment in volcanic gases, rainwater and groundwaters in the area. Nevertheless, this is the first study focussing on the Se content and its mobility in the soils. Acid rain-soil interaction experiments were performed under controlled conditions with soils collected at the flanks of the volcano and synthetic rainwater. The results showed that exposure to the volcanic plume did not correlate with Se release during soil-rain interaction. Selenium leaching towards the aquifer is expected to occur during increased volcanic activity at sites close to the craters for three reasons. First, the interaction with the volcanic plume results in rain enriched in sulphate close to the craters. In contact with the soil sulphate desorbs selenate due to its chemical competition for adsorption sites. Second, the soils in these sites have a high amorphous Al content and low contents of soil organic matter (SOM), related to the regular input of fresh ash. These characteristics allow the mobilization of high levels of Se during acid events. Third, the dominance of selenate in the leaching solutions will prevent re-adsorption and promote transport towards the groundwater. Further away from the craters only a small amount of Se will be released, because soil properties prevent significant leaching and the rainwater is not as strongly influenced by the volcanic plume.

At Mount Teide previous works showed the strong influence of climate and corresponding weathering regimes on the soil characteristics. However, the effect of weathering on Se distribution has not been evaluated previously. In this study elemental composition, soil parameters and Li-Sr isotopic signatures have been obtained for soils collected along a NE-SW transect in Tenerife Island. A range of factors, such as variations in parental rock elemental concentrations, weathering and the input of Saharan dust and/or marine aerosols, were identified as affecting soil compositions. Nevertheless, there was no clear evidence that these factors play a key role in the Se content or mobility. Two extreme Se distributions were recognized. At the top of Mount Teide, with low precipitation and a low weathering regime, soils have a low Se content with relatively high mobility. In contrast soils collected in high weathering regimes were characterized by high Se contents, but low mobility. These differences could be explained by variations in SOM and amorphous Fe compound contents. Both field studies (Mount Etna and Mount Teide) showed that sorption processes control the Se mobility and soil content. Therefore, soil mineralogy, which changes during its development, plays a major role in the Se behaviour in volcanic soils.

Resumen

El selenio (Se) es un elemento con importantes implicaciones en salud pública que es emitido por los volcanes en cantidades significativas. Atraída por la fertilidad de los suelos volcánicos, un 10% de la población mundial vive a menos de 100 km de volcanes activos. La actividad volcánica produce fuertes gradientes tanto en las condiciones de pH como de Eh en tiempo y espacio, y estos parámetros determinan la movilidad del Se. Sin embargo, el comportamiento geoquímico del Se en ambientes volcánicos es aún poco conocido. El objetivo de esta tesis doctoral es contribuir al estudio del ciclo del selenio (Se) en medios volcánicos. Con este fin se estudiaron suelos volcánicos provenientes de dos sitios europeos con características muy distintas: el Monte Etna en Sicilia (Italia) y el volcán Teide en Tenerife (España) combinando estudios de terreno y de laboratorio bajo condiciones controladas.

Previo a la realización de los estudios geoquímicos que se presentan en esta tesis, se desarrollaron algunos métodos analíticos para la cuantificación de Se. Las medidas de Se en muestras geológicas son muy dificultosas debido a las bajas concentraciones y a la complejidad de las matrices. En el caso específico de las determinaciones de concentraciones totales se desarrollaron dos protocolos. En primer lugar se analizaron concentraciones totales de Se en digestiones ácidas mediante espectrometría de masas con plasma acoplado por inducción (ICP-MS). Monitorizando el $^{82}Se^{+}$ sin el uso de una celda de colisión-reacción se sobreestima considerablemente el contenido de Se debido a las interferencias espectrales de HBr^{+} y ZnO^{+}. Los mejores resultados (Se=1,31 ± 0,20 mg/kg) para el material de referencia certificado JSAC-0411 (Se = 1,32 ± 0,27 mg/kg) correspondiente a un suelo volcánico se obtuvieron con $^{78}Se^{+}$ usando una sistema de reacción de octapole (ORS) presurizado con hidrógeno. Se recomienda el agregado de un 2% de metanol a las soluciones, ya que mejora las estadísticas de medida de la señal. Sin embargo, algunas alícuotas sin metanol deben ser medidas para evaluar si las interferencias han sido adecuadamente resueltas. Por otro lado, en este trabajo se exploraron también las posibilidades analíticas de la Fluorescencia de Rayos X por Reflexión Total (TXRF) para la determinación de Se. Los análisis directos con TXRF son rápidos, sencillos y requieren poca muestra (20 mg o 10 µl). Los resultados muestran que el límite de detección (LOD) depende significativamente de la matriz ya que el fondo se incrementa notablemente y y se produce una disminución automática de la corriente de excitación del tubo de rayos X cuando se encuentran presentes elementos (como Fe, y Zn) en concentraciones altas. Por lo tanto, el análisis directo de soluciones con matrices complejas presenta a menudo problemas de LOD para la determinación de Se. No obstante, usando una micro-extracción dispersiva líquido-líquido (DDLME) con ammonio pyrrolidina ditiocarbamato amónico (APDC) como agente acomplejante, se obtuvieron un LOD adecuado (0.7 µg/L y 0.05 mg/kg para extracciones ácidas y muestras suelos respectivamente) y resultados exactos para las muestras naturales.

La especiación química controla la movilidad del Se. Sin embargo, las determinaciones de especiación en muestras ácidas pueden verse obstaculizadas por la precipitación de fases minerales de Al y Fe, lo que suele provocar la adsorción de Se y transformaciones. Dado que el APDC solo acompleja el ión selenito, la aplicación del método DDLME con y sin un paso previo de reducción de la solución de lixiviación puede ser usado para cuantificar las especies inorgánicas de Se sin necesidad de

modificar las condiciones de pH. Además, se desarrolló un nuevo protocolo para la determinación de la especiación de Se mediante cromatografia líquida de alta resolución (HPLC) acoplada a un ICP-MS para muestras ácidas. Una fase móvil citrato atómico 20 mM y 2% de metanol a pH =3 es capaz de separar la especie selenito del selenato en 10 minutos con un LOD de 0.1 µg/L usando ORS presurizada con hidrógeno y $^{78}Se^{+}$ para la detección. Las relaciones isotópicas de Se se puede usar como trazadoras de fuentes y también para monitorear procesos que involucran transformaciones redox en medios geológicos. En esta tesis se evaluaron dos nuevos métodos para la determinación de isótopos de Se usando un ICP-MS con colector múltiple: pseudo-alta resolución de masas y plasma mezclado con metano. Se observó que el uso de pseudo-alta resolución de masas no puede resolver los iones poliatómicos de árgon y, por lo tanto, no es adecuado para determinaciones de isótopos de selenio. Sin embargo, en el segundo caso, la adición de pequeñas cantidades de metano resultó beneficiosa para este tipo de medidas ya que incrementa la sensibilidad, las señales debidas a las interferencias disminuyen y la precisión mejora en un factor de tres.

Una vez completado el desarrollo analítico, se estudió la movilidad química del Se en dos sitios volcánicos de Europa con el objetivo de identificar los procesos determinantes en estos medios volcánicos. En el Monte Etna la actividad volcánica provoca fuertes gradientes químicos tanto temporal como espacialmente. En el volcán Teide la variación de la altitud y los vientos alisios provocan un fuerte gradiente climático y, por ende, un amplio rango de condiciones de meteorización. Trabajos previos realizados en el Monte Etna mostraron un enriquecimiento en Se en los gases volcánicos, en el agua de lluvia y en los acuíferos de la zona. Sin embargo, éste es el primer estudio que se centra en los contenidos de Se y su movilidad en los suelos alrededor de un volcán activo. Se realizaron experimentos en condiciones controladas de laboratorio simulando la interacción entre la lluvia ácida y los suelos con muestras tomadas en los flancos del volcán y usando agua de lluvia sintética. A partir de estos estudios se puede concluir que los aportes directos de la pluma volcánica no controlan la movilidad del Se durante la interacción suelo-lluvia. La lixiviación de selenio hacia los acuíferos se espera que tenga lugar durante los periodos de mayor actividad volcánica en sitios próximos a los cráteres por tres razones. En primer lugar la interacción de la lluvia con la pluma volcánica produce un agua de lluvia rica en sulfato. El sulfato, una vez en contacto con el suelo, desorbe el selenato por competición química por los mismos sitios de adsorción. En segundo lugar los suelos próximos a los cráteres tienen altos contenidos de Al amorfo y bajos contenidos en materia orgánica debido a los aportes regulares de cenizas frescas. Estas características permiten la movilización de altos contenidos de Se durante los eventos de lluvia ácida. En tercer lugar el predominio del ion selenato en las soluciones de los lixiviados evitaría fenómenos de re-adsorción y favorecería el transporte hacia los acuíferos. A mayor distancia del cráter solo pequeñas cantidades de selenio son movilizadas. Las características de los suelos impiden la lixiviación de Se y además, en estas zonas las lluvias no se encuentran tan fuertemente afectadas por la pluma volcánica.

Trabajos previos realizados en el volcán Teide mostraron una influencia de los fuertes gradientes climáticos y los correspondientes regímenes de meteorización sobre las características de los suelos. A pesar de esto, los efectos de la meteorización en la

distribución de Se no han sido previamente evaluados. En este estudio se combinaron datos de composición elemental, parámetros de los suelos y relaciones isotópicas de Li-Sr a lo largo de una transecta NE-SW en la isla de Tenerife. Se identificaron, como responsables de la composición de los suelos, una serie de factores que incluyen las variaciones en la composición de las rocas madre la meteorización y los aportes de polvo del Sahara y de aerosoles marinos. Sin embargo, no existe una clara evidencia de que estos factores tengan un rol mayor en el control de las concentraciones de Se y su movilización. Se reconocieron dos casos extremos en relación con las distribuciones de Se. En la cima del Monte Teide, con bajas precipitaciones y un bajo grado de meteorización, los suelos presentan bajos contenidos de Se con una relativamente alta movilidad. Por otro lado, los suelos colectados en zonas con un alto grado de meteorización se caracterizan por tener altas concentraciones de Se aunque con una baja movilidad química. Estas diferencias pueden explicarse por las variaciones en los contenidos de materia orgánica y compuestos de Fe amorfo. En ambos emplazamientos estudiados (Monte Etna y Monte Teide) se evidencia claramente que los procesos de adsorción controlan tanto los contenidos como la movilidad de Se en los suelos. Por lo tanto, la mineralogía de los suelos, que cambia durante el desarrollo de los estos, tiene un rol central en el control del comportamiento del Se en los suelos volcánicos.

Resum

El seleni (Se) és un element amb importants implicacions en salut pública que és emès pels volcans en quantitats significatives. Atreta per la fertilitat dels sòls volcànics, un 10% de la població mundial viu a menys de 100 km de volcans actius. L'activitat volcànica fa que existeixin forts gradients en las condicions tant de pH como d'Eh en el temps i l'espai, i aquests paràmetres determinen la mobilitat del Se. No obstant, el comportament geoquímic d'aquest element en ambients volcànics és encara poc conegut. L'objectiu d'aquesta tesi doctoral és contribuir a investigar el paper del sòl en el cicle del seleni (Se) en ambients volcànics. Amb aquesta finalitat es varen estudiar sòls provinents de dos emplaçaments europeus amb característiques diferenciades: el Mont Etna a Sicília (Itàlia) i el volcà Teide a Tenerife (Espanya), combinant estudis sobre el terreny i de laboratori sota condicions controlades.

Prèviament a la realització dels estudis geoquímics que es presenten en aquesta tesi, va ser necessari desenvolupar mètodes analítics exactes i precisos per a la quantificació de Se en sòls volcànics. Cal dir, que les mesures de Se en mostres geològiques són molt dificultoses degut a les baixes concentracions i a la complexitat de les matrius. En el cas específic de les determinacions de Se total en sòls, es varen desenvolupar dos protocols. Per una banda, les mesures de concentració total es varen dur a terme mitjançant espectrometria de masses amb font de plasma induït per alta freqüència (ICP-MS) després d'una digestió assistida per microones. Es va observar que amb la monitorització de $^{82}Se^+$, sense pressurització de la cel·la de col·lisió-reacció, es sobreestima considerablement el contingut de seleni degut a les interferències espectrals produïdes per HBr^+ i ZnO^+. En canvi, es varen obtenir bons resultats (Se=1,31±0,20 mg/Kg) utilitzant $^{78}Se^+$ amb un sistema de reacció d'octapol (ORS) pressuritzat amb hidrogen pel material de referència certificat JSAC-0411 (Se=1,32±0,27 mg/Kg) consistent en un sòl volcànic. A més, es recomana l'addició d'un 2% de metanol a les solucions, ja que millora les estadístiques en la mesura del senyal. Tot i així, algunes alíquotes sense metanol han ser mesurades per avaluar si les interferències han estat adequadament resoltes. Per altra banda, en aquets treball també es varen explorar les possibilitats analítiques de la Fluorescència de Raig X per Reflexió Total (TXRF) per a la determinació de Se. Les anàlisis directes amb TXRF són ràpides, senzilles i requereixen poca mostra (20 mg o 10 µl). Tot i això, els límits de detecció (LOD) obtinguts depenen significativament de la matriu, degut a que es produeix un augment del fons i una disminució automàtica de la corrent d'excitació del tub de raig X, per la presència d'elements, com el Fe i el Zn, a concentracions elevades. Així doncs, l'ús d'aquesta tècnica per a l'anàlisi directa de mostres de matriu complexa es veu limitada pels LOD, sobre tot per a la determinació de Se en mostres ambientals. No obstant, la utilització d'una micro-extracció líquid-líquid dispersiva (DDLME) amb pyrrolidinditiocarbamat amònic (APDC) com agent complexant, va donar uns LODs adequats (0,7 µg/L i 0,05 mg/kg per a extraccions àcides i mostres de sòls respectivament) i una bona exactitud per a mostres d'origen ambiental.

L'especiació química juga un paper fonamental en la mobilitat del Se. Tot i això, l'especiació de seleni en mostres àcides pot veure's obstaculitzada per la precipitació de fases minerals d'Al i Fe, la qual cosa pot donar lloc l'adsorció de Se i transformacions redox. Donat que l'APDC només complexa l'ió selenit, l'aplicació del mètode DDLME, amb i sense un pas previ de reducció de la solució de lixiviació, pot ser utilitzat per a quantificar les espècies inorgàniques de Se a pH baix. A més, es va desenvolupar un nou protocol per a la determinació de l'especiació de Se mitjançant cromatografia líquida d'alta resolució (HPLC) acoblat a un ICP-MS per a mostres àcides. Una fase mòbil 20 mM de citrat amònic al 2% de metanol a pH =3, és capaç de separar el selenit del selenat en 10 minuts amb un LOD de 0,1 µg/L utilitzant ORS pressuritzat amb hidrogen i mesurant $^{78}Se^{+}$. Les relacions isotòpiques de seleni es poden utilitzar com a traçadores de fonts o pel monitoratge de processos que involucren transformacions redox. En aquesta tesi s'han avaluat dos nous mètodes per a la determinació d'isòtops de Se utilitzant un ICP-MS amb detector multi-col·lector, un mitjançant pseudo-alta resolució de masses i un segon utilitzant un plasma amb addició de metà. En el primer cas, l'us de la pseudo-alta resolució de masses no pot resoldre els ions poliatòmics d'argó dels isòtops de seleni i per tant no és adequat per a la determinació d'aquests. Tot i això, en el segon cas, l' addició de petites quantitats de metà va resultar beneficiós per dur a terme aquestes determinacions, donat que incrementa la sensibilitat, els senyals deguts a les interferències disminueixen i la precisió millora en un factor de tres.

Després del desenvolupament analític, es va estudiar la mobilitat química del Se en dos emplaçaments volcànics a Europa, amb l'objectiu d'identificar els principals processos en entorns volcànics. En el Mont Etna, l'activitat volcànica provoca forts gradients químics, tant temporalment com espacial. En el volcà Teide, la variació de la altitud i els vents alisis provoquen un fort gradient climàtic. Treballs previs realitzats en el Mont Etna han mostrat un enriquiment en Se dels gasos volcànics, l'aigua de pluja i els aqüífers de la zona. Tot i això, aquest és el primer estudi centrat en el contingut de Se i la seva mobilitat en els sòls pròxims a un volcà actiu. Es varen dur a terme experiments, en condiciones controlades de laboratori, simulant la interacció del sòl amb la pluja àcida amb mostres preses als flancs del volcà i aigua de pluja sintètica. Els estudis mostren que l'exposició al núvol volcànic no es correlaciona amb l'alliberament de Se en la interacció sòl-pluja. La lixiviació de seleni cap als aqüífers es preveu que es produeixi durant els períodes de major activitat volcànica en llocs pròxims als cràters per tres raons. En primer lloc la interacció de la pluja amb el núvol volcànic produeix una pluja rica en sulfat, el qual, en contacte amb el sòl, desorbeix el selenat per competició amb els mateixos punts d'adsorció. En segon lloc els sòls pròxims als cràters tenen alts continguts d'Al amorf i baixos en matèria orgànica (SOM), degut a les aportacions regulars de cendres fresques. Aquestes característiques permeten la mobilització d'alts continguts de Se durant esdeveniments de pluja àcida. En tercer lloc, el predomini de l'ió selenat en les solucions dels lixiviats evita els fenòmens de readsorció i afavoreix el transport cap als aqüífers. En augmentar la distancia al cràter només petites quantitats de seleni són mobilitzades, donat que les característiques dels sòls eviten la seva lixiviació i l'aigua de pluja no està tan fortament afectada pel núvol volcànic.

Treballs previs realitzats en el volcà Teide, varen mostrar una forta influència del clima i dels règims de meteorització sobre les característiques del sòl. Tot i això, els efectes de la meteorització en la distribució de Se no han estat prèviament avaluats. En aquest estudi es varen obtenir dades de composició elemental, paràmetres dels sòls i relacions isotòpiques de Li-Sr per sòls recollits al llarg d'un transecte NE-SW a l'illa de Tenerife. Una sèrie de factors que inclouen les variacions en la composició elemental de les roques mare, la meteorització i les aportacions de pols del Sahara, així com de aerosols marins, es varen identificar com a responsables de la composició dels sòls. No obstant, no existeix una clara evidència de que aquests factors tinguin un paper rellevant en el contingut de Se i la seva mobilitat. Es varen reconèixer dos casos extrems en relació amb la distribució de Se. En el cim del Mont Teide, amb baixes precipitacions i un baix grau de meteorització, els sòls presenten baixos continguts de Se però amb una relativament alta mobilitat. Per contra, els sòls col·lectats en zones amb un alt grau de meteorització es caracteritzen per tenir alts continguts de Se però una baixa mobilitat. Aquestes diferencies poden explicar-se per les variacions en els continguts de matèria orgànica i compostos de Fe amorf. En els dos emplaçaments estudiats (Mont Etna i Mont Teide) s'evidencia clarament que els processos d'adsorció controlen tant el contingut como la mobilitat del Se en els sòls. Per tant, la mineralogia dels sòls, que canvia durant el desenvolupament dels mateixos, té un paper central en el control del comportament del Se en sòls volcànics.

Résumé

Le sélénium (Se) est un élément chimique qui peut avoir de graves conséquences sur la santé produit par les volcans. De plus, 10% de la population mondiale vit à moins de 100 km d'un volcan en activité, du fait de la fertilité de ce type de sols. Les activités volcaniques produisent de forts gradients de pH et d'Eh, à la fois dans le temps et l'espace, et ces paramètres exercent un contrôle direct sur la mobilité du sélénium dans les sols. Le comportement du Se dans les environnements volcaniques reste très peu connu à ce jour. C'est pourquoi l'objectif principal de cette thèse est d'étudier le comportement du sélénium dans les sols volcaniques, pour ce faire: nous avons étudié deux systèmes volcaniques aux propriétés et aux caractéristiques très différentes en Europe: le volcan Etna (Sicile, Italie) et le volcan Teide (Ténérife, Espagne), à la fois par une approche de terrain et des expériences en laboratoire.

Au préalable à ces études géochimiques, nous avons développé puis validé différentes méthodes justes et précises pour la mesure des concentrations en sélénium dans les sols volcaniques. En effet, la mesure des teneurs en sélénium dans les matériaux géologiques est un vrai challenge analytique du fait des faibles concentrations en Se dans ces matrices complexes. Pour la mesure du sélénium total dans les sols, deux protocoles analytiques ont été développés dans cette thèse. D'une part, les concentrations sont mesurées par spectrométrie de masse à source plasma (ICP-MS) après mise en solution de l'échantillon par micro-ondes. La mesure de l^{82}Se^{+} sans cellule de collision met en évidence une surestimation de la concentration du fait des interférences (HBr^{+} and ZnO^{+}) à cette masse. Par contre, des résultats justes précis sont obtenus en mesurant l'isotope 78 (^{78}Se^{+}) et en utilisant une cellule de collision sous pression d'hydrogène. Concernant le matériau de référence JSAC-0411 (sol de cendres volcaniques), la valeur que nous obtenons (Se=1.31±0.20 mg/kg) est en parfait accord avec la valeur certifiée (Se=1.32±0.27 mg/kg), de plus, le blanc associé à ce protocole analytique est très faible (<0.03 mg/kg). Nous avons également testé l'ajout de méthanol (2%) à la solution d'analyse et cela s'avère efficace, puisque cela a pour effet d'améliorer la statistique de mesure. Mais dans ce cas, des mesures sans ajout de méthanol doivent aussi être réalisées afin de vérifier que la résolution des interférences est correcte. D'autre part, les possibilités analytiques de la fluorescence X à réflexion totale (TXRF) ont aussi été évaluées pour la mesure des teneurs en sélénium total. Ces analyses sont rapides, simples et ne nécessitent que très peu d'échantillon (20 mg de solide ou 10 µL de liquide). Toutefois, les limites de détection avec cette technique sont très dépendantes de la matrice de l'échantillon à cause de l'augmentation du bruit de fond instrumental et de la réduction du courant d'excitation des rayons X du fait de la matrice en présence (p.e. les éléments Fe et Zn). Ainsi, les analyses directes de suspensions de sol ou de solutions liquides complexes à faibles teneurs en sélénium ne peuvent être réalisées avec cette technique du fait des limites de détection. Toutefois, en utilisant au préalable une micro-extraction liquide-liquide dispersif (DDLME) en présence de pyrrolidinedithiocarbamate d'ammonium (APDC) en tant qu'agent complexant, nous obtenons une meilleure limite de quantification et des résultats justes pour des échantillons naturels (respectivement 0.7 µg/L et 0.05 mg/kg pour les lessivats acides et les échantillons de sols).

La spéciation joue une rôle clef dans la mobilité du sélénium. Toutefois, les analyses de spéciation peuvent être perturbées dans des échantillons acides par la précipitation de composés d'aluminium et de fer qui peuvent provoquer l'adsorption du sélénium mais aussi des changements d'états rédox. La méthode de micro-extraction liquide-liquide (DDLME) à faible pH (avec ou sans étape de réduction) peut être utilisée pour la mesure de la spéciation inorganique du sélénium, dès lors que APDC permet de complexer uniquement l'espèce sélénite. De plus, un nouveau protocole a été développé concernant la mesure de spéciation du sélénium par chromatographie liquide (HPLC) couplée à une ICP-MS. Avec une élution en citrate d'ammonium (20 mM) et 2% de méthanol à pH=3, les espèces sélénite et sélénate peuvent être éluées séparément et mesurées en 10 minutes avec une limite de détection de 0.1 µg/L, en mesurant la masse 78 du sélénium ($^{78}Se^{+}$) et avec cellule de collision.

Les isotopes du sélénium peuvent être de bons traceurs de source et également un outil de choix pour caractériser les processus et réactions de changements d'états rédox. Dans le cadre de cette thèse, nous avons mis en œuvre deux nouvelles approches pour évaluer la mesure des isotopes du sélénium par Multi Collecteur ICP-MS : la technique de « pseudo haute résolution » et la méthode d'ajout de méthane. Nous avons pu montrer que l'approche de « pseudo haute résolution » ne permet pas de résoudre totalement les interférences polyatomiques d'argon pour les masses du sélénium lors de la mesure isotopique. Toutefois, l'ajout en faible quantité de méthane dans le plasma d'argon est bénéfique, en ce sens qu'il permet à la fois d'augmenter la sensibilité du sélénium mais aussi de réduire significativement les interférences, la précision de la mesure isotopique s'en trouve ainsi améliorée d'un facteur 3.

Suite à tous ces développements analytiques, nous nous sommes intéressés à l'étude du sélénium dans deux environnements volcaniques très différents dans le but de déterminer les processus de contrôle de cet élément dans les sols volcaniques. Pour le Mont Etna, l'activité volcanique provoque de très forts gradients chimiques autour du cratère à la fois dans l'espace et le temps. Pour le volcan Teide, il existe un fort contraste des conditions climatiques du fait des variations d'altitude et d'intensité des précipitations au niveau du volcan. Les études précédentes de l'Etna, ont montré que le sélénium était enrichi dans les gaz volcaniques, les eaux de pluies et les eaux souterraines. Quoiqu'il en soit, notre étude est la première de ce type à se focaliser plus précisément sur le sélénium et sa mobilité dans les sols d'un volcan en activité. Nous avons mené une série d'expériences en laboratoire reproduisant les interactions eau/sols entre une eau de pluie synthétique et des sols prélevés à différentes distances du cratère du volcan. Les résultats de ces expériences montrent que le flux et la dispersion d'éléments traces à partir du panache ne corrèle pas directement avec la mobilisation du sélénium lors des interactions eau de pluie/sol. Il est attendu que d'avantage de sélénium soit transféré vers l'aquifère lors des pics d'activité du volcan pour trois raisons principalement : tout d'abord, l'interaction de la pluie avec le panache volcanique produit une eau de pluie très riche en sulfates. Or, la présence abondante de sulfates entraine une désorption préférentielle du sélénium (sélénate) à cause de la compétition chimique entre ces deux éléments lors des processus d'adsorption. En deuxième lieu, les sols les plus proches du cratère présentent à la fois des fortes concentrations en aluminium amorphe et des faibles teneurs en matière organique (SOM), du fait de l'apport régulier de cendres fraiches. Ces caractéristiques ont pour effet une très forte mobilisation du sélénium lors des épisodes de pluies acides. Enfin, troisièmement, le fait que l'espèce sélénate prédomine dans les solutions lixiviées va réduire sa réadsorption et favoriser son transport vers les eaux souterraines. A plus grande distance du cratère, seulement une faible quantité de sélénium va être relargué, du fait des caractéristiques des sols et aussi parce que les eaux de pluies sont aussi moins influencées par la panache volcanique dans ces zones.

Concernant le volcan Teide, des études précédentes ont montré qu'il existait une fort effet du climat sur la distribution des sols et des conditions d'altération. Toutefois, ces effets concernant les régimes d'altération et la distribution du sélénium dans les sols n'ont pas été évalués pour les précédentes études. A partir d'un échantillonnage de sols le long d'un transect NE-SW, nous avons déterminé les compositions chimiques, les paramètres physico-chimiques ainsi que les compositions isotopiques du lithium et du strontium. Nos résultats montrent qu'il existe un certain nombre de facteurs et/ou paramètres qui contrôlent la composition chimique de ces sols: la variabilité chimique de la roche mère soumise à l'altération, le régime d'altération, et les apports externes tels que les particules atmosphériques en provenance du désert saharien ou des apports marins. Parmi ces paramètres de contrôle, aucun n'apparait être déterminant en ce qui concerne le contrôle des teneurs et la mobilité du sélénium dans ces sols. En réalité, nous avons pu mettre en évidence deux types différents de distribution du sélénium : au sommet du volcan Teide, du fait des faibles précipitations et du régime d'altération très superficiel, les sols présentent des teneurs basses en sélénium, mais en revanche la mobilité est importante. Au contraire, les sols qui sont soumis à une altération plus poussée possèdent de plus fortes teneurs en sélénium associées à une mobilité plus faible. Ces différences peuvent s'expliquer par des variations de teneurs en matière organique des sols et par la présence abondante de composés de Fer amorphe. En effet, à la fois les études de terrain et les expériences en laboratoire montrent que les processus d'adsorption constituent le facteur de contrôle principal de la teneur et de la mobilité du sélénium dans les sols. Ainsi, la minéralogie du sol, qui évolue du fait lors du développement du sol, est le paramètre principal de contrôle du comportement du sélénium dans les sols volcaniques.

Samenvatting

Seleen (Se) is een belangrijk element voor de gezondheid van de mens dat in aanzienlijke hoeveelheden door vulkanen wordt uitgestoten. De vruchtbaarheid van vulkanische bodems maakt dat 10% van de wereldbevolking minder dan 100 km van een actieve vulkaan woont. Vulkanische activiteit veroorzaakt grote verschillen in de zuurgraad en de reductiepotentiaal, die op hun beurt bepalend zijn voor hoe Se zich verplaatst. Toch is het gedrag van Se in vulkanische omgevingen nauwelijks bestudeerd. Daarom wordt in dit proefschrift de rol van bodems in de seleencyclus rond vulkanen beter onderzocht. De resultaten werden verkregen door een combinatie van veldonderzoek en laboratoriumexperimenten met bodems van twee sterk verschillende vulkanen: de Etna op Sicilië (Italië) en de Teide op Tenerife (Spanje).

Seleenmetingen in geologische materialen zijn uitdagend vanwege de lage concentraties binnen een complexe matrix. Daarom moesten er voorafgaand aan mijn geochemische studies nauwkeurige en accurate methoden worden ontworpen. Er werden twee protocollen ontwikkelt om de totale hoeveelheid Se in bodems te bepalen. Het eerste protocol betreft concentratiemetingen die werden uitgevoerd met inductief gekoppeld plasma massaspectrometrie (ICP-MS) na een magnetron-geassisteerde ontsluiting. Bij het gebruik van $^{82}Se^{+}$ zonder een reactie-botsingscel (ORS) werd het Se gehalte aanzienlijke overschat door de aanwezigheid van spectrale overlappingen (HBr^{+} en ZnO^{+}). Uitstekende resultaten Se=1,31±0,20 mg/kg) werden vekregen voor de JSAC-0411 vulkanische asbodem (gecertificeerde Se=1,32±0,27) met een ORS met waterstofdruk en $^{78}Se^{+}$. Bovendien was de blanco van deze analytische prodedure laag (<0.03 mg/kg). De toevoeging van methanol (2%) verbeterd de meetstatisitieken. Toch moeten er sommige ontsluitingen zonder methanol gemeten worden om de aanwezigheid van spectrale interferenties uit te sluiten. Ten tweede werden de analytische mogelijkheden van röntgenstraling-fluorescentie met totale relectie (TXRF) onderzocht. Directe TXRF analyses zijn snel, eenvoudig en geschikt voor kleine monsterhoeveelheden (20 mg of 10 µl). De verkregen Se detectiegrens (LOD) hangt echter sterk af van de matrix. Dit komt door een verhoogde spectrale achtergrond en een automatische vermindering van de excitatie-energie door de overvloedige aanwezigheid van andere elementen (bijv. Fe en Zn). Daarom hebben directe TXRF analyses geen adequate Se LOD voor natuurlijke monsters. Met behulp van een dispersieve vloeistof-vloeistof microextractie (DDLME) met ammoniumpyrolidinedithiocarbamaatoplossing (APDC) als complexvormende agens werden er wel geschikte LODs (0,7 ug/L voor een uitloogoplossing en 0,05 mg/kg voor een bodemmonster) en accurate resultaten verkregen.

Speciatie speelt een belangrijke rol in de mobilisatie van Se. Speciatiemetingen in zure monsters worden echter gehinderd door het neerslaan van aluminium- en ijzermineralen, die adsorptie en redoxtransformaties kunnen veroorzaken. Doordat APDC zich alleen met seleniet bindt kan de DLLME procedure (met en zonder reductiestap) worden gebruikt voor het bepalen van de anorganische seleenverbinding zonder dat een pH verhoging nodig is. Bovendien werd er speciaal voor zure monsters een nieuw protocol ontwikkelt met hoge prestatie vloeistofchromatografie (HPLC)-ICP-MS. Een mobiele fase met een pH van 3 die 20 mM ammoniumcitraat en 2% methanol bevat, kan seleniet en selenaat binnen 10 minuten scheiden. De LOD is 0,1 µg/L met gebruik van een ORS en $^{78}Se^{+}$ voor detectie.

Natuurlijke variaties van seleniumisotopen kunnen worden gebruikt om de oorsprong van Se te bepalen of om redoxtransformaties te monitoren. In dit proefschrift werden twee nieuwe benaderingen geëvalueerd voor Se isotopenmetingen met een multi-collector ICP-MS: 'pseudo-hoge' massaresolutie en methaanmenging in het plasma. De argon polyatomische ionen konden met ´pseudo-hoge´ massaresolutie niet van Se isotopen worden onderscheiden. Daarom is deze aanpak niet geschikt voor Se isotopenmetingen. De toevoeging van een kleine hoeveelheid methaan lijkt echter gunstig. Aangezien de Se gevoeligheid toeneemt en het signaal van de interferenties afneemt, kan de nauwkeurigheid drie maal worden verbeterd.

Met de nieuw ontwikkelde analytische methoden kon de mobiliteit van seleen onderzocht worden in twee sterk tegenstelde Europese vulkanische gebieden. Op de Etna veroorzaakt de vulkanische activiteit grote chemische gradienten in tijd en ruimte. Rond de Teide is er een groot onderscheid in de klimatologische omstandigheden. Eerder onderzoek rond de Etna liet al seleenverrijking zien in vulkanische gassen, regenwater en grondwater. In het huidige onderzoek staat voor het eerst het seleengedrag in bodems centraal. Experimenten die de interactie tussen zure regen en bodem simuleerde werden uitgevoerd in het laboratorium met bodems verzameld rond de vulkaan en synthetisch regenwater. De resultaten tonen aan dat er geen relatie is tussen de blootstelling aan de vulkanische pluim en het vrijkomen van Se tijdens de interactie. Seleenuitspoeling naar het grondwater zal naar verwachting dicht bij de kraters plaatsvinden tijdens verhoogde vulkanische activiteit om drie redenen. Ten eerste heeft de vulkanische pluim meer invloed vlakbij de vulkaan, wat resulteert in sulfaatrijke regen. Tijdens het contact met de bodem mobiliseert sulfaat selenaat door chemische concurentie voor adsorptieplekken. Ten tweede zijn de bodems dicht bij de kraters rijk aan amorfe aluminiummineralen en arm aan organisch materiaal (SOM) door de regelmatige toevoer van vulkanisch as. Deze bodemkarakteristieken veroorzaken hogere Se mobilisatie tijdens het contact met zure regen. Ten derde zal de overheersing van selenaat in de uitloogoplossingen het heradsorberen voorkomen en het transport naar het grondwater bevorderen. Op afstand van de kraters zal slechts een kleine hoeveelheid Se vrijkomen, doordat de bodemeigenschappen uitspoeling voorkomen en het regenwater minder door de vulkaan wordt beïnvloedt.

Uit eerder wetenschappelijk werk is gebleken dat klimaat een sterke invloed heeft op de bodems rond de Teide. Het effect van verwering op het seleengedrag is echter niet geëvalueerd. In deze studie zijn de chemische samenstelling, bodemeigenschappen en Li-Sr isotopische verdelingen verkregen voor bodems die verzameld zijn langs een NO-ZW transect over Tenerife. Veranderingen in de samenstelling van het moedergesteente, verwering en de toevoer van stof uit de Sahara en/of zeewaterdruppels beinvloedde de bodemsamenstelling. Toch was er geen duidelijk bewijs dat deze factoren het seleengedrag bepalen. Er werden twee extreme Se distributies gevonden. Op de bergtop, waar weinig neerslag en verwering plaatsvindt, hebben bodems een laag seleengehalte met relatief hoge mobiliteit. De bodems met hoge verwering worden juist gekenmerkt door een hoog seleengehalte, maar lage mobiliteit. Deze verschillen kunnen worden verklaard door varieties in de hoeveelheid SOM en amorfe ijzerverbingen.

Beide veldstudies tonen aan dat sorptieprocessen de Se mobiliteit en concentratie in bodems bepalen. Daarom speelt de bodemmineralogie, die verandert tijdens de bodemontwikkeling, een belangrijke rol in het gedrag van seleen in vulkanische bodems.

Introduction

1 Selenium and volcanic soils

Selenium (Se) is a biologically essential element with a very narrow concentration range between deficiency (< 40 µg/day) and toxic levels (>400 µg/day; Fordyce, 2005; Hartikainen, 2005). Selenium is needed for the proper functioning of the immune system, successful reproduction and thyroid-hormone metabolism (Rayman, 2000). However, high selenium concentrations are toxic and diseases characterised by dystrophic malformations, hair losses, blindness, ataxia, disorientation and respiratory distress have been associated to Se poisoning (Rosenfeld and Beath, 1964). Although the scientific community is clearly aware of the consequences of the distribution of this element, only a relative small amount of studies deals with the Se behaviour of in geochemical materials, including soils.

It is extremely important to understand the chemical status and fate of Se within soil systems because they are (1) a medium of plant growth (thereby the main supply for our food), (2) a regulator of water supply, (3) a recycler of nutrients, (4) a habitat for billions of micro-organisms, (5) an engineering medium and (6) an environmental interface between the lithosphere, atmosphere, hydrosphere and biosphere (Brady and Weil, 2002). Although Se contents in soils are strongly dependent on the geological parental material, sorption processes play a key role in Se mobility (Fordyce, 2000). In this light, volcanic soils are particularly interesting, since volcanoes emit significant quantities of Se. As a result, Se contents in volcanic soils can be high. However, in contradiction, Se mobility is often low (Byers et al., 1936, Fernández-Martínez and Charlet, 2009).

Volcanic soils are found in areas where significant depths of volcanic ejecta have been accumulated in recent geological times. Although they globally make up less than 1% of the earths surface, they are important and productive soils that support intensive agriculture, because they usually have a high natural fertility (Shoji et al 1993). For that reason around 10% of the global population lives in areas with volcanic soils (Small and Naumann, 2001). Therefore, an understanding of the geochemical controls on the Se distribution and mobility in volcanic soils is a key issue to the assessment of selenium-related health risks. Volcanic soils have very specific properties due to the rapid weathering of volcanic material and therefore the Se behaviour differs from other soils. However, at present Se behaviour in volcanic soils is poorly studied and there is a lack of the mechanistic understanding of the processes influencing Se mobility.

2 Objectives of this study

The principle goal of this study is to explore the mobility of selenium in volcanic soils. Key issues addressed are (a) how mobile is Se within volcanic soils from different European settings and (b) which processes affect Se mobility. However, since Se is analytically difficult to measure new analytical protocols are required to investigate these questions. Selenium determinations in soils and other geological materials are challenging due to the complex matrix and low Se content. Hence, an important part of this study is devoted to develop simple methods to accurately quantify trace level Se contents, as well as Se speciation and Se isotopic signatures in soils and soil solutions. These analytical methods have been applied to study (a) Se mobilization processes within active volcanic systems, in particular the interaction between soil and (acid) rain and (b) the influence of weathering on Se concentrations and mobility.

In summary, the aims of this study can be divided in two main objectives:

1) To develop analytical protocols for Se determinations in complex matrices
2) To improve the understanding of the processes affecting the mobility of Se in volcanic soils

3 Study areas

As discussed above worldwide only 1% of the soils are volcanic. Within Europe volcanic soils are widely scattered, but most of these areas are relatively small. Iceland represents by far the largest volcanic area, while the largest area on the continent is in France (Massif Central, Arnalds et al., 2007). For this study two contrasting European field sites have been selected:

1) *Etna volcano, Sicily Island, Italy.* Active volcanism causes strong gradients in redox and pH conditions, both in time and space. Volcanogenic pollution has been reported in this area (Aiuppa et al., 2000a; Aiuppa et al., 2003b; Bellomo et al., 2007; Calabrese, 2009), but the role of soils in the trace element cycling has been barely studied before.
2) *Teide volcano, Tenerife Island, Spain.* On Tenerife Island the parental materials are relatively uniform. However, strong climatic gradient exist in the island, causing diverse soil characteristics (Tejedor et al., 2007). Therefore, Tenerife Island is an excellent field site to study the influence of climate and weathering.

4 Outline

This PhD thesis consists of four different parts: (1) two chapters dealing with the scientific background (Chapter 1 and Chapter 2), (2) three chapters focused on the analytical aspects of Se determination (Chapter 3, 4 and 5), (3) two chapters wherein the results of the field studies are presented and discussed (Chapter 6 and 7) and (4) one part where results are discussed and summarized.

Chapter 1 reviews previous work on Se in volcanic systems. It discusses the Se content and behaviour in different compartments within volcanic systems, compares its behaviour with the more abundant and well-studied sulphur system and mentions the implication for Se cycling and human health. ***Chapter 2*** gives the background on a range of analytical tools used for Se determinations in soils.

Chapter 3, Chapter 4 and ***Chapter 5*** deal with analytical improvements for Se determinations. In ***Chapter 3*** the focus is on total soil Se determinations using two different techniques: inductively coupled plasma mass spectrometry (ICP-MS) and Total Reflection X-ray Fluorescence (TXRF). In ***Chapter 4*** total and speciation Se determinations in soil extractions are discussed. Again two different techniques are assessed: TXRF and High Performance Liquid Chromatography (HPLC) – ICP-MS.

Chapter 5 presents analytical improvements for the determination of selenium isotopic signatures using multi collector ICP-MS. Two different approaches have been evaluated: the application of pseudo-high mass resolution and the use of a methane-mixed plasma.

Chapter 6 and ***Chapter 7*** present the field studies focussing on which processes influence the Se mobility in volcanic soils. Two distinct field areas have been selected: Mount Etna at Sicily (Italy) and Mount Teide at Tenerife (Spain). Mount Etna is an active volcano and soils in this area are regularly exposed to fresh ash input during volcanic activity. As a result, soils are generally poorly developed. ***Chapter 6*** introduces the effect of the interaction between volcanic soils and volcanic-derived acid rain on Se mobility. In contrast, Teide volcano erupted last in 1798. The island has a strong climatic gradient and a wide range of weathering regimes is recognized in this area. In ***Chapter 7*** the spatial distribution of selenium within soils from Tenerife Island is discussed in order to better understand the effect of weathering. With this aim, the effect of different factors that might additionally influence Se behaviour, such as bedrock variations, weathering and dust and marine aerosol input, will also be evaluated.

Afterwards, the implications of the results will be discussed and indications for future work will be given in the general discussion. Finally, the analytical methodologies developed and the processes controlling the Se behaviour in volcanic soils will be summarized in the conclusions, highlighting the importance of sorption processes and soil mineralogy.

Chapter 1

Selenium in volcanic environments

G.H. Floor, G. Román-Ross. Selenium in volcanic environments: a review. *Applied geochemistry,* submitted.

1 Introduction

Volcanic eruptions are the clear and dramatic expression of dynamic processes in planet Earth. The majority of them happen at plate boundaries. Volcanoes at diverging plate boundaries (e.g. Mid Oceanic Ridges) predominantly occur on the seafloor. Although submarine volcanism emits similar amounts of Se (Rubin, 1997) as subaerial volcanism (Mosher and Duce, 1987; Nriagu 1987; Mather et al., 2003), it has little direct impact on human lives. Subaerial volcanism is mainly concentrated along subduction zones at convergent plate boundaries (e.g. the so-called Ring of Fire around the Pacific Ocean basin, Figure 1). Moreover, these eruptions are normally more explosive than the effusive lavas at divergent plate boundaries (e.g. Iceland) and intraplate settings (e.g. Hawaii).

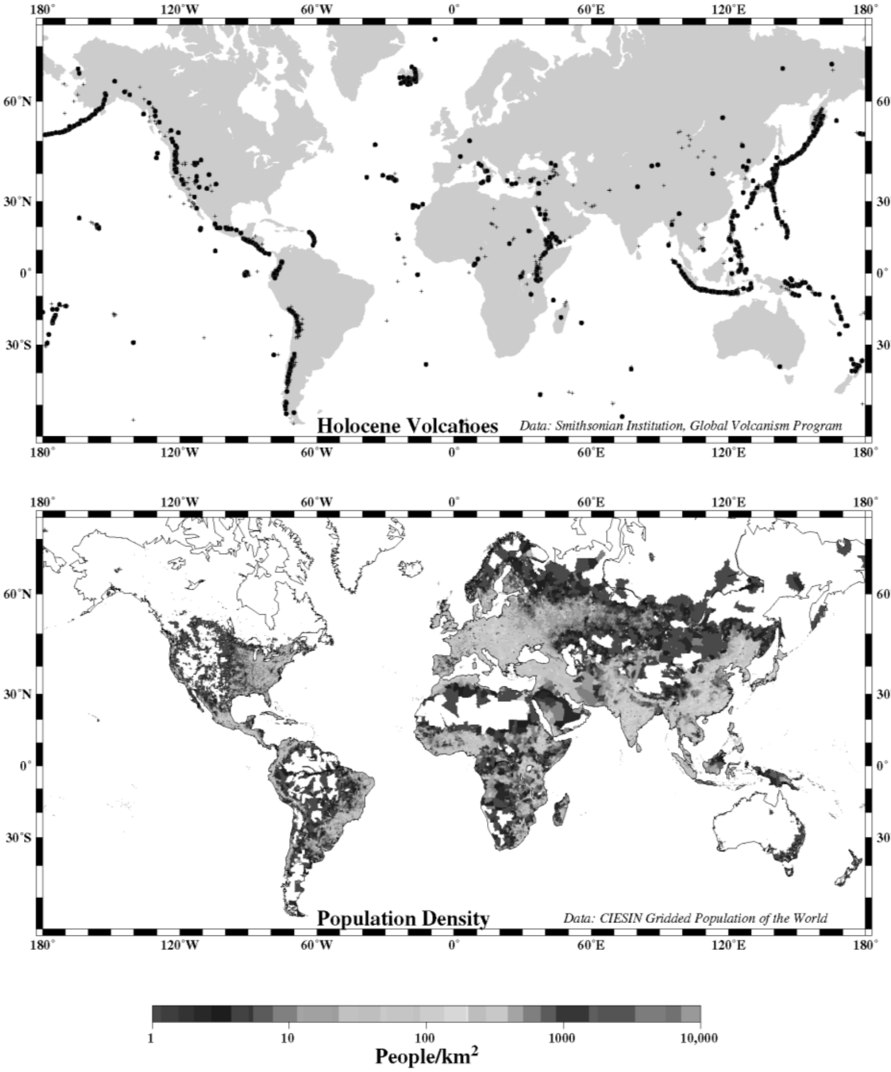


Figure 1: The global distribution of Holocene volcanoes and human population. Red: Historically active volcanoes Blue: Holocene volcanoes without historical eruptions are shown as crosses. Population density is shown on a logarithmic scale. Reproduced from Small and Naumann, 2001.

Volcanic areas are very often densely populated. Nine percent of the world's population (455 million) lives within 100 km of a historically active volcano. Up to 12% lives within 100 km of volcanoes with Holocene eruptions (Small and Naumann, 2001, Figure 1). Populations are attracted by the nutrient rich soils which form on rapidly weathered ash and lava ejected from volcanoes. However, volcanoes can also have negative consequences. Although volcanoes are well known for the immediate destructive behaviour during eruptions, such as lava flows, ash falls and pyroclastic flows, additional important health impact may occur slowly and further away from the craters. The environmental impact of volcanic emissions was first described for the 1783 Laki eruption (Thordarson and Self, 2003; Witham and Oppenheimer, 2004). Since then major eruptions such as Mount St Helens (1980), El Chicón (1982), Galunggung (1982) and especially Pinatubo (1991) increased the scientific interest on potential effects of volcanic activity on human health and the environment (Figure 2). The concern about the negative effects of volcanic emissions keeps growing due to recent eruptions, including the Chilean volcano Chaiten in 2008 (Martin et al., 2009b) and the Icelandic volcano Eyjafjallajökull in 2010 (Gertisser, 2010).

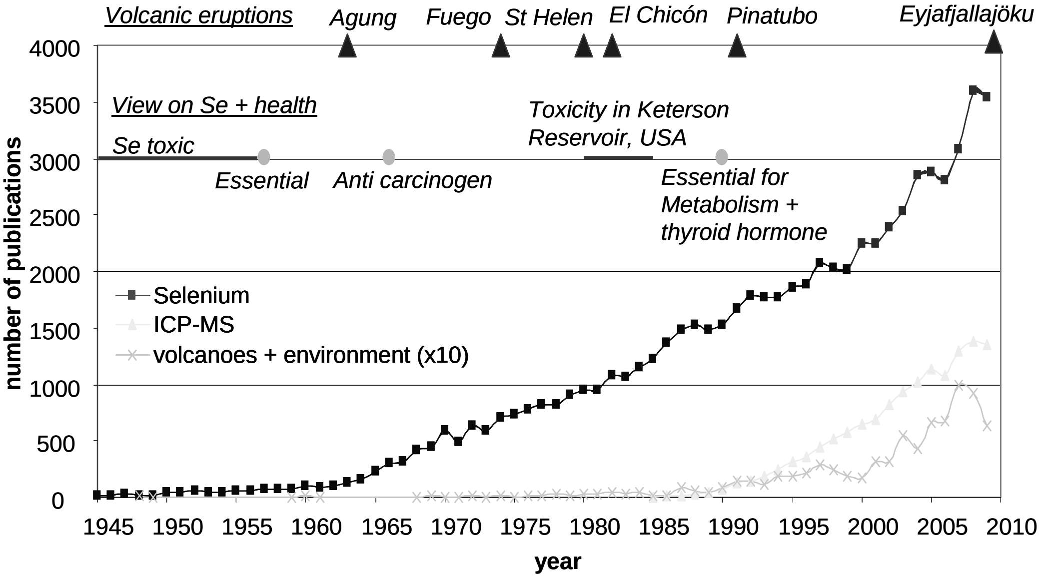


Figure 2: number of publications per year for different topics with important volcanic eruptions and changing view on effect of Se on health indicated. Data on number of publications: ISI web of knowledge.

Even in the absence of obvious physical volcanic eruptions, volcanoes emit significantly amounts of potentially toxic elements, including selenium (Se), arsenic (As), lead, mercury and cadmium during passive degassing (Oppenheimer, 2003). Selenium is an element with great environmental implications. Although Se is an essential element for animals including humans, ingestion of an excess amount of Se can produce adverse effects. Compared to other essential elements, Se has a very narrow range between essential and toxic concentrations (Hartikainen, 2005). The number of publications dealing with Se started to increase since the discovery of its essential character in 1957 (Figure 2). The discovery of the role of Se in health (Section 2) is not the only reason for the increasing number of publications about Se.

Additional, the appearance of new analytical techniques for the sensitive, accurate and precise determination of Se (Chapter 2), such as ICP-MS, opened the possibilities to determine Se at trace levels. Selenium is particularly interesting in volcanic environments due to its geochemical properties (Section 3) that show similarities with sulphur, one of the most important elements within volcanic systems.

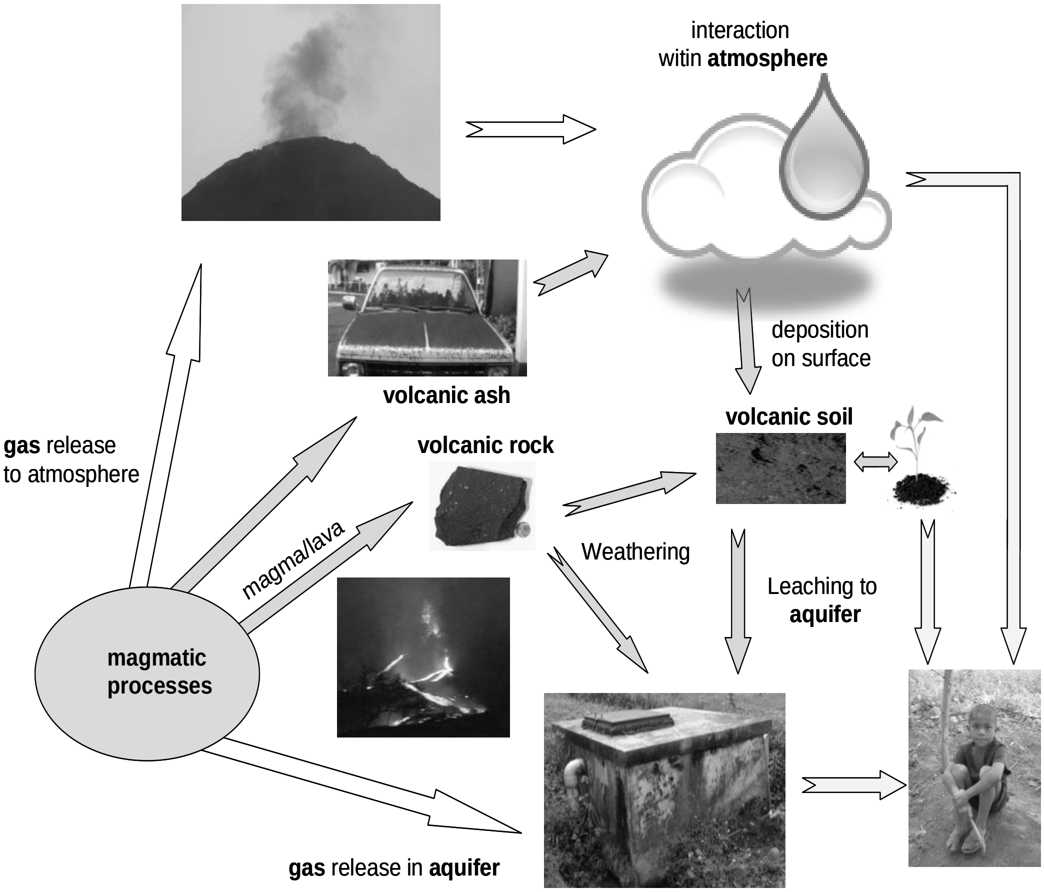


Figure 3: Se transport pathways in volcanic environments

Although this PhD thesis focuses on the processes within volcanic soils, they are just one part of the Se cycling in volcanic system (Figure 3). Therefore, in this chapter I will follow the Se cycle to discuss the most relevant processes affecting the Se behaviour in volcanic systems. Magmatic processes determine the Se distribution in lava and gases. As a result they control the composition of the emitted lava, forming volcanic rocks (Section 4). Moreover, they cause degassing, giving gas emissions towards the atmosphere (Section 5). Additional, volcanoes also emit volcanic ashes (Section 6), an important parental material for volcanic soils (Section 7). Leaching processes from soils and ashes towards groundwaters control together with direct gas input and host rock weathering the chemical composition of volcanic waters (Section 8). The Se cycle in volcanic environments impacts on human health (Section 9), through Se content in drinking water and food (depending on the soil characteristics) and the direct inhalation or ingestion of volcanic gases and ashes.

2 Selenium and health

Of all trace elements, Se has one of the narrowest range between dietary deficiency (<40 µg/day) and toxic levels (>400 µg/day). The link between Se biogeochemistry and health has been documented for many years and numereous papers on this topic exist (Foster and Sumar, 1995; 1997; Rayman, 2000; Brown and Arthur, 2001; 2007; Hartikainen, 2005; Fordyce, 2005). The perspective of Se and its health effects has a very interesting history. The first case of Se toxicity was reported by Marco Polo during his travels in China in the 13th century when he noted that certain plants had serious effects on animals. However, it took until 1930 until the link was made with Se (Hartikainen 2005). At around the same time the occurrence of ´alkali disease´, a disorder producing necrotic and sloughed hoofs, hair loss, poor growth and reproduction in cattle, occurred in the western United States (Rosenfeld and Beath, 1964). From that moment selenium was considered a dangerous substance.

The view that Se was a toxic element changed around 1957, when Schwarz and Foltz identified selenium as essential to animal health when they discovered that trace amounts protect against liver necrosis in vitamin E deficient rats (Schwarz and Foltz, 1957). In 1966 it was revealed that Se is anti-carcinogen and in 1990 that it is essential for metabolism and thyroid hormone synthesis (Arthur et al., 1993). Nowadays, Se receives a lot of attention in veterinary science, because Se deficiency causes skeletal muscle calcification in sheep and cattle, known as white muscle disease, which can be easily prevented by Se supplementation (Brown and Arthur, 2001). Selenium supplementation was also proven to be useful to avoid Kashin-Beck and Keshan diseases (Moreno-Reyes et al., 2003; Xia et al., 2005).

However, an example of Se toxicity was clearly demonstrated in the 1980s with the death of aquatic birds, malformation of bird embryos and poisoning of fish in Kesterson Wildlife Refuge due to Se excess (Presser, 1994). In Hubei Province in China a human disease characterized by loss of hair and nails with a peak prevalence in the 60s was also linked to Se toxicity (Yang et al., 1983). As a result, at the present time Se has received extensive attention in medical studies and is famous as a so-called *double-edged sword*. Another reason for the interest in Se is that its intake influences the toxicity of other elements, such as As and Hg (Yang et al., 2003; Gailer, 2007; Huang et al., 2007; Ralston and Raymond, 2010; Wang and Guo, 2010).

3 Geochemistry of selenium

Selenium is a non-metal of group sixteen in the period table having an atomic number of 34. In natural settings, Se can be found in +6, +4, 0, and -2 valences (Johnson and Bullen, 2004) and in a variety of organic compounds (Muños-Olivas et al., 1995). The chemical form is important, since it strongly influences Se mobility and toxicity (Hartikainen, 2005; Gonzalvez et al., 2009). Chemical reactions in volcanic environments are controlled by the strong pH and Eh gradients in space and time depending on the volcanic activity. For example, the rainwater pH at Mount Etna varies between 2 and 6 in less than ten kilometres or within several months at one location (Calabrese, 2009). Since pH and Eh control the elemental speciation, redox transformations of trace elements are expected to occur in volcanic environments.

Chemically Se is often compared to sulphur, which is immediately above it in the periodic table. As a result, Se forms similar compounds to S. For instance Se^{2-} substitutes for S^{2-} in minerals like sphalerite ((Zn,Fe)S), due to comparable ionic radii (C.N. = 6) of 184 and 170 pm (Shannon, 1976, a difference of <10%), and similar atomic electronegativities of 2.45 and 2.48. However, several chemical dissimilarities exist between Se and S. The electronegativities and ionic radii vary much more for other redox states (Shannon, 1976), and therefore substitution between S and Se is not favoured. Other disparities can be observed comparing the Eh-pH stability diagrams for the aqueous speciation of Se and S (Figure 4). The biggest differences in the thermodynamically stable redox species occur under moderately reducing conditions when Se is stable as Se(IV) or as Se(0). However, S(IV) is not a thermodynamically stable species and S(0) is only stable at restricted settings. As a result, the behaviour of Se during oxidation and reduction processes is more complicated compared to S. In strongly reducing circumstances Se(-II) and HSe^- chemically resemble sulphide. Under oxidizing conditions, Se(VI) is thermodynamically favoured and will form selenate ions (SeO_4^{2-}), which are chemically similar to sulphate ions. However, all these considerations are only valid during thermodynamic equilibrium, while in nature kinetics must also be considered. Moreover, volcanic settings are extreme environments, while the Pourbaix diagrams are valid for standard conditions (T=25°C, 1 bar). The extended use of these graphs could produce a misunderstanding of the geochemical processes occurring at high temperature and pressure (Brandtley and Conrad, 2008). Although extrapolation of equilibrium constants at elevated temperatures exists, it has only been performed for relatively simple systems. Therefore, these databases lack thermodynamic data for potential species such as metal selenides (D´yachkova and Khodakovsky, 1968; Xiong et al., 2003; Akinfiev and Tagirov, 2006).

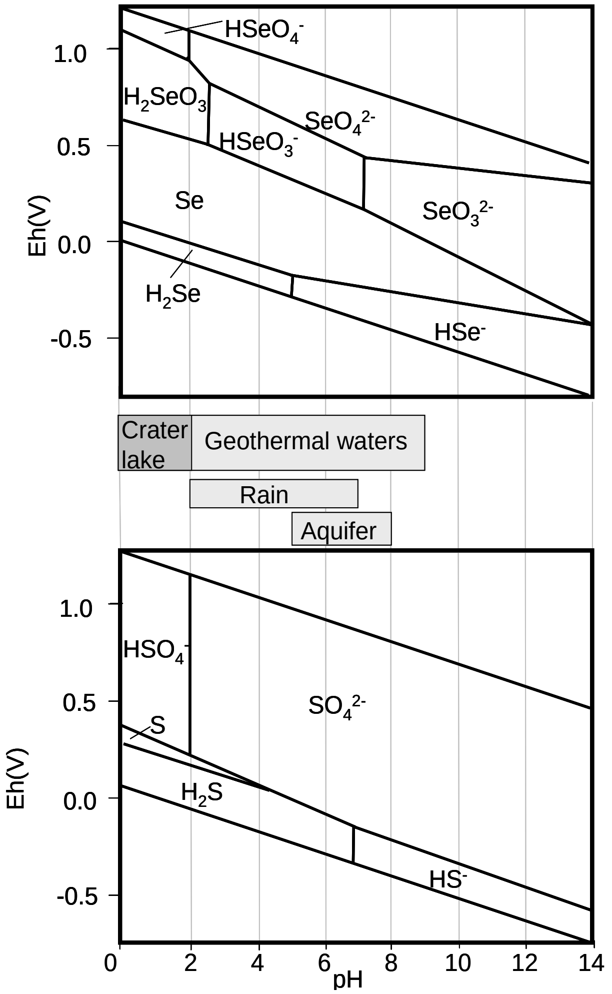


Figure 4: Se and S speciation in aqueous solutions at 25°C (Brookins, 1988) and pH range for different types of volcanic waters.

In general, Se compounds have vaporization temperatures low enough to be volatilized during volcanic activity (and other processes like coal burning (e.g. Zeng et al., 2001, Yan et al., 2001, 2004; Monahan-Pendergast et al., 2008). Nevertheless, important differences exist between the vaporization temperatures of S- and Se-compounds (Table 1). The biggest dissimilarity is observed between SO_2 and SeO_2. While SO_2 is a widespread volcanic gas, being in the gas form even at ambient temperatures, SeO_2 has a vaporization temperature of 315°C. This means that during cooling processes within a volcanic plume, SeO_2 is very unstable in the atmosphere and can usually readily transform to particulate phases (Wen and Carignan, 2007).

Table 1: vaporization temperature of some S and Se compounds

Sulphur			**Selenium**		
Compound	Boiling T in °C	Solubility in g/100 mL (T °C)	Compound	Boiling T in °C	Solubility in g/100 mL (T °C)
H_2S	-60	0.25 (40)	H_2Se	-41	0.7 (25)
S (0)	445		Se(0)	680	
SO_2	-10	9.49 (25)	SeO_2	315 (subl)	3.95 (25)
H_2SO_4	290	Miscible	H_2SeO_4	260	130 (30)

4 Selenium in magmatic systems

Selenium escapes as high-temperature gases during volcanic activity due to its volatility (Section 3). Therefore, Se concentrations left behind in volcanic rocks are commonly very low (Davidson and Power, 1959; Fordyce, 2005). Average Se concentrations of igneous rocks have been estimated to be between 0.05 and 0.09 mg/kg (e.g. Tamari et al., 1990 and references therein). Davidson and Powers (1959) studied igneous rocks from the USA (including Hawaii) and concluded that all crystalline volcanic rocks had low Se contents (below the detection limit of 1 mg/kg). Icelandic and USSR volcanic rocks generally have Se concentrations below 0.4 mg/kg (Koljonen, 1973, Sindeeva, 1964; Unni and Schilling, 1976). Reported Se concentrations in Japanese igneous rocks average 0.01 mg/kg, with only seven samples with Se contents above 0.05 mg/kg (Tamari et al., 1990). Reference basalts (BHVO-2 BIR-1 BE-N) have values <0.2 mg/kg (e.g., Forrest et al., 2009; Jenner et al., 2009; Wombacher 2009). Jenner et al. (2008) determined values below 0.6 mg/kg for Atlantic and Pacific MORB, Hawaiian glasses and Back-arc Basin magmas from the SW Pacific. Selenium isotopic analyses (Chapter 2) of terrestrial igneous mantle rocks and iron meteorites show very limited variations of less than 0.5‰ (Rouxel et al., 2002).

Due to analytical difficulties for trace Se determinations (Chapter 2), Se data for magmatic systems are scarce (e.g. Savard et al., 2006; 2009; Forrest et al., 2009; Jenner et al., 2009; 2010; Wombacher et al., 2009). Even nowadays, standard techniques for elemental analyses of volcanic rocks lack suitable detection limits for Se, and therefore Se concentrations are normally not reported. Moreover, the information obtained from early studies is limited because most volcanic rocks have reported Se concentrations below the detection limit of the used techniques. As a result, trends in Se fractionation during magmatic processes such as partial melting and phase assemblages are still unclear (e.g. Koljonen, 1973; Tamari et al., 1990;

Malisa, 2001; Lorand et al., 2003; Jenner et al., 2008; 2010). The cosmic or mantle abundance of Se is also a point of discussion (Greenland, 1977; Morgan et al., 1981; Lorand et al., 2003; Palme and O´Neill, 2003; Rose-Weston et al., 2009; Jenner et al., 2010). Clearly more research is needed to fully understand the partition of Se in magmatic systems. However, since Se concentrations are low, most magmatic processes have little impact on the cycling of Se in volcanic environments and its health impact.

The only important magmatic process from an environmental point of view is magmatic degassing. Degassing will transfer Se from the magmatic system into the environment. Even so, the behaviour of Se at high temperatures is poorly understood (Forrest et al., 2009). Jenner et al (2008; 2010) showed that S concentrations in SW Pacific back-arc basin and Hawaiian glasses are considerably lower than in MORB glasses, while Se contents are comparable. Moreover, Se follows the behaviour of other chalcophile elements such as Au, Ag and Cu. This indicates that Se is not as volatile as S and that Se/S increases during degassing. This is supported by the observation that reference materials prepared from basaltic rocks at atmospheric pressure and high temperatures have lost almost all S, but retained Se (Jochum et al, 2006; Jenner et al., 2009). The lower volatility for Se than for S is also sustained by data from fumaroles where lower Se and Se/S are observed for lower temperatures (Section 4.2). Furthermore, these observations are in line with the higher vaporization temperatures for Se than for S compounds (Table 1, Section 3).

5 Volcanic gases

5.1 Volcanoes as source of selenium

Volcanic emissions play a key role in geochemical cycling of several elements (Oppenheimer, 2003). Volcanic gases mainly consist of H_2O, CO_2, SO_2, HCl, H_2S and HF (Faivre-Pierret and Le Guern, 1983; Symonds et al., 1994), but also contain minor components such as vaporized metals (Nriagu, 1989). High concentrations of Se in shales and atmospheric deposition from volcanoes were already linked in studies from the 1930s (Byers, 1936; Manville, 1939). Nriagu (1989) compared the natural and anthropogenic fluxes of trace metals to the atmosphere and was the first to recognize that volcanoes are important emitters of trace metals at the global scale. Volcanoes also emit Se in substantial concentrations (Table 2 and 3). For that reason volcanism globally contributes significantly to the atmospheric input of Se.

Table 2: Estimated global atmospheric Se fluxes. Data from Wen and Carignan, 2007.

Natural sources		**Anthropogenic sources**	
Source	Flux (Gg/yr)	Source	Flux (Gg/yr)
Volcanoes (see Table 3)	**0.1 - 1.8**	Combustion (coal, oil and others)	4.09
Marine biosphere	0.4 - 9		
Continent biosphere	0.15 – 5.25	Non-ferrous metal production	1.713
Sea salt spray	0.04 - 1.1		
Wild forest fires	0 – 0.52	Manufacturing	0.2441
Total (average)	**9.4**	**Total**	**6.05**

The main sources of atmospheric Se are anthropogenic (especially coal combustion), marine derived biogenic Se and volcanic emissions (Table 2). It has been estimated that in total between 13,000 and 19,000 tons of Se are annually cycled through the troposphere (Wen and Carignan, 2007). Volcanoes emit annually globally approximately 100-1800 tons of Se (Mosher and Duce, 1987; Nriagu, 1989; Mather 2003, Table 3) and are thus the most important natural source of inorganic Se. Release also occurs in the absence of obvious volcanic activity (so called passive degassing). A similar amount of Se is emitted during submarine degassing at mid-ocean ridges (Rubin, 1997; Table 3).

Table 3: Worldwide volcanological Se fluxes and Se/S

Location		Se (Gg/yr)	Se/S x 10^{-4}	Reference
Subaerial	Worldwide	0.4 -1.2		Mosher and Duce, 1987
		0.3-0.5		Mather et al., 2003
		0.1-1.8	0.007 – 0.35	Nriagu, 1989
Submarine (to seawater)	Hydrothermal flux mid ocean ridges	0.042		Rubin, 1997
	Degassing flux mid-ocean ridges	0.83		

Although at global (Mosher and Duce, 1987; Nriagu 1989) or subglobal (Ross, 1985) scale anthropogenic are dominant over volcanic emissions (Table 2), this may be different at a regional scale. This is for example the case for Etna volcano. Mount Etna is considered to be the major volcanic gas emitter in the world on the long term average (tens of years), accounting for about 10% of worldwide average volcanic emission of CO_2 and SO_2 (D'Alessandro et al., 1997; Caltabiano et al., 2004). It has been shown that Etna volcano emits one order of magnitude more Se than all anthropogenic sources on the island, even during passive degassing. As a consequence, Etna is the main point source of Se in the Mediterranean area (Calabrese, 2009).

However, estimates of global volcanic fluxes contain large uncertainties and vary widely. Only a few of potential sources in the world have been measured (Hinkley et al., 1999; Oppenheimer, 2003). Fluxes are mostly based on metal/sulphur ratios, which vary significantly from volcano to volcano but also temporally and spatially within one volcanic system (Table 4). Furthermore, there is significant uncertainty concerning the amount of S emitted by volcanoes (Mather et al., 2003). Additionally, it is difficult to obtain quantitative data for Se in volcanic gases (Finnegan et al., 1989). A potential tool to better discriminate between the contribution of volcanoes and other sources of atmospheric Se, is the use of isotopic signatures. Most of the reactions that affect Se in the atmosphere involve oxidation (Section 4.2). These reactions should not lead to isotope fractionation (Johnson, 2004). However, volatilization and condensation in industrial processes and during volcanic activity, may lead to kinetic isotope effects characteristics of a given activity (Wen and Carignan, 2007). As a result, the isotopic composition of Se comprised in aerosols should reflect its source emission and may help to discriminate the different sources, as has been previously done for other isotopic systems such as Pb and Cd (Erel et al, 1997; Cloquet et al, 2006). Nevertheless, despite the high variability in the current budget estimations, in all cases volcanoes are important emitters of inorganic Se.

Table 4: Se fluxes and Se/S for some volcanoes

Location				Period	Se (Gg/yr)	Se/S x 10^{-4}	Comment on methodology and volcanic acitivity	Reference
Antarctica	Mount Erebus			1986-1991	0.002	0.2 – 30	Filter pack - INAA	Zreda-Gostynska et al., 1997
				1997-2000	0.0001	0.1	Chemical trap with NaOH – HGAAS	Wardell et al., 2008
New Zealand	White Island			2000-2001	0.0005	0.06 – 0.009		
Indonesia	Merapi			1984 (Jan-Feb)		3 – 60	Sublimates by silica tubes – INAA and XRF	Symonds et al., 1987
Russia	Kurile Island			1990-1993		~0.1	Chemical trap with NaOH – ICP-MS	Taran et al., 1995
USA	Kilauea			1983 (Nov)		0.6	LiOH-impregnated filters – INAA: Max value. System not quantitative for Se	Finnegan et al., 1989
				1983 -1984		6-30	Filter pack – INAA	Olmez et al.,1986
				1984-1996	0.023	0.64	Filter pack - INAA or ICP-MS	Hinkley et al., 1999
	St Helens			1980 (May)		~1.3	Filter pack – INAA: collected with aircraft just after major eruptions	Vossler et al., 1981
				1980 (Sept)	0.037	3.55	Filter pack – INAA: collected with aircraft during stable plume emission	Phelan et al., 1982
	Augustine			1976		5-10	Filter collection - INAA: collected with aircraft	Lepel et al., 1978
Mexico	El Chicón			1982	0.0014		Filter pack – INAA: collected with aircraft, particulate only	Kotra et al., 1983
Caribbean	Montserrat			1996		0.4 - 4	PTFE-coated glass-fibre filters – ICP-MS	Allen et al., 2000
Italy	Stromboli			1993-1997	0.055	0.3-46	Filter pack – INAA	Allard et al., 2000
	La Fossa, Vulcano			1994	0.0008		filters + condensate trap – INAA	Bichler et al., 1995
	Etna	Total		1976	0.23	15	Eruption	Faivre-Pierret and Guern, 1983
		Main plume		1976 (June)		6.77	Filters – INAA: Moderately pyroclastic activity	Buat-Menard and Arnold 1978
		Lava vents				32.1		
		Bocca Nuova		1987 (July)	0.016	1.16	Filter packs – INAA: Relatively quiet activity	Andres et al., 1993
		SE Crater			0.002	0.24		
		Total			0.018	0.86		
		Bocca Nuova		2001 (3 May)		18.2	Filter packs – INAA: Before eruption	Aiuppa et al., 2003b
				2001 (18 May)		8.39		
				2001 (5 June)		9.27		
				2001 (29 June)		50.8		
				2001 (12 July)		5.84		
		Lava flow		2001 (19 July)		15.0	Filter packs - INAA: Eruption	
		Monti Carcazzi Vent				1.12		
				2001 (25 July)		20.0		
				2001 (1 August)		14.3		
		Crater rims	Min	2004-2007	0.0003	0.001	Filters – ICP-MS: Passive Degassing	Calabrese 2009
			Max		0.216	0.25		
			Mean		0.019	4.15		

5.2 Chemistry of selenium within volcanic plumes

Selenium is enriched in volcanic plumes compared to volcanic rocks (Buat-Menard and Arnold, 1978; Phelan et al, 1982; Crowe et al, 1987; Allard et al, 2000; Toutain et al, 2007), suggesting volatilization of Se during volcanic activity. As stated above, the composition of the emissions (e.g. Se/S ratio) and the amount of emitted Se varies considerably during different eruptive periods of the same volcano and even between sample locations within one volcano (Table 4). Data on fumarole gases and volcanic gas condensates show lower Se contents and lower Se/S ratios for lower temperatures (Suzuoki, 1964; Murata and Richter, 1966). This indicates that Se and S do not behave the same during volatilization processes in the magma chamber. Most Se/S ratios observed in volcanic plumes (Table 4) are below the Se/S in the primitive mantle or continental crust (with Se/S in the order of $*10^{-4}$). This (again) suggests that S is more readily volatilized in magmatic systems than Se, related to their differences in vaporization temperatures.

Not many data are available for Se speciation in volcanic plumes. Since volcanic sulphur species are H_2S, S(0) and SO_2, volcanoes will probably emit Se as H_2Se, Se(0) and SeO_2. Thermodynamic calculations on volcanic gas compositions from Mount St Helen shows that in contrast to S, Se is not transported as the dioxide but as H_2Se at high temperatures (930°C, 1 atm). At lower temperatures the main gases of S and Se, H_2S and H_2Se respectively, are chemically similar (Symonds and Reeds, 1993). Modelling on gases from two Japanese volcanoes predicted that most Se is present as free Se (Suzuoki, 1964). The appropriateness of such modelling depends on whether volcanic gases approach chemical equilibrium (i.e. if kinetically retarded reactions are present), the quality of the input gas composition and the quality and quantity of the thermodynamical data (i.e. missing species). For example, metal selenides might form, which are not included in thermodynamic databases. However, measurements of the fumarolic gas at Vulcano also indicate the presence of elemental Se, since the Se is trapped on the filter rather than capped in the condensate as would be expected for SeO_2 or H_2Se (Bichler et al., 1995).

Although little attention has been paid to the reactivity of Se within volcanic plumes, volcanic emissions and coal combustion share both elevated temperatures and the excess of SO_2 which may act as a reducing agent. Therefore, coal combustion can be used as analogue to predict the behaviour of Se in volcanic emissions. Also for this process thermodynamical predictions on the behaviour of Se exist (e.g. Yan et al. 2001; Monahan-Pendergast et al., 2008). In coal combustion gases H_2Se, SeO, SeO_2, $SeCl_2$ and elemental Se were all found to be possible stable species (Monahan-Pendergast et al., 2008 and references therein). Moreover, some experiments simulation this combustion confirmed the presence of elemental Se and its oxides (Yan et al., 2001; 2004; Senior et al., 2000).

The convergence of high temperature and reduced volcanic gases with the atmosphere triggers a series of cooling and oxidation reactions (Figure 5). Although performed combustion simulations did give insight into the possible species released, they do no provide comprehension on the atmospheric lifetime and pathways. There is a lack of knowledge on the reactions of volatile inorganic selenium within the atmosphere. Nevertheless, a preliminary model can be discussed. Selenium dioxide can be transformed to elemental Se by reactions with SO_2, with or without water (Andren and

Klein, 1975; Wen and Carignan, 2007). However, whether thermodynamic equilibrium occurs during this process is untested and kinetic investigations need to be carried out on the thermodynamically favoured pathways. Due to the relatively high vaporization temperatures, both elemental Se and SeO_2 can be condensed and rapidly form particulate Se under normal atmospheric conditions (Zhang, 2002). Selenium dioxide is soluble in water and can dissolve in rainwater to form H_2SeO_3 (Zhang, 2002). Experimental data between volatile inorganic Se and various atmospheric oxidant radicals show fast reactions (Dobson et al., 1975; Agrawalla and Setser, 1987; Ongstad et al., 1990). The reaction between elemental Se and sulphoxy radicals transforms insoluble elemental Se to soluble Se(IV) and Se(VI) with unstable polyselenodithionates as intermediate products (Bronikowski et al., 2000).

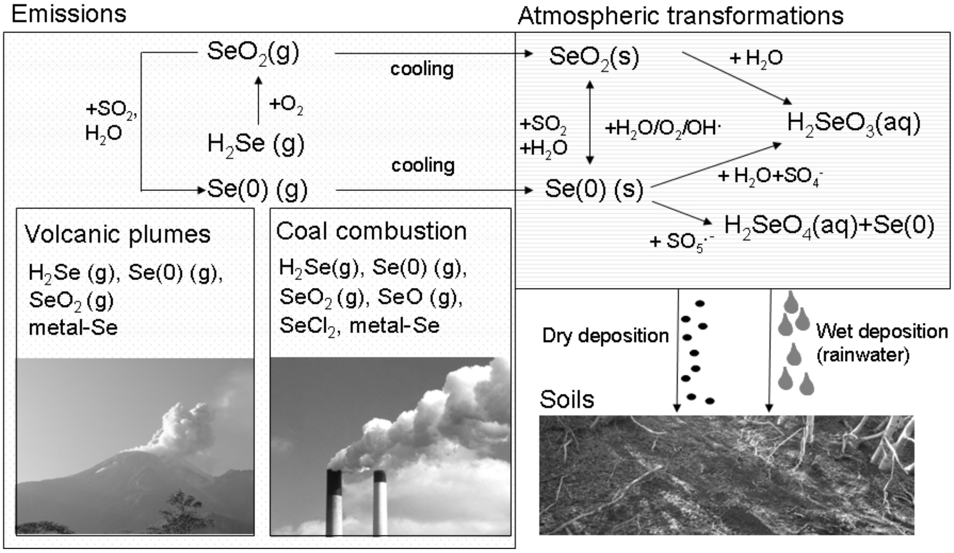


Figure 5: Atmospheric transformations of Selenium

5.3 Gas-water interactions in the atmosphere

The impact of volcanic gases on rainwater composition has been widely recognized (e.g. Kilauea, Hawaii (Eriksson, 1957; Scholl and Ingebristen, 1995), Masaya, Nicaragua (Johnson an Parnell, 1986; Delmelle, 2001), Nevado de Ruiz, Colombia (Parnell and Burke, 1990); Poás, Costa Rica (Rowe et al.,1995); Soufrière Hills, Montserrat (Edmonds et al., 2003) and several volcanoes in Japan (Kawaratani and Fujita, 1990; Okuda et al., 2005) and Italy (Capasso et al., 1993; Aiuppa et al., 2006; Liotto et al., 2006). However, there is a scarcity of trace element data. Selenium deposition has only been investigated for Etna volcano during relative quiescent degassing activity (Calabrese, 2009). This study shows that for most elements the highest concentrations have been found close to the emission vent. Moreover, elemental distrbutions closely follow the plume composition, confirming the prevailing volcanic contribution to rainwater composition. The Se content rapidly decreases with distance from the volcanic source of Etna (Figure 6). The concentrations in the rain water close to the crater depend strongly on volcanic activity, but are up to 13 µg/L. This is significantly higher than most worldwide reported values (generally below 1 µg/L, Conde and Sant Aleojos, 1997 and references therein). Also in anthropogenic acid rain water samples from Canada much lower Se contents were detected (Milley and Chatt, 1987).

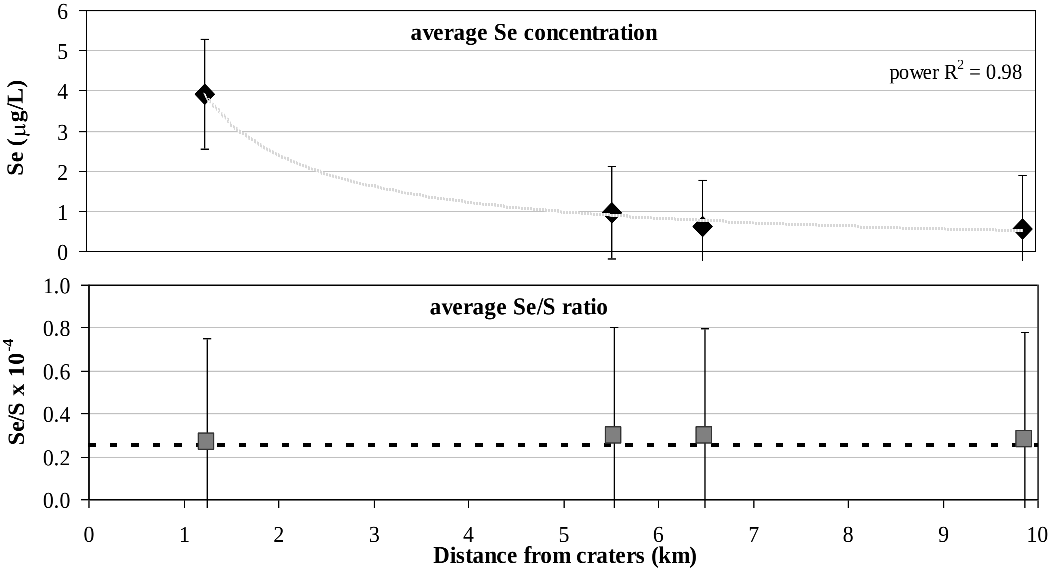


Figure 6: Average Se and Se/S in Etna rainwater and its changes with distance from the volcano. For comparison the average Se/S ratio within the plume (Table 4) for the same period is indicated with a dashed. line Data from Calabrese, 2009.

Although the measured concentrations in Etnean rainwater correspond to significant deposition of Se (up to 15 µg/m^2 per day), only 0.8-2.2% of the total Se emitted is locally deposited. The low percentages of local deposition have been related to the high altitude of the volcano, with the consequence that the volcanic output is directly injected above the boundary layer (Calabrese, 2009). Since this is only measured at Mount Etna during low levels of volcanic activity, there is a need to investigate Se around other volcanoes and during eruptions to identify the general trends of local deposition. For example, at Masaya volcano in Nicaragua the surface occurs at the same altitude of the plume vent. For that reason direct plume fumigation takes regulary place (Delmelle et al., 2001). In contrast, Mount Etna has a conical form with the plume vents at the top. This geometry does not allow frequent direct fumigation of its flanks, significantly reducing the deposition of acidic compounds.

Se/S ratios in the rainwater vary significantly between |x·10^{-3} and |x·10^{-5} (Calabrese, 2009). However, no systematic changes in Se/S are observed with location (Figure 6) or with volcanic activity (i.e. no clear correlation with F^-). Moreover, rainwater Se/S ratios are in the same range as the ratios in the plume (Table 4; Figure 6). This would indicate that deposition processes produce no evident S-Se fractionation (Calabrese, 2009). The study at Mount Etna shows that rainwater-gas interaction is an active process for Se deposition. However, the deposition alone is not enough to understand the environmental impact of the rainwater. Processes occurring between rainwater and soils or volcanic ashes are important for the cycling of Se (Section 5 and 6). As a result, it is important to understand the interaction between volcanic gases and water present in the atmosphere. Changes in this process will affect the rainwater composition, which in its turn will induce changes in the interaction between soils and rainwater. In this, Se speciation will play an important role.

6 Volcanic ash

Weathered ash has often been mentioned as being an important Se source in selenosis areas such as Ziyang Country in China and the Kesterson reservoir in the USA (Presser, 1994; Kulp and Pratt, 2004; Kunli et al., 2004). However, the chemical fate of Se in volcanic ashes has not been extensively studied. In contrast to volcanic rocks which are generally low in Se, volcanic ashes can contain relatively high Se concentrations (Table 5). Moreover, it might be readily mobilized from fresh volcanic ash upon exposure to water (Witham et al., 2005 and references therein). The presence of soluble compounds on ash is believed to originate from the interaction between gases/aerosols and ash within eruption plumes (Rose, 1977; Oskarsson, 1980, Delmelle et al., 2007). Volcanic salt aerosols can adsorb on the volcanic ash within the volcanic plume (Taylor and Stoiber, 1973; Smith et al., 1982). Moreover, the condensation of sulphuric acid onto ash may drive dissolution reactions, thereby providing the source of the soluble cations measured in ash leachates (Rose 1977, Hinkley and Smith 1982, Delmelle et al., 2007). Most studies dealing with volcanic gas-ash interaction have focussed on the adsorption of sulphates and halides. The formation mechanisms of sorbed complexes onto the surface of volcanic ash are unclear (Delmelle et al., 2007). The interaction between Se compounds and volcanic ash particles within the volcanic plume has not been studied at all. However, to study gas-ash interaction, more detailed information on the Se speciation within the volcanic plume (Section 4.2) is needed.

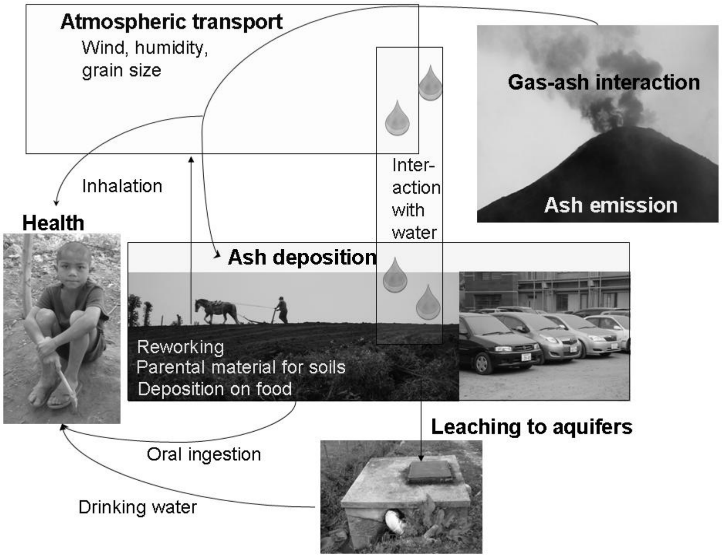


Figure 7: Cycling of volcanic ash

Fresh volcanic ashes influence the Se status in the environment. Volatiles scavenged by ash particles reach the ground more rapidly because of faster deposition velocities of the ash (Witham et al., 2005). Many adsorbed elements are highly soluble, so they can be easily dispersed into the environment, where they have the potential to impact soils, vegetation, livestock, water sources and people (Figure 7; Cook et al., 1981; Cronin et al., 1997; 1998; Stewart et al., 2006; Jones and Gislason, 2008; Martin et al., 2009b). However, ash also releases bio-limiting micronutrients and therefore has a large fertilization potential (Jones and Gislason, 2008; Duggen et al., 2010).

Table 5: Total and leachable Se concentrations in volcanic ash in mg/kg. For comparison, the WHO guideline for drinking is 0.01 mg/kg.

Volcano	Distance crater (km)	Date	Se conc (mg/kg)	Se/S x 10^4	Comments on methodology	Reference
Se total concentration (in mg/kg)						
Raupehu New Zealand	15	1995 (11 Oct)	3.7	1.2	Nitric digest – ICP-MS	Cronin et al., 1997 Cronin et al., 1998
	155	1995 (11 Oct)	3	0.98		
	18	1995 (14 Oct)	3	3.9		
	48	1995 (11 Oct)	2.5	7.2		
	36	1996 (17 June)	2	2.8		
	38	1996 (17 June)	2.4	0.74		
	80	1996 (17 June)	2.2	0.78		
	141	1996 (17 June)	2.4	1.7		
Mount St Helens USA	100	1980	0.5		Spark Source Mass Spectrometry (not further specified)	Taylor and Lichte, 1980
	400		2			
	790		<0.2			
Augustine Alaska		1976	0.34	2.0	INAA (filter): Average value	Lepel et al., 1978
El Chicón Mexico		1982	7		INAA (filter)	Kotra et al., 1983
Mount Etna Sicily Italy Europe	6.5	2006 (Nov)	0.9		ICP-MS (total digestion with HF, HClO4, HNO3 and HCl): Encountered interaction with rainwater	Calabrese 2009
	5.5	2006 (Nov)	0.8	16		
	7.3	2006 (Dec)	0.7	14		
	5.5	2007 (Mar)	0.9	90		
	5.5	2007 (April)	0.7			
	9.5	2007 (April)	0.3			
	5.5	2007 (May)	1.1			
	1.2	2007 (May)	0.8	2.2		
	1.2	2007 (Sep)	0.9	45		
	1.2	2007 (Oct)	0.7			
Se leaching concentration (mg/kg expressed per weight ash)						
Popocatépetl Mexico	13.4 km	1997 (12 May)	0.09		Ratio 1:25 2h agitated ICP-MS	Armienta et al., 2002
	15.9 km		0.04			
	21.5 km		0.03			
	25.5 km		0			
Fuego Guatemala		1974 (14 Oct)	0.36 (0.22-0.48)	6.3	Methodologies not specified	Rose et al., 1978
		1974 (17 Oct)	0.27 (0.16-0.40)	4.3		
		1974 (19 Oct)	0.55 (0.32-0.64)	9.7		
		1974 (23 Oct)	0.20 (0.06-0.48)	7.4		
Ruapehu New Zealand	Several distances	1995 and 1996	0.1 or <0.1	X	Ratio 1:25, 24h agitated ICP-MS (close to DL)	Cronin et al., 1997 Cronin et al., 1998
Mount St Helens USA	5 different locations	1980	<0.025		Ratio 1:2.5;, 1 hr agitated Spectrophotometer	Nehring and Johnston, 1981
	110 km		0.001	10	Ratio ~1:0.6 4 hr in column Spark Source Mass Spectrometry?	Taylor and Lichte, 1980
	115 km		0.003	0.12		
	250 km		0.003	0.17		
	400 km		0.002	0.11		

For example, Cronin et al., (1997) showed that Se concentrations in pasture increased markedly after the 1995 eruption of the Ruapehu volcano (New Zealand). Thicker tephra deposits lead to higher Se concentrations, as observed both field and glass house experiments. Stewart et al. (2006) modelled the impact of volcanic ash from the same volcanic eruption on water supplies. They predict that ash fall has a strong influence on the Se concentration in the waters and that high ash fall (10 mm during one single eruption) in small open water supplies causes Se concentrations which exceed the recommended WHO values. However, to understand the environmental impact of ash fall, the mobility of the deposited Se is more important than the total concentrations. For example for the 1995 Ruapehu eruption, the total Se deposition rate for 1 mm tephra thickness greatly exceeded the recommended amount of Se fertilization for agricultural soils. Nevertheless, only up to 5% of the Se in the tephra was leachable. Therefore, the bioavailable Se was just 11-22% of the normally applied Se deposition by fertilizing (Cronin et al., 1997).

To study the mobility of the elements adsorbed on the ash, ash leachate experiments have been performed. These experiment are used to estimate the environmental impact (Taylor and Lichte, 1980; Croninet al., 1997, 1998; Armienta et al., 2002) or as a plume proxy (Rose 1978; Nehring and Johnston 1981), although some problems exist with the latter approach (Witham et al., 2005 and references therein). Only some of the published ash leachate studies include Se data (Table 5). Additional, for some studies the detection limit of the analysis method is close to or above the concentrations. The concentrations in ash leachates strongly depends on the characteristics of the volcanic eruption (i.e. magma type, mode of eruption, concentration of the plume, ratio of particles to gas, particle size-fractions, temperature within the plume, environmental conditions including wind and humidity) and the experimental approach (e.g. leaching solution used, ash/leach-solution ratio, reaction time, ash grain-size fraction used). Therefore, the number of variables is much higher than the number of data for Se concentrations in ash leachates, making systematic interpretations impossible with the current data. The limited available data show that Se/S ratios vary between different volcanoes and also slightly within one volcanic system. Se/S ratios are in the same order of magnitude in the ash as in the leachate solutions (Table 5).

7 Volcanic soils

The behaviour of Se in soils is the basis of the Se cycle in a geo-ecosystem. Soils play a key role in trace element cycling, because they are an important environmental interface between the lithosphere, atmosphere, hydrosphere and the biosphere. They determine the Se level in food and water and thereby human health. In this perspective, volcanic soils are particularly significant due to their high potential for agricultural production. Although they globally make up less 0.8% of the Earth’s surface, volcanic soils host around 10% of the world population due to their high agricultural productivity (Small and Naumann, 2001). In Indonesia there is a strong relationship between the population density and the input of volcanic ash with 3 to 4 times higher population density around Merapi volcano compared to areas without young volcanic ash (Mohr, 1938).

Nevertheless, volcanic soils did not receive worldwide recognition among the soil scientist community until the mid 20th century. Nowadays there are many names to refer to volcanic soils. Volcanic ash soils refers to soils formed from tephra or pyroclastic material, and is a more general term which includes andosols (FAO-Unesco 1974), andisols (soil survey staff, 1998) and Kurobokado (3rd division of soils, 1973). However, not all volcanic ash soils fall within one of these groups and vice versa (Shoji et al., 1993). Soils formed in volcanic areas have many distinctive properties that are rarely found in soils derived from other parent materials. Due to the rapid weathering of volcanic material they have a high content of amorphous and poorly crystallized silicate minerals, such as allophane, imogolite and ferrihydrite. The accumulation of organic matter is fast mainly because of its protection in aluminium-humus complexes. They have a high water retention (due to allophonic clays), a large total porosity, good drainage, high phosphate retention and a low bulk density. Moreover, volcanic soils have a low permanent charge and a high pH dependent charge (Shoji et al., 1993). These properties strongly control the trace element behaviour.

The Se content of most soils is very low; commonly 0.01 – 2 mg/kg with a world mean of 0.4 mg/kg. However, Se concentrations vary widely and amounts up to 1200 mg/kg have been reported in Ireland (Fordyce, 2005). It was already early recognized that volcanic soils from Hawaii have relatively high Se content (1-20 mg/kg) compared to other USA soils, but that its mobility is low (Byers, 1935; 1936; Byers et al., 1936). The parent material plays an important role on selenium concentrations in soils (Fordyce, 2005). As shown in Section 5, not all volcanic ashes are high in Se. This will probably explain the differences in Se concentrations in volcanic soils. However, currently it is unknown what controls the Se content of volcanic ashes (Section 6).

In contrast to the total concentration, the mobility and bioavailability (the uptake of selenium into plants and animals) is determined by bio-physiochemical parameters such as pH and redox conditions, selenium speciation, soil texture, mineralogy, organic matter content and competitive ions (Fordyce, 2005). Sorption processes (dependent on the chemical form of selenium) are central in the Se mobility. Studies on volcanic soils from New Zealand (John and Saunders, 1976) point out the importance of poorly crystalline iron oxides (e.g. ferrihydrite) for the Se adsorption properties. Nakamaru et al. (2005; 2006) demonstrated with the combination of adsorption experiments and sequential extractions analyses that high correlation exist between Se adsorption and the presence short-ranged-ordered aluminosilicates (e.g. allophone, imogolite) for Japanese volcanic soils. Soil adsorption can have a strong effect on the environmental effects of volcanoes. At Mount Etna strong fluoride adsorption within the soils acts as a natural barrier that protects the groundwater system (Bellomo et al., 2007; Section 7.2). For Se a similar process could occur. However, this strongly depends on Se speciation in the rainwater, competitive anion concentrations and potential adsorption phases within the soils.

Weathering is an important process that controls elemental transport towards oceans, soil formation and earth morphology. At a global scale, about 45% of the suspended river material carried to the ocean comes from volcanic island (Milliman and Syvitski, 1992; Dessert et al., 2003). Around 30% of the long term sequestration of carbon fixed by chemical weathering of silicates in the terrestrial environment of the Earth occurs on basaltic rocks and volcanic soils store about 5% of the Earths carbon

(Milliman and Syvitski, 1992; Eswaran et al., 1993; Dessert et al., 2003). The effect of weathering on the environmental fate of Se within volcanic soils is currently unknown. Since the mineralogical composition of volcanic soils changes with weathering and minerals have different affinity for Se, the mobility of Se is expected to change. Volcanic glass is usually the first component of volcanic rocks to undergo weathering and will form short range order clays (SROCs) such as allophane, imogolite and ferrihydrite. Organic matter content also increases with weathering. In older volcanic soils that are in more advanced stages of weathering, halloysite and gibbsite appear more common as SROCs decrease (Shoji et al., 1993). Moreover, redox changes could occur during soil formation.

Because abiotic and biotic reduction processes affect the Se isotopic signature (Johnson, 2004), Se isotopes could be used to better understand the effect of weathering. Previous works show the potential of isotopic changes within soil profile for different isotopic systems, such as for lithium (Huh et al., 2004; Kisakürek et al., 2004). Soils and sediments are isotopically heterogeneous for Se with variations of up to 10‰ (Carignan and Wen, 2007). However, Se isotope data in soils are only present for a few sites and it is currently unidentified how weathering contribute to these variations and which part is controlled by other factors, such as the parental material.

Despite the limited studies dealing with Se adsorption in volcanic soils, experiments on pure mineralogical phases present in these soils can indicate which sorption mechanisms are important. These have been extensively discussed for different mineral phases in the review of Fernández-Martínez and Charlet (2009). Iron (Fe) and aluminium (Al) oxides are minerals in volcanic soils that form important adsorption sites for selenium. Higher selenate and selenite adsorption occurs at lower pH (Yu et al., 1977; Neal et al., 1987; Barrow and Whelan, 1989) and under most circumstances the affinity of selenite is much higher than of selenate for Fe and Al oxides. Few studies exist on the kinetics of Se adsorption processes, but most show fast kinetics (< 2h). Organic matter also can provide immobilization of Se due to sorption processes (Fernández-Martínez and Charlet, 2009 and references therein). Moreover, both Fe oxides and organic matter can induce redox changes (Myeni et al., 1997; Bruggeman et al., 2007, Scheinost et al., 2008). However, Se adsorption has not yet been studied for all compounds relevant in volcanic soils. For example, the adsorption capacity of volcanic glass remains unknown. The competition of other ions, such as sulphate (SO_4^{2-}), fluoride (F^-) and phosphate, strongly influences Se sorption. Fertilizers containing significant amounts of phosphate might reduce selenite adsorption (He et al., 1994; Dhillon and Dhillon, 2000; Goh and Lim, 2004; Nakamura et al., 2006; 2008). Sulphate and fluoride are widely abundant in volcanic environments. Fluoride is especially competitive with selenite, while selenate is similar to sulphate and therefore similar surface complexes form with both oxyanions (Balistri and Chao, 1990; Wijnja and Schultless 2000; Peak and Sparks, 2002). During acid rain events (Section 4.3) and direct plume fumigation (Delmelle et al., 2002) the compounds might be transferred from the atmosphere towards soils. For example rainwater around Mount Etna has up to 450 and 65 mg/L of SO_4^{2-} and F^- respectively (Calabrese, 2009). It also means that adsorption mechanism of SO_4^{2-} (Delmelle et al., 2003; Delfosse et al., 2006) or F^- (Delmelle et al., 2003; Bellomo et al., 2007) can be used as chemical analogous to better understand the selenate oxyanion behaviour on volcanic soils.

Although the discrepancy between enriched Se concentrations and low bioavailability is known, the processes and mechanisms are not well identified. Moreover, Se specific studies in volcanic soils were only performed in Hawaii, New Zealand and Japan (Byers, 1935; 1936, Byers et al., 1936; John and Saunders, 1975; Nakamaru et al., 2005; 2006; Nakamaru and Sekine, 2008). Taking into the account the importance of volcanic soils for the Se levels in food and water, the main human Se sources, it is a critical issue to better investigate how different processes influence the mobility of Se within volcanic soils.

8 Volcanic waters

Volcanic gases interact with water at the earth surface or at depth, affecting hydrothermal and groundwaters. Leaching from host rock additional plays a major role in the chemical properties of groundwater. In this section the Se contents of the waters resulting from these interactions will be examined.

8.1 Geothermal waters

Geothermal active areas occur where an above average geothermal gradient allows hot water or steam to emerge at the Earth’s surface. Although geothermal activity is often associated with recent volcanism, other process such as intrusions, metamorphism, faulting and radioactivity can be involved. High temperature geothermal systems are present throughout the world, generally at tectonic plate boundaries (both at convergent (subduction) and divergent (extension) boundaries) or along hotspots. Geothermal waters can occur at the continent, in shallow-water submarine environments and at mid-ocean ridges. At shallow depth the temperature of fluids ranges between 10 to 119°C. In deep hydrothermal waters the temperature of the fluids can exceed 400°C. Consequently, the chemical composition of the waters is a function of fluid temperature, host rock composition and time. The origin of geothermal fluids was initially reported to be of magmatic origin, but isotopic analyses have confirmed that they are mostly derived from meteoric waters (Webster and Nordstrom, 2003 and reference therein). When the geothermal fluids rise through the crust, the fluids separate into steam and water as a response to pressure changes. Accordingly, two endmembers of geothermal fluids can be distinguished. The direct discharge of the hot water phase causes springs with a near-neutral pH and rich in chloride and silica. The steam can interact with shallow aquifer water and cause acidic, sulphate-rich springs (Webster and Nordstrom, 2003). Selenium belongs to the typical ´geothermal suite´ of contaminants, which additionally includes As, V, B, F, Tl, Li, Hg, Sb and H_2S (Webster and Nordstrom, 2003). In continental environments the presence of As in geothermal fluids has been documented since the mid-19th century. However, the occurrence of Se received significant less attention. Some extremely high Se concentrations have been reported, but in general Se concentrations in hydrothermal waters are relatively low with values below the WHO guideline for drinking water of 10 µg/L (Table 6). This might be related to the presence of volatile Se compounds under reducing conditions, which are lost during sampling procedure (Conde and Sanz-Alaejos, 1997) or due to the immobility of reduced forms (Aiuppa et al., 2000b). In thermal groundwaters at Vulcano Island in Sicily Se is enriched in oxidized Cl-rich water and depleted in Fe-S rich waters (Table 5, Aiuppa et al., 2000b).

Table 6: Selenium concentrations in volcanic waters. For comparison: the WHO guideline for drinking water is 10 µg/L.

Location			Water type	Se concentration range (µg/L)	References
USA	Arizona, USA		Thermal waters	<2-256	Callender et al., 1977
	New Mexico, USA			<2-16	
				Up to 300	Summers, 1970
				10	Schulze-Makuch and Kennedy, 2000
	Yellowstone, USA			<1-9	Ball et al., 2008
Latin America	El Chicón, Mexico		Thermal waters and crater lake	0.1-54	Taran et al., 2008
	Póas volcano, Costa Rica		Crater spring	Nd-15	Martínez, 2006
			Crater lake	1-500	Martínez, 2009
	Estado Mèrida, Venezuela		Thermal waters	10.7±0.1	Burguera et al., 1966
	Guadeloupe, Lesser Antilles			Nd – 3	Floor, unpublished data
Africa	Limpopo, South Africa			Nd-1.66	Olivier et al., 2008
Europe	Germany			<2	Grosser and Heumann, 1988
	Hungary			<2	Bozsai and Karpati, 1989
	Catalonia, Spain			Most <1, one 620	De la Fuente et al., 1994
	Tenerife, Spain		Groundwater	Nd – 2.17	Rodríguez-Rodríguez, 2003
	Gran Canaria, Spain			Nd – 1.35	
	Italy		Thermal waters	<0.002-0.15	Dall´Aglio et al., 1978
	Vulcano Island, Sicily Italy	Oxidized	Thermal groundwater	1.5-237	Aiuppa et al., 2000b
		Reduced		0.8-16	
	Ischia, Southern Italy			0.6-150.8	Daniele, 2004
	Etna, Sicily Italy		Groundwater	0.6-66.8	Aiuppa et al, 2000A
	Vesuvius, Italy			Nd-24.1	Aiuppa et al, 2005
	Reykjanes , Iceland		Thermal water	0.46-0.83	Ólafsson and Riley, 1978
	Hekla, Iceland		Groundwater	Nd	Flaathen et al, 2009
Asia	Patuha volcano, Indonesia		Flank springs	Nd-1.87	Sriwana et al., 2000
			Crater lake	4.2-23	
	Asia unspecified		Thermal waters	6	Robberecht and Grieken, 1982
	Henan Province, China			<0.1-1.2	Haiyan, 2003
	China unspecified			1.33-1.38	Shaopu et al., 1990
Oceania	North Island, New Zealand			<6	Hirner et al., 1998
				<1	Vega et al., 2007
Ocean	East Pacific Rise			<0.02	Von Damm et al., 1985

Nd not detected

Selenium is scarcely included in trace element analyses of geothermal waters, probably related to the difficulties regarding sampling and measurements (Chapter 2). Thermodynamic modelling can also be used as a tool to estimate Se concentrations in original fluids. However, only a few studies exist on the extrapolation of equilibrium constants at elevated temperatures, which often lack thermodynamic data for metal selenides (D´yachkova and Khodakovsky, 1968; Xiong et al., 2003; Akinfiev and Tagirov, 2006). It is necessary to improve the understanding of Se in hydrothermal waters. Since continental and shallow-marine hydrothermal waters might be used by human for drinking water purposes and bathing (Fridleifsson, 2001; Lund et al., 2005), they might impact human health. Continental geothermal waters are additionally used for energy generation, which might lead to significant contamination (Czernichowski-Lauriol and Fouillac, 1991). A new emerging discipline deals with the industrial applications of bacterial communities. The ability to reduce toxic Se oxyanions to their less toxic elemental forms could play a future key role in bioremediation of highly polluted effluents. In addition, bacteria capable of reducing selenite could prove useful in the applied biometallurgy of Se. Selenium ores are rare and expensive, used extensively for their properties as semiconductors (Shpaisman et al., 2010). The high concentrations of metals and metalloids in fluids and mineral deposits surrounding vents at mid-ocean ridges make them an ideal location for the isolation of metalloid-resistant microorganisms (Rathgeber et al., 2002).

8.2 Volcanic aquifers

Selenium contents in groundwater are often below 1 µg/L and rarely exceed the WHO guideline of 10 µg/L. In contrast to the extensive database of As concentrations in aquifers, Se is often not included in the list of analysed elements. As a consequence, Se concentration data are scarce. Mobility of selenium in groundwater systems is directly related to 1) speciation in aqueous solution, 2) sorption properties of the aquifer substrate and 3) solubility with respect to solid phases. Its geochemical behaviour is often compared to that of As. However, in contrast to As, Se concentrations tend to be higher in oxidizing groundwaters because the dominant present Se (VI) is less prone to adsorption by metal oxides than Se (IV) (Plant et al., 2003). The particular characteristics of volcanic environments can cause an enrichment in trace elements in volcanic aquifers due to different mechanisms: i) magmatic gas input, ii) input of hydrothermal waters, iii) host rock weathering, iv) rain water input and v) leaching processes from soils and volcanic ashes. Direct gas inputs are an active mechanism in thermal waters. The thermal groundwaters at Vulcano and Ischia Islands (Southern Italy) are strongly enriched in Se with values above the WHO guideline of 10 µg/L (Aiuppa et al., 2000b; Daniele, 2004, Table 6). Around Mount Etna volcano the highest Se concentrations (66 µg/L) are observed where thermal saline brines from the sedimentary basement enter into the aquifer (Aiuppa et al., 2000a, Table 6). This shows that magmatic gas or hydrothermal water inputs can enrich aquifers in Se. However, as discussed in Section 8.1, not all thermal waters are enriched in Se.

Magmatic gas input (especially CO_2, e.g. Giammanco et al., 1998; Brusca et al., 2001) can additional enhance leaching from the host rock into water. Although this has often been mentioned to be a controlling factor in trace element composition of volcanic aquifers (Giammanco et al., 1998: Aiuppa et al 2000a,b; Flaathen et al., 2009), it is doubtful if this mechanism plays an important role in the Se distribution. As discussed in Section 3, total Se concentrations in volcanic rocks are low. Tamari et al (1990) showed that for basalts and gabbros less than 10 percent of the total Se was mobilized in contact with CO_2-bubbling water. Flaathen et al (2009) confirm that very low amounts of Se are mobilized during CO_2-rich fluid-basalt interaction in groundwaters around Hekla volcano (Table 6). Therefore, it seems that rock-water interaction is not an important process causing Se enrichment in volcanic aquifers. Nevertheless, the aquifer of Mount Vesuvius encouters intensive groundwater-gas-rock interaction and is enriched in Se (Aiuppa et al., 2005; Table 6).

As described in Section 4.3, rainwater can interact with volcanic gases and can therefore significantly be enriched in selenium (Calabrese, 2009). However, the Se mobility towards the aquifer depends from the processes during infiltration. Bellomo et al (2007) showed that around Mount Etna volcano the fluorine adsorption capacity of the andosols acts as a natural barrier that protects the groundwater system with around 60% of the atmospheric fluorine deposition being adsorbed on the soils. Volcanic soils can also have a high capacity for Se adsorption (Section 6). It has been shown that leaching from volcanic ashes can have an important influence on water sources, as discussed in Section 5.

The aquifers of Tenerife and Gran Canaria have, with average Se concentrations of respectively 1.78±0.50 and 1.84±0.78 µg/L (Table 6), a higher Se content compared to most other European countries. Nevertheless, the concentrations are below the WHO guideline. Most Se was present as selenite (Rodriguez-Rodriguez, 2003). The source of this Se has not been investigated. Selenium isotopes (Section 9.3) could be a useful tool to better understand the sources and reactions of Se in volcanic aquifers. As discussed for the atmosphere in Section 4.1, Se isotopes could give insight in the Se source within the aquifer and potentially separate between hydrothermal input, rock weathering and anthropogenic influences. Moreover, Se isotopes are sensitive for reduction processes within the aquifers (Johnson, 2004). Therefore, Se isotopes might significantly improve the understanding of the Se enrichment observed in some volcanic aquifers.

9 Volcanoes and health

As shown in Figure 3 and 7, there are different pathways how volcanic activity can impact human health: direct exposure, intake by drinking water and food consumption. Drinking water and food are traditionally considered as the most important sources of trace elements for humans. Soils and volcanic ashes actively act as determining factor in the chemical composition of groundwater and plants (Sections 5 and 6). Volcanic aquifers can be strongly enriched in Se with values about the WHO guideline for drinking water of 10 µg/L. However, for most volcanic aquifers Se concentrations are unknown (Section 8.2). Given the fact that Se has an important health effects and that it influences the As toxicity (Section 2) it is important to evaluate the Se content in more volcanic aquifers. Geothermal waters (Section 8.1) are also used for bathing, but the effects of dermal exposure to selenium-rich water remains unstudied.

In volcanic environments direct exposure could also play a significant role in trace element status. Inhalation of volcanic gases and ashes can affect human health, as respiratory problems have been reported around different volcanoes (Horwell and Baxter, 2006). It has also been shown that trace elements are enriched in urine after exposure to volcanic gas (Durand et al, 2004). Nevertheless, Se uptake during inhalation of volcanic gases has not been adequately measured. Although air around volcanoes is enriched in Se, in populated volcanic areas Se concentrations in air are expected to be below Se exposure limits in most cases. Populations live several kilometres from the crater and concentrations significantly decrease with increasing distance (Allen et al., 2000). Ash fall can readily affect a lot of people, because wide areas can be covered by ash fall-out (Witham et al, 2005), as illustrated by the 2008 eruption of the Chilean volcano Chaiten (Martin et al., 2009b) and the 210 eruption of the Icelandic volcano Eyjafjallajökull (Gertisser, 2010). However, the contribution of volcanic ash inhalation or ingestion on the trace element status in human populations remains unstudied.

Selenium is also an anti-carcinogen element (Section 2). A possible relation between volcanic activity and cancer has been studied in the geothermal area Rotorua in New Zealand (Bater et al., 2002) and at the Azores, Portugal (Amaral et al., 2006). Increased incidence rates of thyroid cancer have been reported in volcanic areas such as Hawaii, Philippines and Iceland and around Mount Etna (Kung et al., 1981; Arnbjornsson et al., 1986; Goodman et al., 1988; Truong et al., 2007; Duntas and Douman, 2009; Pellegriti et al., 2009). The mechanism by which the volcanic environment favours tumorgenesis is unknown. Different authors indicate the trace metals content of the drinking water as potential factor. However, the role of Se is unclear. Selenium has been proven to play a central role in cancer development (Patrick, 2004; Rayman, 2005). For example, it has been shown that cases with thyroid cancer have lower Se serum levels compared to a control group (Glattre et al., 1989). Therefore, the low Se bioavailability has been suggested as potential factor for the development of thyroid cancer in volcanic areas (Duntas and Douman, 2009). Nevertheless, a high incidence of thyroid cancer has been reported in the Etna area (Pellegriti et al., 2009), while Se levels in the drinking water in this area are high (Aiuppa et al., 2000a). Clearly, more studies are needed to investigate the relation between the Se status of populations and cancer incidence around volcanoes.

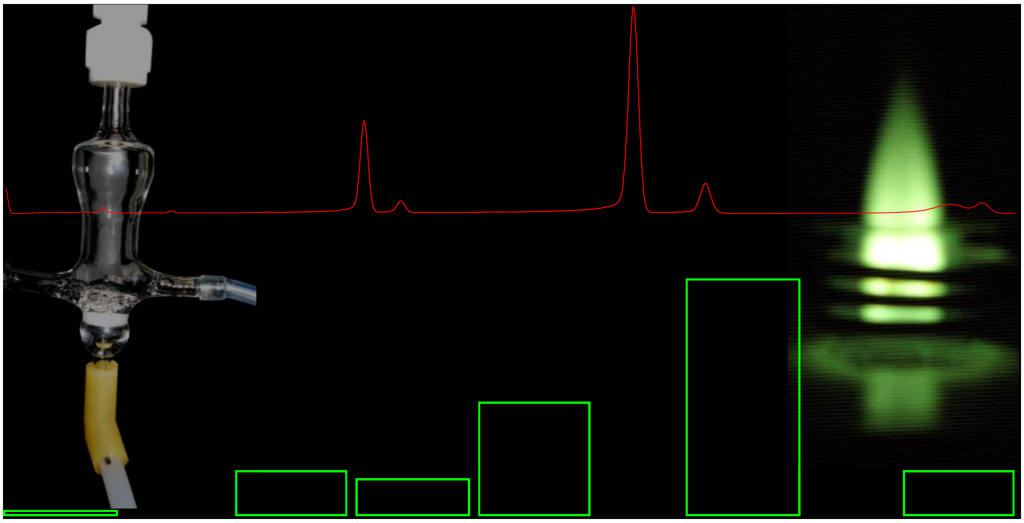
10 Concluding remarks

In this chapter I discussed the behaviour of Se within volcanic settings. The understanding of the Se cycle is also needed to evaluate how the health of populations is affected by volcanic-derived Se. Although Se and S chemistry are often compared, the existing data show a different behaviour compared to S in volcanic environments. A preliminary model shows that concentrations in volcanic rocks are in general low, because a significant amount of Se has been reported to be volatilized during volcanic activity. Selenium concentrations in gases are correlated with the temperature, suggesting more volatilization at higher temperatures. The interaction of volcanic gases with water strongly affects the rainwater composition. However, if is currently unknown how this impacts the aquifer, since this strongly depends on processes in the soils. Geothermal waters and volcanic aquifers have sometimes high Se concentrations, but the controlling processes are poorly constrained. Hence, there are several processes which require more investigation in the next future. Soils have a key position in the trace element cycle around volcanoes, forming a link between volcanic rocks, volcanic products released towards the atmosphere (gas and ash), plants and groundwater (Figure 1). Their physicochemical characteristics determine Se mobilization towards the aquifer and the uptake in food, and therefore have a major role in human health. Taking into account that 10% of the worldwide population lives within 100 km from an active volcano (Small and Neumann, 2001), it is essential to understand the processes affecting Se mobility in volcanic soils. Nevertheless, currently there is a very limited amounts of studies focussing on this topic (Section 7).

Therefore, in this PhD thesis I focused on the role of soils on the Se cycle in volcanic environments. Two contrasting volcanic settings have been studied. Mount Etna at Sicily (Italy) is an active volcano with continuous degassing and regular volcanic eruptions. Soils downwind from this volcano are regularly exposed to volcanic-induced acid rain and fresh ash input. Mount Teide at Tenerife (Spain) has a strong climatic gradient, caused by different exposure to the trade winds, the marine current, a thermic inversion layer and orography. Since Teide volcano had its most recent eruption in 1798, differences in weathering regimes rather than volcanic activity causes strong variations within the soils. The combination of these two sites allows the comparison of Se mobility in soils with a wide range of characteristics: from poorly-developed, ash-like soils around Mount Etna to highly weathered andosols at Tenerife Island.

Chapter 2

Analytical methods for selenium determinations in soils



1 Introduction

In Chapter 1, it was mentioned that a limited amount of Se data are currently available within volcanic environments. This is probably related to the fact that Se measurements are extremely challenging. Selenium concentrations are generally low in geological materials with a worldwide mean Se content in soils of only 0.4 mg/kg (Fordyce, 2005). This is up to 5 orders of magnitude lower than the content of major elements forming the main constituents within the soil matrix, such as Si, Fe, Al, Na, Ca and K. This complex matrix hampers analysis. Therefore, Se concentrations are often below the limit of detection (LOD) of standard techniques. Yet, recent advances in instrumentation have decreased the LOD to the lower µg/L range for waters and lower mg/kg range for solids. Additionally, analytical developments have opened the possibilities for Se speciation and isotopic determinations in environmental samples. The progress within the analytical field is probably one of the main reasons of increasing Se research interest in the last years. Although significant analytical development occurred in the last decades, most scientific work has focussed on the biological properties of Se and its analysis in biological samples. Geochemical studies represent only a small percentage of all published works. Recently there is a growing interest in the geochemistry of Se. Nevertheless, still a significant amount of analytical development is required to improve knowledge on Se cycling in volcanic environments. Moreover, it is essential to know the possibilities and limitations of current available techniques. This will help to prevent analytical errors, to obtain accurate Se data at low concentrations and to choose the most suitable analytical protocol. Therefore, the analytical methods for total Se, speciation and isotope ratio determinations will be discussed below. Sample preparation and chemical pretreatment before analyses is a critical aspect and will be explained too. Rather than giving a comprehensive review, the aim of this chapter is to provide the current relevant background for analytical methods used within this thesis.

2 Total selenium determinations

Solid samples can be measured directly or in solution after digestion. In Table 1, the most relevant analytical procedures published in the past decade for Se determination in soil samples are summarized.

2.1 Direct analysis

The advantage of direct techniques is that no sample decomposition is needed, avoiding the risk of contamination and Se volatilization. Moreover, the response of chemical treatment can strongly depend on the matrix and chemical Se form. Additionally, direct methods are often faster and cheaper compared to analyses of a soil digest. However, disadvantages are the strong matrix effects and calibration problems. Most techniques need matrix-matched standards, which can be difficult to obtain (Günther et al., 2001; Montaser, 1998). Direct analyses include Instrumental Neutron Activation Analysis (INAA), X-ray Fluorescence (XRF), Electron Microprobe Analyses (EMPA) and Laser Ablation (LA)-ICP-MS (Table 1). Moreover, after preparation of a slurry (thick suspension of the soil in a liquid) samples can be analyzed by Graphite Furnace Atomic Adsorption Spectrometry (GFAAS), Electrothermal Vaporization ICP-MS (ETV-ICP-MS) or Total reflection XRF (TXRF).

Table 1: Some literature from the last decade about analytical techniques for the Se determination in solids

Detection	**Details** (advantage/disadvantage)	**LOD (mg/kg)**	**Reference**
Direct analyses (prevents contamination)			
INAA	Irradiation 6 hr, cooling 21 d, measurements 0.5 hr (long analyses times)	0.1	El Ghawi et al., 2007
ED-XRF (lacks sensitivity)	Laboratory EDXRF	8	EPA/1540/R-06/002
	Field portable EDXRF, Miniature X-ray tube	6	EPA/1540/R-06/002
	Field portable EDXRF, isotope source	40	EPA method 6200
TXRF	Slurry preparation: Mo X-ray tube, 50 kV, 1 mA, Si detector (lacks sensitivity)	9	Stosnach. 2006
EMPA	Se Kα X-ray line, HV=25 kV, current 100 nA, spot size 20 µ (lacks sensitivity, spatial information can be obtained)	40-50	Jenner et al., 2009
LA-ICP-MS	Spot size 105 µm, laser repetition rate 10 Hz, wavelength 193 nm (sensitive for interferences, spatial information can be obtained)	0.02	Jenner et al., 2009
ETV-ICP-MS	Slurry preparation + electrothermal vaporization + dynamic reaction cell	0.02	Tseng et al., 2007
GFAAS	Slurry preparation with acid mixture: matrix modifier needed	0.12	Dobrowolski, 2001
Digestions			
ICP-MS (high argon consumption = expensive)	Octupole reaction cell to reduce interferences	0.07	Shand et al., 2010
	Hydride generation injection (prereduction needed; sensitive for interferences)	0.04b	Moor and Kobler, 2001
	High mass resolution to reduce interferences	?	Moor and Kobler, 2001
ICP-OES	Hydride generator (HG) (sensitive for interferences, only Se (IV))	<0.2a	Yadav et al., 2005
AFS	(Interferences with HG, only Se (IV))	0.005	Fordyce, 2000
HG-FAAS	(Interferences with HG, only Se (IV))	0.006	Terashima and Imai, 2000
GFAAS	Matrix modifier + Zeeman background correction (strong matrix effects)	0.003-0.006	Gonzalez-Nieto et al., 2005
Fluorescence spectrometry	DAN cheleater	0.002	Tan, 2002
Digestion + chemical pretreatment (time consuming)			
INAA	TCF, LOD depends on chalcophile element content	0.002-0.12	Savard et al., 2006
GFAAS	TCF, matrix modifier needed	0.02	Marin et al., 2001
ICP-MS	TCF, Reduction, Isotope dilution hydride generator	<0.006a	Wombacher et al., 2009
ICP-MS	Sintering, dissolution, cation exchange resin added, filtered	0.004	Bing et al., 2002
ICP-MS	Cation Exchange chromatography + reduction, Isotope dilution hydride generator	0.00001	Forest et al., 2009
AFS	Thiol cotton fibre preconcentration with hydride generation injection system	0.00004	Fan et al., 2008

a: lowest reported concentration.
b: procedural blank

Despite the high sensitivity of INAA, a nuclear reactor is needed for irradiation. Moreover, the analyses times are lengthy imposed by the long cooling periods for the decay of short-lived radioisotopes. This has restricted its use in Se determinations. In LA-ICP-MS a laser is used to vaporize the surface of a sample and this ablated material is carried into the ICP-MS. A big advantage is that spatial information can be obtained in this approach. However, interferences occur in the ICP-MS detection, as discussed in more detail in Section 5. Although this technique has been applied to soil analysis (Durrant and Ward, 2005), it has not been used for Se determination in soils. Nevertheless, it has been used for Se quantifications in volcanic glasses (Jenner et al., 2009), aerosols (Okuda et al., 2004) and fly-ashes (Spears, 2004). With EMPA also spatial information can be obtained. This technique has been used for Se determination in sulphide deposits (Auclair et al., 1987) and references glasses (Jenner et al., 2009), but lacks adequate detection limits for the application to uncontaminated soils.

X-ray fluorescence spectrometry is a popular technique for major elemental analysis in geological samples. In particular, the speed, accuracy, and versatility of XRF are the most important features that have made it a very mature analytical tool in this field. In-situ analysis with field-portable XRF equipment are possible and have become a common technique for on-site screening and fast turnaround analysis of contaminant elements in environmental samples (EPA 6200; Kalnicky et al., 2001). Nevertheless, the major shortcoming of Energy Dispersive XRF (ED-XRF) has been the poor elemental sensitivity. This is mainly a consequence of high background noise levels, resulting from instrumental geometries and sample matrix effects (Mukhtar et al., 1991). A reduction of spectral background can be effectively achieved by using Total reflection X-ray Fluorescence (TXRF) geometry. In this configuration, the primary beam strikes the sample at a very small angle (~0.1°) and the solid-state energy-dispersive detector is accommodated very close to the sample (~0.5 mm). Consequently, an improvement of detection power is achieved compared with conventional XRF (Klockenkämper, 1996). To perform analysis under total-reflection conditions, samples must be provided as thin films, depositing 5-50 µL of sample on a reflective carrier with a subsequent drying by applying heat or vacuum. Preparation of samples as thin layers excludes matrix effects, such as absorption and secondary excitation. As a result, the quantification in TXRF analysis can be done directly by the addition of an internal standard to the sample. One typical application field for TXRF is the analysis of aerosol filters (Schmeling, 2001; Dudzinska–Huczuk and Bolalek, 2007). Although reported, the analysis of soil and sediment samples by TXRF is less common (Stosnach, 2006). In a first approximation, the direct solid analysis can be reached by means of an adequate suspension followed by internal standardization (Fernández-Ruiz, 2009). Selenium determinations in soils have been performed only once by TXRF (Stosnach, 2006). In these on-site analyses of contaminated soils, a Se LOD of 9 mg/kg was obtained, which is significantly higher than the world wide average soil concentration (0.4 mg/kg, Fonovocs, 2007). Soil suspensions can also be analyzed by ETV-ICP-MS and GFAAS, in which soil slurries are vaporized for sample introduction (Dobrowolski, 2001; Tseng et al., 2007). However, matrix effects are strong in these approaches.

2.2 Soil digestion analyses

Since most direct analyses lack adequate LOD, common used techniques for Se determination in soils include inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS) and atomic fluorescence spectroscopy (AFS). These types of instruments are basically designed for the analysis of liquid samples, and thus, soil samples have to be brought into solution by means of a wet digestion procedure prior to the spectroscopic analysis. Nowadays microwave-assisted digestion is often preferred since this approach is rapid and reduces the risk of contamination and volatile loss. Different acid mixtures are used for total digestions, such as HNO_3:HCl (aqua regia, Martens and Suarez, 1997; Moor and Kobler, 2001; Gonzales-Nieto et al., 2005; Shand et al., 2010), HNO_3:H_2O_2 (EPA method 3051; Johnson 2000), HNO_3:HF (EPA method 3052; Yadav et al., 2005), HNO_3:HF:$HClO_4$ (Fordyce, 2000) and HNO_3:H_2SO_4 (Bujdos et al., 2005). The selection of the acid mixture should be based on the extraction efficiency and the suitability of the final matrix for the subsequent Se analysis with the selected technique.

Atomic absorption spectrometry can be either performed using a graphite-furnace (GFAAS, also called Electrothermal Atomization AAS (ETA-AAS)) or a hydride-generation injection system combined with Flame Atomic Adsorption Spectrometry (HG-FAAS) (Verlinden et al., 1981; D´Ulivo, 1997). The main drawback concerning the use of AAS when dealing with Se determination in soil samples is the presence of severe interferences that significantly hamper the analysis. During the hydride generation step, the reaction between the reducing agent and Se is subject to acute interferences. Especially the presence of transition metals and nitric acid (commonly used for soil digestions) leads to a significant signal suppressions (Verlinden et al., 1981). In addition, hydride generation is only sensitive for Se(IV), and thus, a reduction step is necessary if total Se has to be determined (Terashima and Imai, 2000). When using a graphite furnace, strong interferences occur during the atomization step and therefore background corrections and chemical modifiers are needed (Gonzalez-Nieto et al., 2005). Atomic fluorescence spectrometry is a very sensitive and selective technique with a high linear range (Cai, 2000). Since the availability of commercial AFS is relatively new, it has not yet been widely applied to geochemical studies. The system consists mainly of two parts, the hydride generator and the AFS detector (Fordyce et al., 2000). As for HG-AAS, the hydride generation step is susceptible to interferences. Since TXRF spectrometry is, in contrast to XRF systems, capable for the trace element analysis in liquid, soil digestions can also be measured with this technique (Stosnach, 2006). Nevertheless, this has not been commonly applied. During the last decades ICP-MS has become a popular technique for elemental determination, due to its sensitivity, accuracy, linear range and multi-elemental capacities. However, the measurements of Se by ICP-MS are not straightforward. Given the importance of ICP-MS in Se determinations and the extensive use of ICP-MS based techniques in this thesis, the analytical problems encountered with ICP-MS detection systems and its solutions are discussed in more detail in Section 5. Since the above techniques all suffer from matrix-derived interferences, sometimes chemical pretreatment is performed to eliminate Se from the sample matrix (Table 1, Section 6).

3 Selenium mobility

To understand the environmental implications of the Se in soils, chemical mobility must be considered as a more determining factor than total Se concentrations. Speciation analysis is the determination of individual physical-chemical forms (species) of elements present in the samples. Different definitions of speciation exist, depending on different levels of molecular structures. However, I refer to speciation as inorganic and organic compounds and their complexes. To refer to the elemental distribution in the solid phase and the identification of carries, I will use ´fractionation´. Nowadays, fractionation and speciation can be obtained using in-situ measurements by spectroscopy techniques. However, the fractionation of Se in soils has been traditionally employed using indirect methods such as specific or sequential extraction. This approach is still commonly applied. Additionally, several studies include the determination of Se speciation within soil extractions.

3.1 In-situ measurements

In the same way as in total Se determinations, direct measurements avoid the risk of chemical changes during extraction. This is extremely important in speciation and fractionation analysis, since extractions often lack selectivity and redox transformation can be easily induced (Section 3.2). Another advantage of direct analysis is that molecular-scale information can be provided by some in-situ spectroscopy techniques, such as X-Ray absorption fine-structure spectroscopy (XAFS), Fourier Transformation Infra-Red Spectrometry (FTIR) and Raman Spectrometry.

X-Ray absorption Spectroscopy (XAS), which includes X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Adsorption Fine Structure (EXAFS), is a powerful analytical tool that provides detailed information regarding the average electronic and molecular energy levels associated with a specific element. This permits determinations of oxidation state by XANES and coordination number, identification of nearest neighbours and bond lengths using EXAFS (Brown et al., 2006). Such data are crucial for understanding the geochemical properties and structure of complex minerals. Under optimal conditions speciation measurements can be obtained for trace elements in liquid and solid samples down about 10 mg/kg with or without spatial resolution (Martens and Suarez, 1997; Tokanuga et al., 1994). Taking into account that the average world wide concentration of soil Se is 0.4 mg/kg, this is a limiting factor in the XAS applications for most environmental samples. However, Se in sulphides and hydrothermal systems, where Se is strongly enriched, have been successfully studied by several authors using XAS methods (Ryser et al., 2005, 2006 and reference therein). Moreover, XAS is very useful to obtain insight in the processes controlling Se in soils under non-natural conditions such as adsorption processes on soils and pure mineral phases (Fernández-Martínez and Charlet, 2009). The development of microscopically resolved XAFS spectroscopy created new opportunities for interpreting speciation and spatial heterogeneity within natural and synthetic materials, since chemical and structural information can be obtained on the micrometer-scale typical of mineral grains or smaller (Kirpichtchikova et al., 2006, Cancès et al., 2008; Tokunaga, 1998, Fernández-Mártínez and Charlet, 2009). The disadvantage of XAS-techniques is the limited availability of sensitive apparatus.

Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. As a result, with the measured frequencies structural information can be obtained, including element speciation. Selenium investigations by FTIR have only been applied in geochemistry to study adsorption on pure mineral phases (Peak and Sparks, 2002; Su and Suarez, 2000; Wijnja and Schulthess, 2000). A disadvantage of FTIR is that the spectral region where the fundamental vibrations of SeO_4 appear can be obscured by the strong adsorption of the mineral lattice (Wijnja and Schulthess, 2000). Raman spectroscopy is a scattering technique that probes molecular and crystal lattice vibrations. Therefore it is sensitive to the composition, bonding, chemical environment, phase and crystalline structure. In environmental sciences, its use includes mineralogical identification and in situ examination of mineral surfaces. Moreover, investigations of aqueous systems are straightforward because water is only weakly Raman scattered (Wijnja and Schulthess, 2000). Nevertheless, since the general sensitivity in Raman studies is poor it cannot be applied to the low levels normally present in environmental waters. For this reason this technique has a large application in Se studies in material science and synthetic samples but its relevance in natural systems is limited.

The development of the new synchrotron generation with higher brightness and consequently greater spatial and time resolution will largely enhance the XAS, FTIR and RAMAN application in Earth Sciences. Integration of these beam facilities with new sample preparation protocols, complementary analytical tools (such as FTIR and Raman with high lateral resolution) and innovative sample environments (e.g. high temperatures, on-site kinetic experiments) will enable unique experiments. As Se is one of the most challenging elements for these analytical methods, geochemical studies on Se will significantly profit from these technical advances.

3.2 Chemical extractions

The fractionation of trace elements within soils can be investigated using reagents to selectively mobilize Se from different mineralogical fractions. However, sequential or specific extraction schemes have been widely criticised because they lack selectivity. In addition, re-adsorption and re-distribution can occur during the extraction and results are strongly influenced by the operating conditions, such as the extraction time and solid-to-liquid ratio (Bacon and Davidson, 2008). The complexity of the problem is reflected by the great variety of protocols that have been used in published studies and the diversity makes comparison of different studies impossible. Although for cationic species some attempts exist for the harmonization of sequential extraction procedures (e.g. BCR scheme, Hernandez-Moreno, 2007), no standard protocol is available for Se. Moreover, it has been shown that the sequential schemes devised for transition metals are not applicable to Se extraction (Weres et al., 1989). Some consensus exists on how to access the more labile forms of Se. However, there is less agreement on how to target the less mobile forms (Wright et al., 2003). Most Se sequential extraction protocols have been applied to soils with different characteristics from volcanic soils. Nevertheless, Nakamura et al (2005) have adapted a sequential extraction method for volcanic soils which included a separate extraction for Al and Fe oxides.

3.3 Speciation

The mobility of Se is also strongly influenced by its speciation. Selenium has a complex chemicistry in natural waters. Its speciation depends mainly on the pH and redox potential, influenced by the presence of reducing and oxidizing compounds. The most common Se species within surface waters and soils are selenite and selenate (Pyrzynska, 2002). Speciation analyses are even more demanding than total concentration measurements, since they involve the determination of individual species which are fractions of low total Se concentration (Gonzalvez et al., 2009). Although the impact of speciation on the environmental fate was already recognized early, it was not until the last decades that analytical advances have enabled Se speciation measurements at sufficiently low concentrations to be of true interest to environmental studies (Gonzalvez et al., 2009; B´Hymer and Caruso, 2006). Selenium speciation in solutions is currently measured primarily by the coupling of the different types of high performance liquid chromatography (HPLC), such as ion exchange, size exclusion, ion pairing liquid chromatography with a detector technique, for example ICP-MS (B´Hymer and Caruso, 2006). Most papers dealing with Se speciation measurements by HPLC-ICP-MS focus on biological samples rather than in environmental samples. Also some non-chromatographic methods exist for Se speciation determination (Gonzalvez, 2009). In these approaches, the chemical pretreatment (e.g. liquid-liquid extraction, Section 6.1) or measurement technique (e.g. those with a HG injection system, Section 5.1) is only sensitive for one specific form of Se. A sequential reduction can then be used to obtain information on the Se speciation (Gonzalvez, 2009). Similar results can be obtained by the selective retention on solids (such as silica gel, activated Al_2O_3 and nanometer sized TiO_2). Although these methods are often simple and cheap, the performance in complex matrices has not been evaluated and their sensitivity is generally inferior to the HPLC-ICP-MS technique.

A key issue in speciation analyses is to preserve the integrity of the samples, which is particularly challenging in complex chemical matrices (Wrobel et al., 2005; Hymer and Caruso, 2006; Gonzalvez et al., 2009). In volcanic environments, sample locations can be difficult to reach, making frequent sampling complicated. As a result, redox transformations can occur during sampling and storage. Species interconversion depends on the analyte itself (selenite is less stable than selenate, less stable at lower concentrations), the solution characteristics (pH, suspended matter, microorganism), the container (more adsorption on container walls in the case of polypropylene compared to Teflon) and external factors (species more stable at 4°C than at room temperature, storage time as short as possible, dark better than light; Cobo et al., 1994; Héninger et al., 1997). It has been shown that the transformation of selenite to selenate occurs at low pH in the presence of chloride (Héninger et al., 1997). This could be problematic in volcanic environments since samples are often acidic and chloride-rich. Moreover, volatile species of Se present under reducing conditions could be lost during sampling (Conde and Sanz-Alaejos, 1997). Pretreatment of samples is needed especially for chromatography to obtain a clear solution without microparticles (Gonzalvez et al., 2009). During this pretreatment analyte lost and/or species interconversion must be avoided. Speciation analyses of soil extractions have received growing interest (Séby et al., 1997; Jackson and Miller, 1997; Ponce de Leon et al., 2003). The major issue in this approach is that the extraction must not modify the speciation. Therefore, often weak extractions (i.e. hot water extraction) are used (Jackson and Miller, 1997; Séby et al., 1997; Ponce de Leon et al., 2003). However, these extractions generally only release a low percentage of the total Se (Séby et al., 1997; Ponce de Leon et al., 2003). Other extractions which have been measured for Se speciation include phosphate buffer extractions and basic extractions (Séby et al., 1997; Ponce de Leon et al., 2003). Soil extractions often have a complex matrix. For example, acidic extractions are rich in dissolved iron (Fe) and aluminium (Al), which can precipitate during chromatographic separation when the samples are adjusted to the mobile phase pH (Table 2). These precipitates form adsorption sites for selenite in particular (Balistrieri and Chao, 1990; Parida et al., 1997; Wijnja and Schulthess, 2000; Duc et al., 2003). In consequence, measurements can be biased by the decrease of total dissolved Se and by changes in the relative abundance of the Se species. Moreover, Fe oxides can induce Se redox transformations (Myneni et al., 1997, Scheinost et al., 2008) and the chromatographic column can be damaged. The problem of speciation change induced by the presence of Fe has received significant attention for arsenic speciation. In an attempt to prevent this arsenite oxidation several strategies have been developed, such as addition of inorganic acids (HCl, HNO_3, adsorbic acid, H_2SO_4, H_3PO_4) and/or ethylenediaminetetraacedic acid (EDTA) and the use of a cation-exchange resin, with varying success (Georgiadis et al., 2006; Sanchez-Rodas et al., 2006; Samanta and Clifford, 2005; Gault et al., 2005; Bednar et al., 2002). However, for Se speciation in acidic environmental samples such strategies have not been used (Orero Iserta et al., 2004; Ochesnkühn-Petropoulou et al., 2003; Séby et al., 1997; Ponce de Léon et al., 2003; Jackson and Miler, 1999 ; Bujdos et al., 2005). Moreover, the potential Al precipitation has not been evaluated in speciation studies. Since samples from volcanic settings are likely to have a low pH and high metal concentrations, this is a major issue in Se speciation analyses in these environments.

Table 2: Examples of mobile phase composition and pH in anion exchange HPLC-ICP-MS for Se speciation in environmental samples in the last decade.

Column	**Mobile phase**		**Reference**
	Composition	***pH***	
Hamilton PRPX-100	5 mM ammonium citrate + 2% MeOH	5.2	Bueno et al., 2007
Agilent G3154A/101	20 mM NH_4NO_3, 10 mM $NH_4H_2PO_4$	5-7	Chen et al., 2008
Hamilton PRPX-100	Gradient: NH_4NO_3/$NH_4H_2PO_4$ mixture	6.0	Tsoi and Leung, 2010
Dionex PA- 100	6 mM salicylic acid-sodium salicylate	8.5	Ponce de Léon, 2003
Hamilton PRPX-100	12.5 mM $(NH_4)_2HPO_4$ + 2% MeOH	8.5	Darrouzes et al., 2007
Hamilton PRPX-100	Gradient: 20-60 NH_4NO_3	8.7	Martínez-Bravo et al., 2001
Dionex AG-11	Gradient: 0-50 mM NaOH	11.7-12.7	Vassileva et al., 2001
Porous graphitic carbon	500 mM HCOOH (formic acid)	ns	Mazan et al., 2002
Dionex AS 11	Gradient*:* 1 mM NaOH + 2% MeOH, 0.5% TMAH.	ns	Ochesnkühn-Petropoulou et al., 2003
IonPac AS-16	Gradient: 10-100 mM NaOH	ns	Wallschlager and London, 2004
Dionex AS-11	20 mM sodium hydroxide	ns	Orero Iserta et al., 2004
Dionex AS-11	20 mM sodium hydroxide	ns	Bednar et al., 2009
IonPac® AS18	23 mM KOH	ns	Hu et al., 2009

ns= not specified

4 Selenium isotopes

4.1 Radioactive isotopes

The radioactive tracer ^{75}Se which has a half life of 119.8 days is used in Se studies for two reasons. Firstly, it can be used as less dangerous proxy for ^{79}Se, a nuclear fission product with a long half-life of 65000 years (Wang and Liu, 2005). Secondly, it is extremely suitable as tracer in adsorption studies (Nakamura et al., 2005; 2006; Nakamura and Sekine, 2008; Dhillon and Dhillon, 1999; Kamei-Ishalawa et al., 2007). The use of radioactive ^{75}Se has the advantage that low (natural) Se concentrations can be used and that the Se present in the system does not influence the results. After the experiments, the Se in solids or solutions can easily be quantified using a gamma counter. The disadvantage of this technique is clearly the special conditions needed and risks related to work with radioactivity. Moreover, it can only be used in lab controlled experiments and not for the determination of Se in natural samples. It has been previously applied to Se adsorption experiments in volcanic soils (Nakamaru 2005; 2006; Nakamaru and Sekine, 2008) and organic matter (Kamei-Ishakawa et al., 2007).

4.2 Fractionation of stable isotopes

Although isotopic abundances are fairly constant in nature, very small variations can occur (isotopic fractionation). Several isotopes of one element have to a large extent the same chemical behaviour. However, due to quantum-mechanical processes as a result of the difference in their number of neutrons (corresponding to a mass variation), the isotopes participate in a different extent in (bio)chemical reactions and processes (Vanhaecke et al., 2009). Therefore, it may be possible to learn about the chemical reactions inducing isotopic fractionation or paleoredox conditions through isotopic measurements. Alternatively, distinct isotopic signatures may enable tracing of various point sources through a system. Since the fractionation depends on the mass, the isotope ratios follow an empirical mass fractionation law. Although different laws exist to describe this mass fractionation, normally the exponentially law is used for Se (Rouxel et al., 2002; Clark and Johnson, 2008; Elwaer and Hintelmann, 2008b; Zhu et al., 2008). Mass-dependent fractionation has been traditionally investigated for light stable isotope such as H, C, N, O and S. There is a growing interest in the last years for ´heavy´ stable isotopes (elements heavier than S, such as Fe, Zn, Hg and Cr). Although their mass-dependent isotopic fractionation is generally smaller and therefore more difficult to measure, the potential geochemical applications are similar to those already established for the light stable isotopes (Johnson, 2004).

Since isotopic variations are small and relative, the variance is often expressed relative to the isotope ratio of a standard in terms of per mil (part per thousands, ‰) known as the delta notation. The Se isotopic variations are nowadays reported using the $^{82}Se\,^{/76}Se$ ratio relative to NIST SRM 3149 as the delta zero material:

$$\delta^{82/76}Se = 1000 \times (^{82/76}Se_{sample}/^{82/76}Se_{NIST\ SRM\ 3149} - 1) \quad (1)$$

Previous work has indicated natural variations up to 13‰ (Carignan and Wen, 2007 and references therein). Some typical values for several solids are given in Figure 1A. Selenium isotopic signatures can be used in two different ways (Figure 2). On one hand, they could be use to monitor redox transformations. Thereby, Se isotopic measurements might be a suitable alternative to speciation analysis to understand the redox transformations in volcanic environments. Previous studies show that fractionation occurs during reduction processes (Figure 1B). Therefore, reduction processes along a flow path in an aquifer or within a soil profile could be monitored using Se isotopic signatures. It is important to realise that kinetic isotopic effects are inherently dependent on the reaction path. In Figure 1B it can be for example observed that biotic and abiotic pathways reveal different fractionation. It means that results cannot be readily extrapolated to conditions who differ from the setting in which they are measured (Johnson, 2004).

On the other hand, oxidation reactions do not induce any fractionation. Since only oxidation processes are expected to occur in the atmosphere (Chapter 1), the atmospheric signature is a combination of the different input sources (Wen and Carignan, 2007). In such way, Se isotopes could be used to trace the contribution of different sources. For example, the isotopic signature within the atmosphere could reveal in more detail the contribution of volcanoes versus anthropogenic pollution (Chapter 1; Wen and Carignan, 2007). A similar approach could be used for aquifers. However, in this case care should be taken since reduction processes can also affect the isotopic variation.

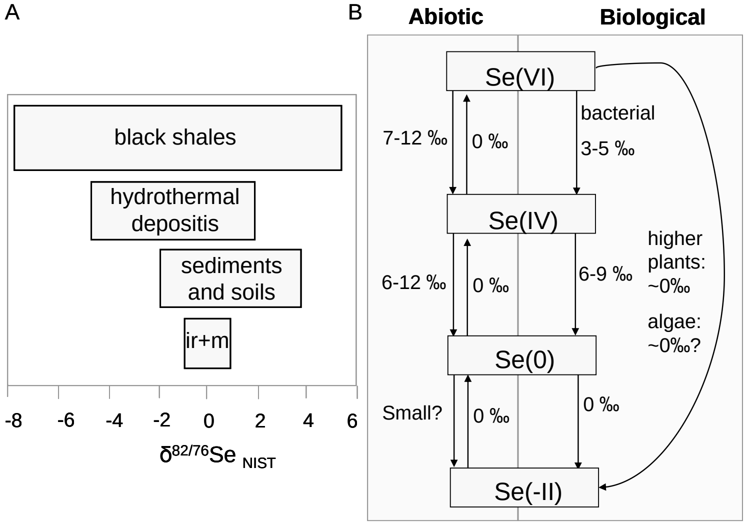


Figure 1: Current knowledge on Se isotope ratio systematics. A: observed fractionation in solids (after Carignan and Wen, 2007). Ir= igneous rocks. M=meteorites. B: expected fractionation during redox transformations (after Johnson, 2004).

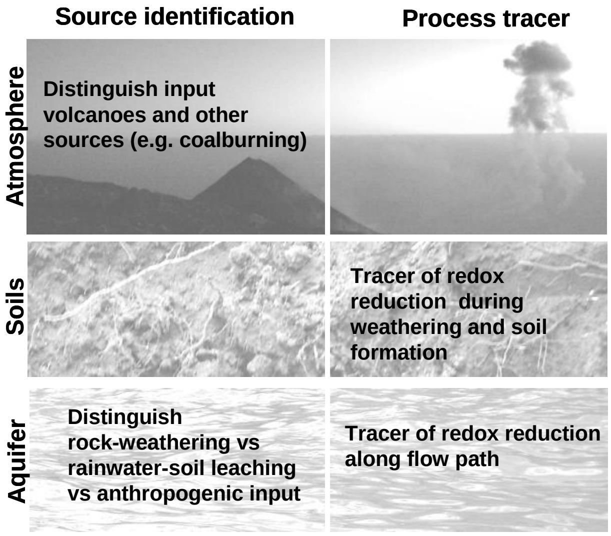


Figure 2: Potential applications of Se isotopic signatures in volcanic environments.

Since the geochemistry of Se is complex, the interpretation of Se isotopic signatures with the current knowledge on Se isotope systematics is still not straightforward. Nevertheless, Se isotopes have a high potential to better constrain the Se cycle.

4.3 Stable isotopic analysis

Selenium isotopes have a relatively long history of investigation compared to other ´heavy´ isotopes (Johnson, 2004). However, the recent development of multi collector ICP-MS (MC-ICP-MS) coupled with a hydride generator injection system (Rouxel et al., 2002) enabled the application to environmental samples. A MC-ICP-MS is a sector field mass spectrometer with several collector cups (Faraday cups). By collecting the different isotopes at the same time, the instrumental noise is reduced and the precision is increased. For isotopic analysis, precision is a key parameter, because the expected Se isotope fractionation is only a few per mil or less in many environmental settings. Current techniques obtain a precision of around 0.2 ‰ (Rouxel et al., 2002; Carignan and Wen, 2007; Clark and Johnson, 2008; Zhu et al., 2008).

Many analytical issues are similar for a MC-ICP-MS compared to a single collection ICP-MS. For example, similar spectral interferences exist (Section 5.3). However, isotopic analyses have some additional problems. One of these problems is instrumental mass bias. As a result of differences in the efficiency of ion extraction, transmission and detection as a function of analyte mass, an isotope ratio measured with ICP-MS may show significant bias with respect to the corresponding true value (Vanhaecke et al., 2009). For high precision isotopic analysis, the accurate correction of instrumental mass bias is essential. However, these corrections are not straightforward. Two different approaches exist to deal with this problem. On one hand an external standard with known isotopic composition can be used to calculate the correction factor based on the difference between the measured and true value. In this sample-standard bracketing each analyses of a sample solution is preceded and followed by a measurement of the isotopic standard (Rouxel et al., 2002; Carignan and Wen, 2007). A major disadvantage of this technique is that it only corrects for the instrumental mass bias and not any further mass discrimination induced by the sample preparation (Section 6). As an alternative, an internal standard can be used. To all solutions a spike solution containing two trace isotopes (^{74}Se and ^{77}Se) in a known ratio is added to the sample which allows correction for the mass bias (Clark and Johnson, 2008; Zhu et al., 2008; Elwaer and Hintelmann, 2008b). An advantage of this technique is that the spike can be added before sample purification and therefore it can correct for additional mass discrimination induced by the sample preparation.

5 Analytical issues in ICP-MS based techniques

Given the importance of ICP-MS based techniques within this thesis, analytical considerations such as sample introduction, analyte sensitivity and spectral and non-spectral interferences will be discussed in this section.

5.1 Sample introduction in ICP-MS

Sample introduction into the plasma plays a key role in the production of ions, and therefore in analyte sensitivity, interfering species and precision (Montaser, 1998). Liquid sample introduction is the most common means for presenting samples to plasmas. It results in excellent measurement accuracy and precision due to the ease of sample handling and calibration for quantification. The dispersion into fine aerosols before introduction into the ICP is essential for the analytical performance. Therefore, a wide range of nebulizers exist suitable for different applications, which optimize at different sample flows and vary in their tolerance of suspended and dissolved solids (Montaser, 1998). In this thesis, a Babington-type nebulizer was used for ICP-MS quantification measurements. The advantage of this nebulizer type is that it does not accumulate salts or clog with high dissolved solids samples, such as soil digests. However, disadvantages are that a peristaltic pump is needed causing signal variations and that the transport efficiency is not 100%. Therefore, for isotopic measurements often micro-concentric types nebulizers are used, which are based on self-aspiration and therefore give more stable signal intensity, eliminate contamination from pump tubing, have lower sample consumption and have a higher nebulisation efficiency limiting mass bias (Todolí and Mermet, 2006).

Introducing the sample into the plasma through the gas phase offers benefits over liquid aerosol introduction. The transport efficiency is nearly 100%, matrix interferences are nearly eliminated and the plasma energy can be more efficiently used for atomization and ionization, since no energy is required for desolvation and vaporization, which improves the LOD (Hwang et al., 1989; Muños-Olivas et al., 1995; Montaser, 1998; Rouxel et al., 2002). This approach is suitable for Se, since Se forms volatile hydrides at ambient temperature. Normally the acid-borohydride reaction is used for hydride-generation (Muños-Olivas et al., 1995; Rouxel et al., 2002). However, as discussed in Section 2.2, the hydride generation step is sensitive for interferences (Verlinden et al., 1981) and a prereduction step is necessary for total Se quantification (Terashima and Imai, 2000). Since the sample treatment prior to Se isotopic analysis eliminates these potential interferences (Section 6) and sensitivity is extremely important in Se isotopic analysis, this injection system is generally used in Se analyses by MC-ICP-MS (Rouxel et al., 2002; 2004; Carignan and Wen, 2007; Elwaer and Hintelmann, 2007; Clark and Johnson, 2008; Zhu et al., 2008). Also in this study this introduction system was used for Se isotopic measurements.

While ICP-MS based techniques generally require liquid samples for analysis, the analysis of solids can also be performed using laser ablation or electrothermal vaporization (Okuda et al., 2004; Spears, 2004; Durrant and Ward, 2005; Tseng et al., 2007; Jenner et al., 2009). Advantages are the reduced sampling handling, reducing time and contamination problems, and the possibility to obtain spatial information. Major concerns are the sample heterogeneity and the lack of primary standards needed for quantification (Montaser, 1998).

5.2 Sensitivity

Selenium has a limited sensitivity in ICP-based techniques due to its high ionization energy which results in a poor ionization yield (≈33%) in an argon plasma (Moellmer et al., 2007). Moreover, Se exists in 6 stable isotopes (74, 76, 77, 78, 80 and 82; Table 3) reducing the response of any individual mass (Moor and Kobler, 2001). The effect of a carbon-loaded plasma in order to enhance the analyte signal in ICP techniques has been evaluated by a number of authors (Muñoz-Olivas et al., 1995; Evans and Ebdon, 1990; Hu et al., 2004; 2005). These studies demonstrated that small amounts of carbon containing compounds enhance element signal. However, higher amounts of alcohol reduce this signal due to resultant cooling of plasma. To explain this enhancement, three mechanisms have been described: (1) charge transfer reaction from C^+-species to analyte atoms, (2) improvement in the nebulisation transport of the sample, and (3) shift of the zone of maximum ion density in plasma (Muñoz-Olivas et al., 1995; Hu et al., 2004).The enhancement of signal in the presence of alcohol depends on the ICP-MS operating conditions and on the volatility, mass and ionization potential of analytes and is higher for Se and As than for most other elements (Allain et al., 1991; Muños-Olivas et al., 1995; Hu et al., 2004; Roduskin et al., 2005). Both organic solvents added to the aqueous solutions or volatile carbon compounds introduced into the spray chamber can be used as carbon source. Although carbon addition has been frequently applied to Se concentration and speciation measurements, a carbon-loaded plasma has not been used in multi-collector ICP-MS. The sensitivity of Se strongly depends on the introduction system. For example, as discussed in 5.1, a hydride generator improves the transport towards the plasma and the ionization process. As a result, the HG injection system is another way to improve the Se sensitivity.

5.3 Spectral interferences

The main problem for Se determination by ICP-MS is that Se isotopes are seriously hampered by spectral interferences (Table 3). Four out of six Se isotopes overlap with common plasma-derived Ar-based polyatomic ions. Additionally, the complex matrix of volcanic soils makes the occurrence of other spectral interferences possible. In speciation analysis some of the matrix derived interferences, such as ZnO^+, $CaAr^+$, HBr^+ and $ArCl^+$, are resolved chromatographically since they are either not retained within the column or elute at different times than the Se species (Vassileva et al., 2001; Martínez-Bravo et al., 2001; Bueno et al., 2007; Darrouzes et al., 2007). In isotopic analysis the complex matrix is removed before measurements by sample preparation (Rouxel et al., 2002; Section 6). For element or speciation determination only the intensity of one single isotope (or two for quality control) is needed. In the case of isotope ratio measurements a minimum of two (using standard bracketing for mass bias correction) or four (using a double-spike for mass bias correction) are necessary. To plot the results on the mass fractionation line as control that interferences are well resolved, even one more interference free isotope is required. Moreover, in MC-ICP-MS interferences must be avoided completely or corrected for in high precision, since a small deviation in signal intensity has a significant impact on the Se isotope ratio.

Due to the presence of the Ar-based polyatomic interferences, $^{82}Se^+$ is the recommended mass for Se quantification using conventional quadruple ICP-MS (Pinho et al., 2005). Sometimes the intensity is corrected for potential interferences using mathematical corrections. De Boer (1999) corrected the presence of $^{34}S^{16}O_3^+$, $^{40}Ar^{42}Ca^+$ or $^{1}H^{81}Br^+$ using the following equation:

$$I(^{82}Se) = I(82)-f_1*I(34)-f_2*I(43)-f_3*I(81) \qquad (2)$$

where I is the intensity and f are empirically determined machine-dependent parameters reflecting the proportion of S, Ca and Br contributing to the interferent species at m/z^+ 82 (De Boer, 1999).

Table 3: Spectral interferences on Se isotopes.

	Selenium		**Interference**		**Resolution**	**Measurements problems**		
	Mass	**n/a**	**Ion**	**Mass**	**m/Δm**	**Total**	**Speciation**	**Isotope ratio**
74	73.9225	0.889	$^{74}Ge^+$	73.9212	56 951	Yes		Yes (Reagent)
			$^{36}Ar^{38}Ar^+$	73.9303	9474	Yes	Yes	Yes
76	75.9192	9.366	$^{36}Ar^{40}Ar^+$	75.9299	7084	Yes	Yes	Yes
			$^{38}Ar^{38}Ar^+$	75.9255	12 141	Yes	Yes	Yes
			$^{75}AsH^+$	75.9294	7438	Yes (more w/ CRC)	? (chrom.sep.)	Yes (several % of original As)
			$^{76}Ge^+$	75.9214	34 682	Yes		Yes
			$^{48}Ti^{14}N^{14}N^+$	75.9541	2176	Yes	No	No
			$^{60}Ni^{16}O^+$	75.9257	11700	Yes (sample)	No (constant)	? (cones, constant)
77	76.9199	7.635	$^{40}Ar^{37}Cl^+$	76.9283	9184	Yes	? (chrom.sep.)	Yes (small w/ HG)
			$^{76}SeH^+$	76.9270	10 796	No (same in stand.)	No (same in stand.)	Yes
			$^{36}Ar^{40}ArH^+$	76.9378	4311	No (small + constant)	No (small + constant)	Yes
78	77.9173	23.772	$^{38}Ar^{40}Ar^+$	77.9251	9979	Yes	Yes	Yes
			$^{77}SeH^+$	77.9277	7471	No (same in stand.)	No (same in stand.)	Yes
			$^{78}Kr^+$	77.9204	25 200	No (small + constant)	No (small + constant)	Yes
			$^{36}Ar^{40}ArH_2^+$	77.9456	2756	No (small + constant)	No (small + constant)	Yes (normally low)
			$^{39}K^{39}K^+$	77.9274	7710	Yes	No	No
80	79.9165	49.607	$^{40}Ar^{40}Ar^+$	79.9248	9689	Yes	Yes	+
			$^{79}BrH^+$	79.9262	8289	Yes (more w/ CRC)	? (chrom.sep.)	? (removed w/ sample prep)
			$^{80}Kr^+$	79.9164	570 832	No (small + constant)	Yes (small + constant)	Yes
			$^{32}S^{16}O_3^+$	79.9568	1 983	Yes	No	No
			$^{40}Ca^{40}Ar^+$	79.9250	9 452	Yes	No	No
			$^{64}Zn^{16}O^+$	79.9241	10 603	Yes	No	No
			$^{32}S^{16}O_3^+$	79.9568	1982	Yes	No	No
82	81.9167	8.731	$^{82}Kr^+$	81.9135	25 472	No (small + constant)	No (small + constant)	? (constant)
			$^{81}BrH^+$	81.9241	11 046	Yes (more w/ CRC)	? (chrom.sep.)	? (removed w/ sample prep)
			$^{40}A^{r40}ArH_2^+$	81.9404	3453	No (small + constant)	No (small + constant)	Yes
			$^{42}Ca^{40}Ar^+$	81.9210	19 033	Yes	No	No
			$^{40}Ca^{40}ArH_2^+$	81.9406	3424	Yes	No	No
			$^{46}Ti^{36}Ar^+$	81.9202	23 548	Yes	No	No
			$^{66}Zn^{16}O^+$	81.9209	19 274	Yes	No	No
			$^{34}S^{16}O_3^+$	81.9526	2281	Yes	No	No

n/a: natural abundance
CRC: collision-reaction cell
Yes: the interference causes problems in this type of determination
No: the interference is not a problem in this type of determination

The intensity at m/z$^+$ 82 is also used for arsenic interference corrections, to correct the signal of ArCl$^+$ at mass 77 for selenium content (Polya et al., 2003; Kershisnik et al., 1992; De Boer, 1999):

$$I(^{75}\mathrm{As}) = I(75) - \mathrm{R}(^{35}\mathrm{Cl}/^{37}Cl) * (I(77) - R\,(^{77}\mathrm{Se}/\,^{82}\mathrm{Se}) * I(^{82}\mathrm{Se})). \qquad (3)$$

where R is the ratio of natural abundances of the indicated isotopes. Nowadays, interference corrections are not often applied in the case of Se quantification since other analytical solutions are available (see below).

However, mathematical corrections are very common in isotopic analysis. Since the Ar dimer beams are significant and drift in the intensity occurs, an on-peak zero correction (blank correction) is unsuitable. Nevertheless, using the signals at 76, 78 and 80 and the isotopic occurrence of Ar dimers and selenium, the difference between blank and sample solutions can be corrected (Clark and Johnson, 2008; Elwaer and Hintelmann, 2008b, Zhu et al., 2008). SeH^+ interferences occur at m/z^+ 77 and 78. Although for concentration measurements this interference is not a problem because it is similar for samples and standards, in isotopic measurements its accurate correction is vital. This can be performed using the ratio I(83)/I(82) with I(83) being corrected for Kr. Even if Ge can be quantitatively removed from the sample matrix using sample preparation, reagents can contain some Ge (Rouxel et al., 2002; Layton-Matthews et al., 2005). Mathematical corrections can be performed using the intensity on m/z^+ 72 or 73 to calculate the Ge^+ contribution of m/z^+ 74 and 76 (Clark and Johnson, 2004; Elwaer and Hintelmann, 2008b; Zhu et al., 2008). Arsenic typically has a one or two order of magnitude higher concentration than Se in geological materials (e.g. Rouxel et al., 2002). Although most As can be removed during the sample preparation step using thiol-cellulose/cotton, several percent of the initial As could remain into the solution. In most samples As concentrations are so low after sample preparation that a correction is not required (Clark and Johnson, 2008; Rouxel et al., 2002; Zhu et al., 2008). However, for samples much more enriched in As than Se, such as shales and hydrothermal waters, interference correction is needed. The assessment of the AsH/As is not easy due to the overlap of AsH^+ with $^{36}Ar^{40}Ar^+$. However, the ratio can be approached using the intensity at m/z^+ 75 and the SeH/Se formation ratio. HBr^+ overlaps with Se isotopes at m/z^+ 80 and 82. However, only volatile species of bromide are transferred to the plasma using a hydride generator which can be removed in the samples by N_2 bubbling (Clark and Johnson, 2008; Zhu et al., 2008; Layton-Matthews et al., 2005; Carignan and Wen, 2007). Although m/z^+ 79 can be monitored as a control, HBr^+ corrections are normally not needed. The Kr interferences on 82 and 78 are normally corrected with an on peak-zero correction, since no difference is expected if samples and blanks are equilibrated with the atmosphere. Nevertheless, Kr can be monitored at m/z^+ 83 or 84 and corrected if needed (Carignan and Wen, 2007; Clark and Johnson, 2008; Elwaer and Hintelmann, 2008b).

There are several ways to reduce interferences in ICP-MS, such as the proper selection of an introduction system (Section 5.1), the use of a collision-reaction cell and high mass resolution sector field ICP-MS. Hydride generation, as commonly used in Se isotopic analyses, only transfers volatile hydride forming elements to the plasma. Thereby it excludes some sample derived spectral interferences. However, as can be observed in Table 3, several interferences can still occur. Carbon loaded plasmas show lower levels of interferences, related to the competitive formation of carbides (Evans and Ebdan, 1990; Hill et al., 1992; Muñoz-Olivas et al., 1995; Roduskin et al., 2005). The use of a cold plasma significantly reduces the intensity of argon dimers, but cannot be used for elements which have high ionization potentials such as Se (Boulyga and Becker, 2001).

Collision-reaction cells can be pressured with a small amount of gases, such as H_2, He, CO, CH_4 Ar, O_2 or a combination of them (Moor and Kobler, 2001; Moellmer et al., 2007, Boulyga and Becker, 2001). The collisions between these gases and the ion beam significantly reduce the occurrence of molecular interferences. This approach is frequently applied in concentration and speciation analysis in quadruple-based ICP-MS (Darrouzes et al., 2007; Chen et al., 2008; Shand et al., 2010). However, only one manufacturer supplies MC-ICP-MS instrumentation that uses a hexapole collision reaction cell (Vanhaecke et al., 2009), which limits its use in Se isotopic measurements. A disadvantage of the collision-reaction cell methodology is that, depending on the gas introduced, new interferences can form within the cell, as for instance HBr and SeH (Rouxel et al., 2002; Ogra et al., 2005). Therefore, in this case for concentration measurements $^{78}Se^+$ is monitored instead of $^{82}Se^+$. For Se isotopic measurements the cell is pressurized with Ar. Although this is less effective than H_2 in the removal of Ar dimers, it prevents the formation of new interferences. With this approach only minor contributions of Ar_2 exist at m/z^+ 76 and 78, allowing a simple blank-correction.

Since interferences often have different masses compared to those of the analyte isotopes, high mass resolution is another potential approach to resolve interferences. For this a sector field mass analyzer rather than a quadruple mass spectrometer is coupled to the ICP source. This approach enables a better resolution and better peak shape (Montaser, 1998). For high mass resolution measurements with a single collector sector field instruments both a narrow entrance slit and a narrow detector slit are used, resulting in separate peaks for the analyte and interferent with triangular shapes. Peaks are considered separated as long as they do not overlap in a mass spectrum by more than 10% of the peak intensities, measured in the valley which is formed between the peaks (Weyer and Schwieters, 2003, Figure 3B). Single collector high mass resolution has successfully applied to resolve Ar dimers, $ArCl^+$, $ArArH_2^+$ and carbon containing polyatomic ions from Se (Moor and Kobler, 2001; Wildner 1998; Feldman et al., 2000; Townsend, 1999; Krachler et al., 1999; Narasaki and Cao, 1996; Elwaer and Hintelmann, 2008a). The $^{40}Ar_2^+$ at m/z^+ 80 is so intense that a background remains (Wildner, 1998, Elwaer and Hintelmann, 2008a). High mass resolution can resolve interferences with a $m/\Delta m$ up to about 10,000. Consequently, as can be seen in Table 3, several matrix derived interferences cannot be resolved using this approach (e.g. elemental interferences and $^{46}Ti^{36}Ar^+$). Moreover, the sensitivity reduces significantly in the high mass resolution mode (Klaue and Blum, 1999; Figure 3).

On the other hand, high mass resolution measurements with a multi collector ICP-MS uses a different approach compared to single collector ICP-MS. For high precision isotopic measurements flat top peak shapes are essential. Moreover, multiple collector arrays are not easily fit with adjustable collector slits. Therefore, wider slits are used in conjunction with a narrow source slit, resulting in a configuration often called ‘pseudo-high mass resolution’. In this case, the analyte and interferent beams can be measured separately, but their peaks are not totally separated in mass scans. A peak plateau is obtained where, over a range of selected mass, only the analyte ions contribute to the signal (Weyer and Schwieters, 2003). The resolving power is defined as:

$$R_{power(5,95\%)} = \frac{m}{\Delta m^*} = \frac{m}{m(5\%) - m(95\%)} \quad (4)$$

where Δm is the mass difference between the points where the intensity of the peak changes from 5 (m(5%)) to 95% (m(95%)) of the maximum (Weyer and Swieters, 2003). The higher the resolving power relative to the mass resolution required to separate two ion species, the broader will be the flat plateau region, which represents the interference-free space between the ion beams. The resolving power has to be at least a factor of 2 higher than the required resolution to ensure a flat plateau section (Weyer and Swieters, 2003). The resolving power of a Neptune MC-ICP-MS (Finnigan, ThermoElectron) using the high mass resolution entrance slit is around 10,000-12,000. Although pseudo-high mass resolution has been recently applied to a range of elements (Weyer and Schwieters, 2003; Stenberg et al., 2004; Wiesser et al., 2004; Van den Boorn et al., 2006;Craddock et al., 2008), the performance of high mass resolution MC-ICP-MS has so far not been explored for Se isotopes.

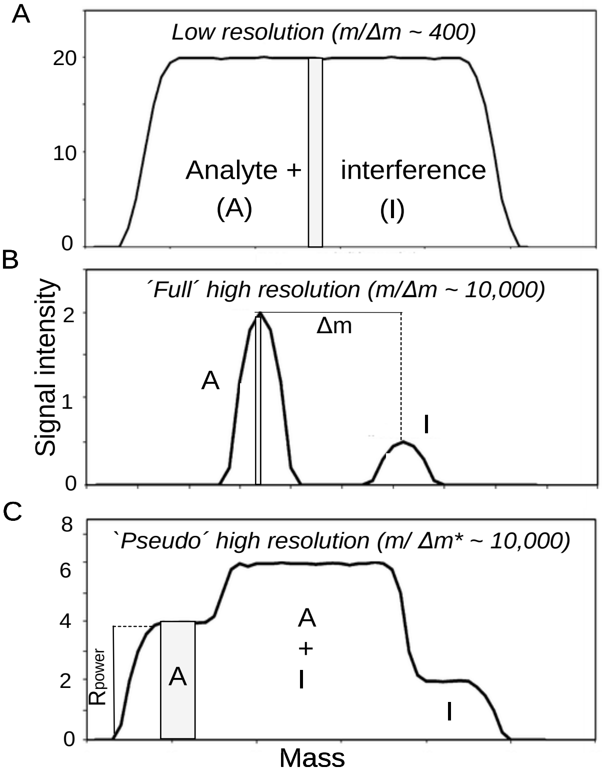


Figure 3: Ion beam profiles for A: low mass resolution, B: (full) high mass resolution (single collector) and C: pseudo-high mass resolution (multi collector). Adapted from Vanhaecke et al., 2009 and Weyer and Swieters, 2003.

5.4 Matrix effects

ICP-MS measurements are also sensitive for non-spectral interferences in complex matrices. In this case the calibration slope is affected by the other elements present. This can be corrected by the intensity differences of a suitable internal standard which is not occuring in the sample matrix (Vanhaecke et al., 1992; Leonhard et al., 2002;

Harris, 2006). Best results are obtained using an internal standard with a mass number close to that of the analyte element. The ionization energy of the internal standard has secondary importance (Vanhaecke et al., 1992). Nevertheless, the response of the internal standard and the analyte can be different. Therefore, as far as possible, it is better to use matrix-matched standards (Lin et al., 2000).

Another method to deal with matrix effects is standard addition, in which the concentration is determined by extrapolation of the intensities measured adding known amounts of analyte to the solution with unknown concentration (Leonhard et al., 2002; Harris, 2006). Although this technique corrects better for matrix effects (exactly same matrix effects and same analyte), it is time-consuming and usually gives a poorer precision. Another approach is isotopic dilution analysis (IDA), which relies on the intentional alteration of the isotope abundances of an endogenous element in a given sample by the addition of a known amount of an enriched isotope of the same element (spike). The element to be analysed must have at least two stable isotopes which are free of spectral interferences. Since the results only depends on the isotope ratio measured, instrumental instabilities such as signal drift or matrix effects will have no influence in the final value for the element concentration in the sample (Rodriguéz-Gonzaléz et al., 2005).

In isotopic analysis, mass bias depends on the matrix and analyte concentration. Therefore, isolation of the target element is a common practice in isotopic analysis in order to eliminate these matrix effects (Section 6). Especially for the standard-bracketing approach a constant matrix is essential, since impurities can bias the final isotope ratio (Barling and Weis, 2008).

6 Chemical pretreatment

As discussed above, the low Se concentrations in a complex matrix significantly hamper Se determinations. Therefore, pre-concentration techniques are often performed (Wake et al., 2004; Savard et al., 2006; Bing et al., 2002; Forrest et al., 2009). Sample pretreatment is one of the most critical steps in an analytical process, since they are very important for the LOD. For example, Gomes et al (2004) improved the Se detection limit by one to two orders of magnitude using a hydride generation pre-concentration step prior TXRF analysis. Sample pre-concentration steps often have the additional advantage that they eliminate the sample matrix. For instance, Aretaki and Kallithrakas-Kontos (2009) developed a methodology for trace Se determination in water samples using TXRF by collecting colloidal Se on quartz reflectors which eliminated the spectral overlap with bromine.

Most sample preparation treatments depend on the Se oxidation state in solution and are usually only effective for selenite. This means that for total Se concentrations, a prereduction step is necessary. However, it also implies that these methods can be used to obtain information on the Se speciation. For example, the adsorption process on the reflectors induced by adsorbic acid, as used by Aretaki and Kallithrakas-Kontos (2009) as pre-concentration step prior to TXRF analyses, is only sensitive for selenite. Therefore, a comparison of the results with and without sample prereduction reveals the abundance of selenite and selenate.

Chemical pretreatments tend to be slow and labour-intensive. Therefore, the simplification of pre-concentration techniques is critical. Although a range of chemical pretreatment techniques exist (Wake et al., 2004), I will focus in this section on liquid-liquid micro-extractions (LLME) and thiol cotton fibre (TCF) procedures. LLME is an emerging field, since these procedures are simple, inexpensive and fast. Moreover, they allow the use of relatively small sample volumes (mLs). Such an approach has been used in Se determinations combined with TXRF in this PhD thesis as described in Chapters 3 and 4. Thiol cotton fibre is often selected for chemical pretreatment in Se determinations, because of its high capacity for Se (IV) ions. It is discussed in more detail in this section, because TCF is commonly used prior to Se isotopic analysis.

6.1 Liquid–liquid micro-extractions

Liquid–liquid extraction (LLE) is a widely used sample preparation technique based on the principle that an analyte can distribute itself in a certain ratio between two immiscible solvents, one of which is usually water (aqueous phase) and the other an organic solvent (organic phase). Recently, three miniaturized methodologies have been developed in order to make such extractions easier, cheaper and more sustainable: single-drop micro-extraction (SDME), hollow fibre liquid-phase micro-extraction (HF-LPME) and dispersive liquid-liquid micro-extraction (DLLME). These pretreatment technique has been mostly applied to the analysis of organics (Ghambarain et al., 2010), but more recently also to trace metals determinations in water or biological samples (Anthemdis and Ioannou, 2009; Pena-Pereira et al., 2009; Rezaee et al., 2010; Dadfarnia and Haji Shabani, 2010).

In SDME a drop of immiscible extracting solvent (about 1–10 µL) is suspended from a syringe into a liquid or gaseous sample medium. After extraction the organic drop is retracted back into the micro-syringe and is injected to the detector for analysis (Dadfarnia and Haji Shabani, 2010). In SDME only a small fraction of the analyte is extracted (Pena-Pereira et al., 2009). Figueroa et al (2005) used in-situ photo-generation of Se vapours, headspace sequestration onto an aqueous micro-drop containing Pd(II) and subsequent analyses by GFAAS for trace level analysis of Se. This method was proven to be suitable for saline matrices, but interferences were observed for transition metals at a relatively low concentration. Since samples from volcanic environments are often rich in Fe and Al, this approach is therefore probably not appropriate for the application to such samples. Fragueiro et al (2006) used a hydride generation-headspace single-drop micro-extraction prior to GFAAS method for determination of selenium in waters. However, as discussed in Section 1, also the formation of hydrides is strongly influenced by the presence of transition metals.

In HF-LPME the analyte is extracted from an aqueous sample by a water-immiscible extractant immobilised within a hollow fibre, which prevents any loss of extracting liquid (Pena-Pereira et al., 2009; Dadfarnia and Haii Shabani, 2010). Xia et al (2006) used HF-LPME combined with electrothermal vaporization ICP-MS for the speciation of inorganic Se in environmental waters. The method has not been applied to other geochemical samples. Saleh et al (2009) developed a method based on the reaction of Se(IV) with *o*-phenylenediamine, extraction of the resulted piazselenol using HF-LPME followed by HPLC-UV analysis. The presence of up to 1 mg/kg of transition metals did not have any significant effect on the complexation and HF-LPME. However, soil digestions or acid soil leachates have much higher levels of transition metals. The effect on the performance of such high levels is unknown.

DLLME is based on the rapid injection of a mixture of an organic solvent with high density as extraction solvent (e.g. tetrachloride or nitrobenzene) and a high miscibility disperser solvent (such as ethanol or methanol) into an aqueous sample containing the analytes of interest. For ionic species, such as selenate and selenite, the addition of a complexing agent to the aqueous sample phase is needed to convert the analytes into neutral, lipophilic forms which are extractable into the organic phase (Dadfarnia and Haji Shabani, 2010). After centrifugation of the cloudy solution, the sedimented phase can be recovered and analyzed (Pena-Pereira et al., 2009). The great advantage of this procedure is that the equilibrium is reached quickly, due to the large surface area between extraction solvent (a few µL) and aqueous sample (a few mL), making the extraction almost time independent (Dadfarnia and Haji Shabani, 2010). Bidari et al (2007) used a DLLME procedure with ammonium pyrrolidinedithiocarbamate (APDC) as chelating agent, carbon tetrachloride as extraction solvent and ethanol as dispersant solvent combined with GFAAS analyses for inorganic Se speciation analyses in water. Another DDLME based on piazselenol formation due to the reaction with 4-nitro-*o*-phenylendiamine and gas chromatography–electron-capture detection also revealed excellent detection limits (Bidari et al., 2008). Both approaches were applied to the determination of selenium in environmental surface water samples with satisfactory recovery. However, the performance in more complex matrices remains untested.

6.2 Thiol cotton fiber

Thiol functional groups have been shown to have a high capacity for Se (IV) ions in a weak acidic medium. Retention capacities in the order of 7-9 mg/g have been found for thioglycollic impregnated cotton fibers (Elwaer and Hintelmann, 2008b). Therefore, TCF can be used as pre-concentration technique for Se. TCF has been used in pre-concentration step in combination with GFAAS (Marin et al., 2001), ICP-MS (Wombacher et al., 2009), AFS (Fan et al., 2008) and INAA (Savard et al., 2006; 2009). The advantage of the later approach is that since INAA can analyze solid samples, a desorption step is not needed.

Moreover, TCF is commonly applied as chemical pretreatment before isotopic analysis by MC-ICP-MS (Rouxel et al., 2002; Clark and Johnson, 2007; Elwaer and Hintelman, 2008b; Zhu et al., 2008). In order to keep mass bias as constant as possible, the sample matrix and Se concentration should be the same for all analyzed samples (Vanhaecke et al., 2009). Furthermore, elements that reduce the efficiency of the hydride generation step (transition metals) or form spectral interferences on Se isotopes (Ge and As) should be removed before Se isotopic analyses. TCF is suitable for this, since it has a high affinity for Se. Additionally, it has a low capacity for transition metals, which can therefore easily be removed from the sample matrix (Rouxel et al., 2002; Elwaer and Hintelman, 2008b; Zhu et al., 2008). Although TCF has an affinity for As (Yu et al., 2002), due to differences in the kinetics only several percent of the initial As concentration will be retained in the column (Rouxel et al., 2002; Elwaer and Hintelman, 2008b).

For both total Se and isotope ratio determinations, recovery yield is a key factor. If the method is not exhaustive it will underestimate the Se concentration. Moreover, the selective adsorption/desorption during sample purification can result in isotope fractionation. In general, reported yields for TCF are high (>85%) and isotope fractionation is not observed (Rouxel et al., 2002; Elwaer and Hintelmann, 2008b; Zhu et al., 2008). Most matrix elements, metal ions, organic compounds, and complexing reagents do not interfere with the quantitative adsorption on TCF (Yu et al., 2001; 2002). However, a high abundance of chalcophile elements could cause saturation of the TCF by occupying most of thiol group sites (Savard et al., 2006). Elwaer and Hintelmann (2008b) showed that the acid concentration in the feed solution had an significant effect on the recovery yield. Not only the adsorption, also the Se desorption from the TCF is an important step in the recovery (Elwaer and Hintelmann, 2008b). Most techniques use nitric acid to desorb the retained Se. In contrast, Wombacher (2009) eluted Se using ammonium hydroxide.

The effects caused by a non-total recovery could be corrected by isotope dilution (quantitative analysis, Rodriguez-Gonzaléz et al., 2005; Wombacher, 2009; Section 5.4) or by a double-spike (isotope ratio measurements, Elwaer and Hintelmann, 2008b; Zhu et al., 2008; Section 4).

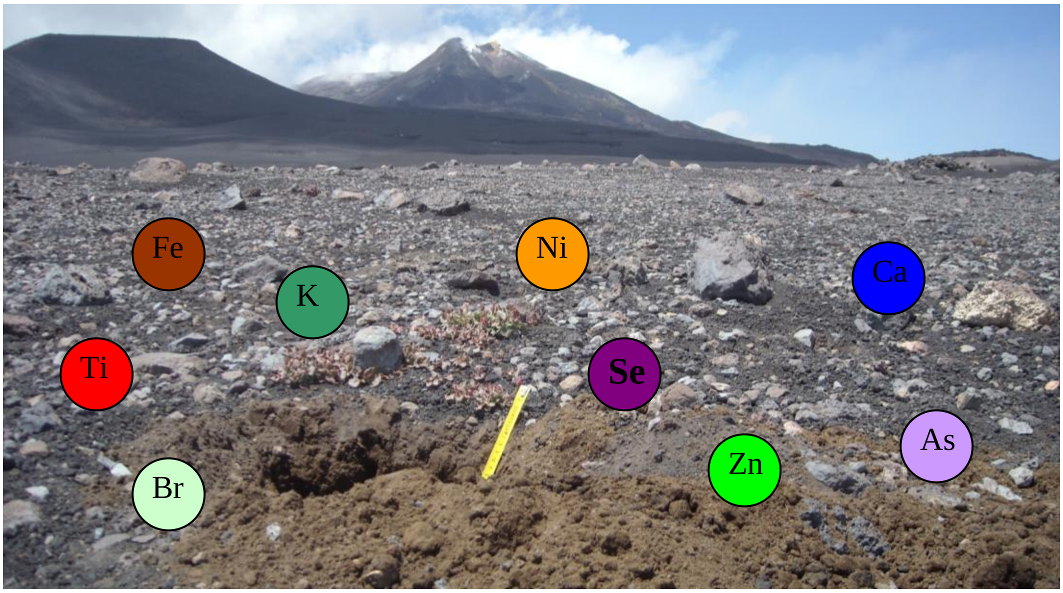
7 Concluding Remarks

The information summarized in this chapter clearly shows that Se determinations are not straightforward. Quantitative trace element measurements are nowadays primarily performed using ICP-MS. However, ICP-MS based techniques suffer from spectral interferences which significantly hamper the analysis. Although analytical tools such as a collision-reaction cell eliminate the Ar-based polyatomic ions, they can also generate new interferences. A systematic study of the effect on measurement conditions in complex matrices such a soil digests is currently lacking. Moreover, there might be other techniques which are suitable for Se determination in complex samples. For example the application of TXRF for Se determinations in geochemical samples have been scarcely explored. Selenium speciation measurements have undergone a significant development in the last decades. Nevertheless, analyses in complex matrices are still challenging. For volcanic environments the adaption of existing Se speciation protocols for the application to acidic samples rich in Fe and Al is especially required. Selenium isotope determinations can be applied to low concentration environmental samples since the development of MC-ICP-MS. Even so, the process of obtaining corrected isotope ratios should be simplified. Also the power of chemical pretreatment before analyses to pre-concentrate Se and eliminate the matrix elements, should be explored in more detail for complex samples.

Clearly the development of new analytical techniques and protocols adapted to Se determinations in complex samples are the key for a more profound understanding of Se cycling within volcanic environments. Therefore, a significant part of this thesis will deal with the development of new analytical protocols for Se determinations in soils.

Chapter 3

Total selenium determination in volcanic soils



G.H. Floor, M. Iglesias, G. Román-Ross. 2009. Selenium determination in volcanic soils by ICP-QMS: influence of reaction cell pressurization and methanol addition on the occurrence of spectral interferences *Journal of Analytical Atomic Spectrometry* **24**, 944 - 948.

E. Marguí, G.H. Floor, M. Hidalgo, P. Kregsamer, G. Román-Ross, C. Streli, I. Queralt, 2010. Analytical Possibilities of Total Reflection X-ray Spectrometry (TXRF) for Trace Selenium Determination in Soils. *Analytical Chemistry* **82(18),** 7744-7751.

1 Introduction

Selenium (Se) determination in soils is a critical issue in geochemistry due to the active role of soils in the selenium biogeochemical cycle and the narrow range between essential and toxic concentrations (Foster and Sumar, 1995; Hartikainen, 2005). However, Se determination in soil samples are difficult because of its low concentration (e.g., worldwide mean concentration of Se is ~0.4 mg/kg, Fordyce, 2005) and the complexity of the matrix. During the last decades ICP-MS has become an accurate and sensitive technique for elemental determination. However, as explained in Chapter 2, Se measurements by ICP-MS are not straightforward because of limited Se sensitivity and the formation of spectral interferences. Due to the presence of Ar-based polyatomic interferences, $^{82}Se^+$ is the recommended isotope to use in conventional ICP-MS (Pinho et al., 2005). The 82 isotope is also used for arsenic interference corrections, to correct the signal of $ArCl^+$ at m/z^+ 77 for Se content (Polya et al., 2003; Kershisnik et al., 1992; De Boer, 1999; see Chapter 2). Collision-reaction cells, which remove interfering ions via collisions or chemical reactions by introducing a small amount of gas have been successfully applied in Se determinations (Moor and Kobler, 2001; Moellmer et al., 2007, Boulgya and Becker, 2001). However, new interferences, as for instance HBr (Ogra et al., 2005), can form within the cell. Therefore in this approach often $^{78}Se^+$ is monitored. On the other hand, the effect of organic solvents on the analyte signal in ICP-MS has been evaluated by a number of authors (Muñoz-Olivas et al., 1995; Evans and Ebdon, 1990; Hu et al., 2004; 2005). These studies demonstrated that small amounts of carbon containing compounds enhance element signal and reduce the formation of polyatomic ions.

An alternative technique for Se determination in soils is Total reflection X-ray Fluorescence (TXRF). Although X-ray Fluorescence (XRF) spectrometry is a popular technique for elemental analysis in geological samples, its application to Se determination in environmental samples is limited due to it poor sensitivity. TXRF has an improvement of detection power compared with conventional XRF as result of a reduction of the background achieved by a different instrumental geometry (Klockenkämper, 1996). In this sense, TXRF is capable for trace element analysis in liquids. Up to now, TXRF has been mostly applied for the determination of trace elements in water samples (Stoessel and Prange, 1985; Prange et al., 1987; Barreiros et al., 1997). Suitable limits of detection (LOD) have also been achieved for the determination of Se in biological samples with and without recourse of pre-concentration strategies (Bellisola et al., 1999; Griesel et al., 2006; Stosnach, 2010). However, relatively few papers exist about Se analysis by TXRF in geological samples (Juvonen et al., 2009).

In this chapter an evaluation of the performance of ICP-MS and TXRF for total Se determinations in soils is presented. The focus is on volcanic soils, but principles are similar for other soil types. For ICP-MS the occurrence of spectral interferences on Se isotopes were evaluated in volcanic soil digestions. Although it is known that interferences can occur during Se determinations, a systematic evaluation of potential interferences under different measurement conditions in soils is missing. The suitability of using a pressurized Octupole Reaction System (ORS), the analyte-interference ratio for the different Se isotopes as well as the presence of small amounts of alcohol in synthetic solutions and real samples have been studied in order to develop a simple procedure to determinate Se in this sample type. Afterwards, the possibilities of TXRF for trace selenium determination in soils as a possible analytical alternative were explored. Direct analysis of soil suspensions were compared with the analysis of digested soil sample. In the latter case, several fast and simple chemical strategies were developed to improve the LOD for Se determination. On one hand, the application of a liquid-liquid extraction procedure using ethyl ether and the introduction of a chromium (Cr) absorbent in the instrument configuration were carried out to avoid the associated problems on TXRF analysis of soil extracts due to high Fe concentrations. On the other hand, the applicability of a Dispersive Liquid Liquid Micro-Extraction (DLLME) procedure to isolate Se from the soil matrix has been tested, since the micro-analytical capability of TXRF spectrometry is very suitable for this approach. The LODs and accuracy were carefully evaluated to test the real capability of the developed TXRF methodologies for the intended purpose.

2 Experimental Section

2.1 Reagents and Materials

Stock solutions of 1000 ± 0.5 mg/L (Spectroscan, TECKNOLAB A/S, Norway) were used to prepare standard solutions, spiked samples and synthetic solutions. High purity water used for dilution of stock solutions and samples was obtained from a Milli-Q purification system (Millipore Corp., Bedford, MA). The commercial nonionic surfractant Triton X-114 (poly(ethylene glycol) *tert*-octylphenyl ether), ethyl ether (>99.9%), ethanol (absolute, >99.5%), carbon tetrachloride (>99.5%), APDC (>99%) and methanol (chromsolv plus, >99.9%,) were purchased from Sigma-Aldrich (Spain). Concentrated hydrochloric acid (Trace Select) was obtained from Fluka, Germany. For microwave assisted sample digestion, analytical grade suprapur quality nitric acid (67-69% Romil SpA, Se < 0.1 mg/kg) and hydrogen peroxide (30%, Merck SpA) were used.

For ICP-MS analyses synthetic solutions with three different concentrations of respectively Zn, Ca, Br, As, K and Ti were prepared in realistic amounts for volcanic soil digests (Table 1), based on the COST 622 database of European volcanic soils (Martínez-Cortizas et al., 2007) and a digestion dilution factor between 100 and 200. All synthetic solutions contain ~5 µg kg^{-1} of Se and Rh internal standard. Two batches of all the solutions have been prepared; one in a matrix of 1% nitric acid, the other in a matrix of 1% nitric acid and 2 % methanol (MeOH). To introduce the sample into the TXRF equipment quartz glass discs with a diameter of 30 mm and a thickness of 3 ± 0.1 mm were used as sample holders. A Cr foil of 25 mm x 25 mm, 10 μm thickness, 99.9% purity with a permanent support of polyester was tested as an absorber between the sample and the TXRF detector to decrease the Fe signal entering the detector when analyzing soil extracts.

Quality assurance was carried out using the certified reference material JSAC-0411 (“Volcanic ash soil”, Japan Society of Analytical Chemistry, Shinagawa, Tokyo, Japan). The Se content of this soil is certified to be 1.32±0.27 mg/kg. The ICP-MS procedure has also been applied to the Se determination in two different volcanic soils (air-dried, <2mm): S1 from Tenerife and S2 from Sicily.

Table 1: Elements with potential polyatomic interferences on Se isotopes, their concentrations in soils (Martínez-Cortizas et al., 2007) and the elemental concentrations used in this study assuming a dilution factor of 100 to 200.

Elements	**Concentration soils (solid phase) mg/kg**		**Concentration synthetic solutions (´soil digestion´) mg/L**		
	Min	**Max**	**Low**	**Intermediate**	**High**
Ca	500	90000	30	100	1000
K	5000	90000	20	200	1000
Ti	2000	100000	10	100	1000
Br	3	700	0.6	7	70
Zn	40	200	3	7	20
Ni	1	400	0.03	0.3	4
As	3	30	0.02	0.1	0.5
Cl	0.13	0.32	-	-	-

2.2 Sample Treatment Procedures

2.2.1 Soil sample digestion

Microwave digestion of soil samples was performed according to the EPA method 3051 (method 3051, US Environmental Protection Agency, 2008) using 0.4 g of soil and an acid mixture of 10 mL of HNO_3 and 2 mL of H_2O_2 in Teflon beakers. This microwave program was also adapted for mass limited samples using 0.1 g of soil, 2.5 mL of HNO_3, and 0.5 mL of H_2O_2 in quartz vessels. For ICP-MS analyses the solutions have been diluted to 50 ml with high purity water (Millipore corp., Bedford, MA, USA) after cooling. Internal standard Rh (5-6 µg/kg) and sometimes MeOH (~2%) have been added to aliquots of these solutions. For TXRF analyses solutions have been used without dilution.

2.2.2 TXRF analyses of soil suspension

To prepare slurries 1 mL of the dispersant solution was added to 20, 50, and 100 mg soil. In the present study, solid suspensions using high purity water or diluted solutions (1% and 10% in high purity water) of a commercial non-ionic surfactant (Triton X-114) were tested as dispersing agents. Then, Ge was added to the slurry sample for internal standardization (final Ge concentration 0.5 mg/L). The resulting mixture was thoroughly homogenized (Vortex device) and an aliquot of 5 μL was transferred onto a quartz glass sample carrier and left to dry at room temperature under a laminar flow hood before TXRF analysis. Finely ground soil material is necessary to obtain reproducible and quantitative results in the TXRF analysis of soil suspensions.

2.2.3 TXRF analyses on soil digest

For the direct TXRF analysis of soil extracts, again Ge was used for internal standardization and added to 0.25 mL of the soil digest (final Ge concentration of 0.5 mg/L). After homogenization, an aliquot of 5 μL was transferred onto a quartz glass sample carrier and dried as for solid suspensions before TXRF analysis. To remove Fe from soil extracts, a liquid-liquid extraction procedure using ethyl ether was carried out (Dulski, 1996). For that, 100 µL of concentrated hydrochloric acid was added to 0.5 mL of soil extract to form the corresponding Fe-chloro complex. Then, 0.5 mL of ethyl ether was added, and the mixture was manually shaken for 2 min. Following the extraction, the mixture was allowed to stand for 10 min for phase separation. Afterwards, the upper organic layer (containing the Fe-chloro complexes) was discarded. This extraction procedure was carried out twice to improve the extraction efficiency. A dispersive liquid-liquid micro-extraction procedure (DLLME) using APDC as complexing agent was employed to separate and pre-concentrate Se from soil extracts. Taking into account that the developed DLLME procedure is only effective for Se(IV), a reduction step of the sample was necessary (Bidari et al., 2007). For that, soil digests were evaporated to incipient dryness at a temperature of 70 °C in Teflon beakers. Afterward, a 6 M hydrochloric acid solution was added, and the sample was heated to ~90 °C for 90 min in closed beakers. After cooling, the sample was diluted with water to the initial volume (final matrix 1 M HCl). To perform the DLLME procedure, 2 mL of the reduced soil extract was placed in a pre-cleaned conical glass. Then, 0.5 mL of ethanol (dispersant solvent), 0.1 mL of carbon tetrachloride (extraction solvent) and 100 mg APDC (chelating agent) were mixed and rapidly injected into the sample solution. The mixture was then centrifuged at 3500 rpm for 1 min to achieve phase separation. After this step, 10 µL of the carbon tetrachloride sedimented at the bottom of the conical test tube, which contains the Se-APDC complex, was deposited onto a quartz glass sample carrier and left to dry at room temperature under a laminar flow hood. Finally, 5 µL of a 1000 ± 0.5 mg/L Y solution was added on the dried sample and left to dry at room temperature under a laminar flow hood before TXRF analysis. In Figure 1, a scheme of the DLLME procedure is displayed.

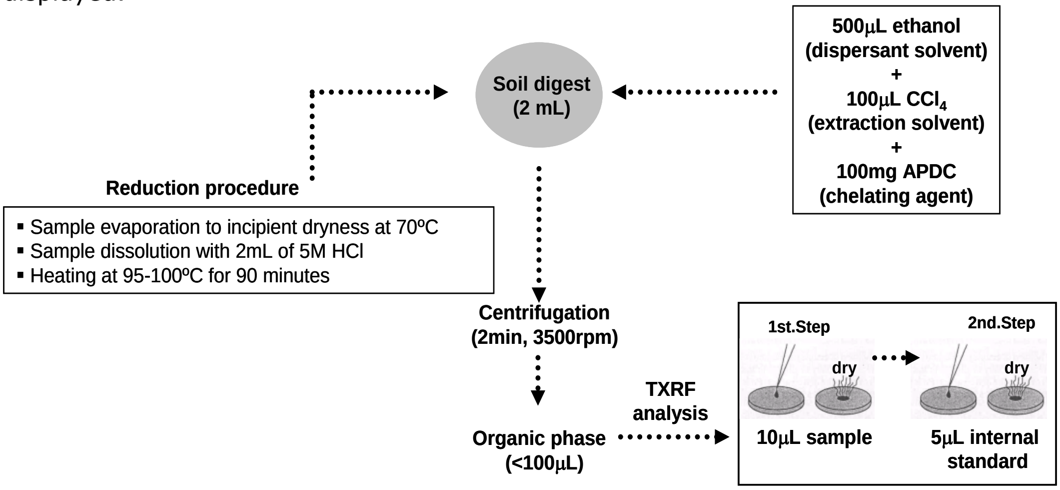


Figure 1: Scheme of the dispersive liquid-liquid extraction (DLLME) procedure used for Se determination in soil digest by TXRF

2.3 Equipment and Instrumentation.

2.3.1 ICP-MS

All data were collected on an Agilent 7500c ICP-QMS. The detected isotopes were $^{76}Se^+$, $^{77}Se^+$, $^{78}Se^+$ and $^{82}Se^+$ for the Se determination and ^{103}Rh as the internal standard. The ICP-MS was tuned daily for highest sensitivity and lowest CeO/Ce ratios (<0.9 and <1.3% in vented/pressurized conditions respectively). The plasma was operated at 1.5 kW with 15 L min^{-1} plasma gas and ~1.0 aerosol carrier gas. Data acquisition was done with 0.5 s dwell time for each isotope and 5 replicates. All solutions have been measured both in the conventional ICP-MS configuration (vented ORS) and with a pressurized ORS. In pressurized conditions 4.0 ml/min of H_2 was used.

2.3.2 TXRF

The TXRF analyses were performed using a TXRF 8030C spectrometer (Atomika Instruments GmbH), equipped with a 3 kW X-ray tube with a Mo/W alloy anode and a double-W/C multilayer monochromator, adjusted to obtain an excitation energy of 17.4 keV (Mo Kα). The characteristic radiation emitted by the elements present in the sample was detected by a Si(Li) detector with an active area of 80 mm^2 and a resolution of 150 eV at 5.9 keV. The measurements were performed working at 50 kV, and the current was adjusted automatically as a trade-off between the detector dead time and total analysis time. A fixed acquisition time of 500 s was used.

3 Results and Discussion

3.1 ICP-MS analyses of synthetic solutions

The interference (*Int)* for the different synthetic solutions measured with vented conditions is shown in Figure 2a. The interference is expressed as the quotient between the measured ratio (analyte/internal standard) in the solution (R_{SOL}) and the expected ratio (R_{Se}): *Int* = R_{SOL}/R_{Se}. The expected ratio was estimated using the Se concentration, the ratio observed in Se standards for m/z^+ 82 and 78 in vented and pressurized conditions respectively and the isotopic abundance. If no interference occured, both ratios are equal and *Int* will equal one. Concentrations of the synthetic solutions increase across the x-axis for each isotope (see Table 1). Nickel and potassium data were not included because their isotopes show no interference different to that coming from argon dimers. Although $ArCl^+$ is a well-known interference in natural samples (Polya et al., 2003; Kershinik et al., 1992; De Boer, 1999), the concentrations are very low (<10 μg kg^{-1}) in volcanic soil digestions (Table 1; Martínez-Cortizas et al., 2007). A solution containing only 5 μg/kg of Se is shown for comparison purposes. The isotope ratio between the excess counts on 76 and 78 and the isotope ratio of Ar clearly demonstrated the occurrence of ArAr ions at m/z^+ 76 and 78. The solutions with methanol (dots) showed lower *Int* than those without the addition of MeOH (lines) due to the Se signal enhancement and the reduction of polyatomic interference itself. Besides the argon dimers, the most abundant interference in the measurements occurred on m/z^+ 82 in the Br-containing solution, related to $^1H^{81}Br^+$. Therefore, the $^{82}Se^+$ isotope is not appropriate to use for Se determination in soils with Br (almost all soils).

The interferences for several elemental solutions using a H_2-presurrized ORS are shown in Figure 2B. The presence of H_2 in the ORS increases the formation of $^1H^{81}Br^+$ (Ogra et al., 2005), causing already small interferences with Br traces. The presence of HBr^+ was confirmed by similar excess counts on 80. Strong interferences occurred in the Br containing solutions. Calcium also produced an interference on m/z^+ 82.

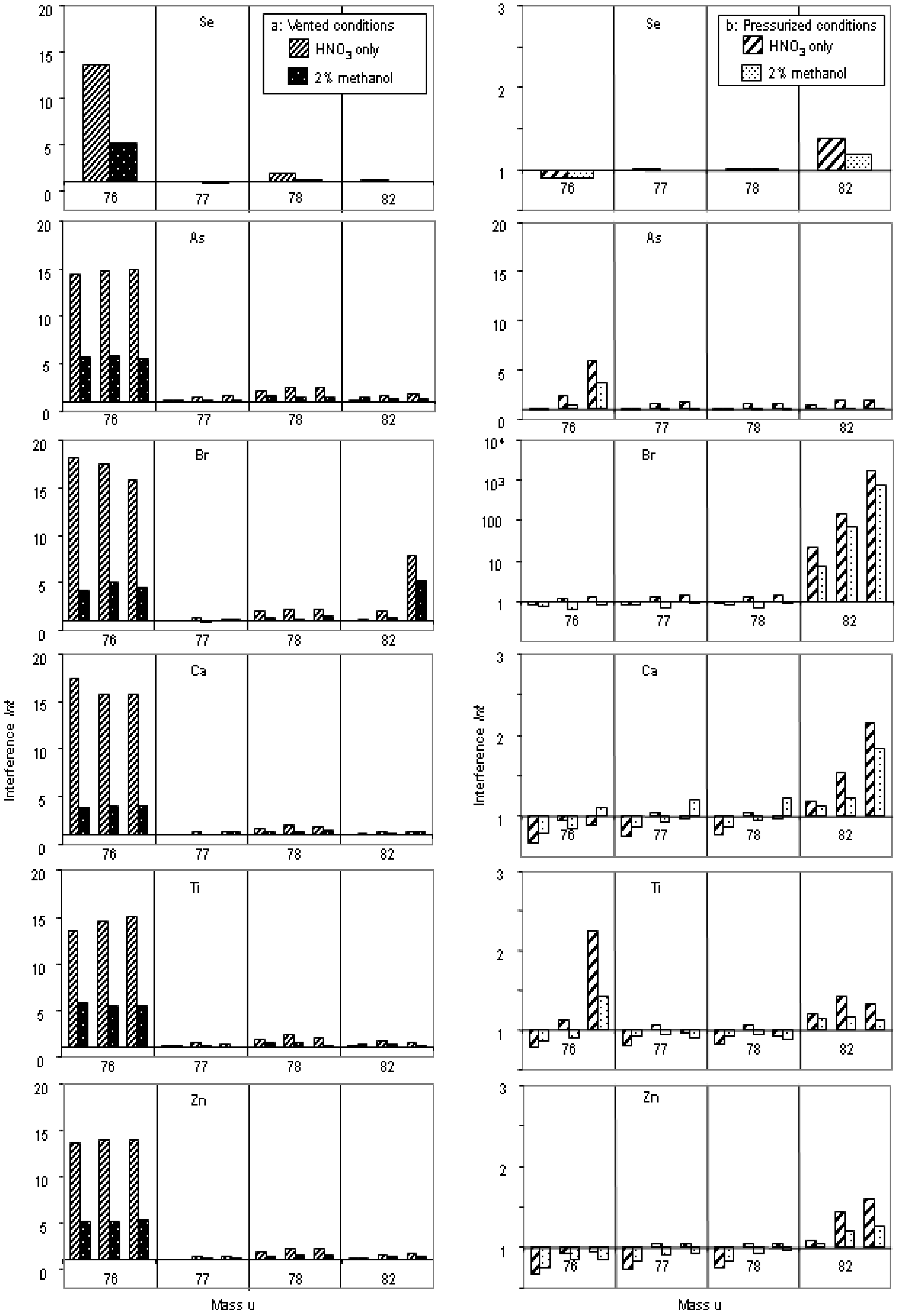


Figure 2: Interference (Int) on different Se isotopes using vented (left) and pressurized (4.0 mL/min H_2) conditions (right).

The origin of this Ca-related interference is not clear, but since this interference was not observed under vented conditions, it is attributed to polyatomic species with H (e.g. $^{40}Ca^{40}CaHH^+$). In addition Zn ($^{66}Zn^{16}O^+$) caused a slightly enhanced signal on mass 82. This showed that even sophisticated interference equations (De Boer, 1999) are not adequate for correction on As measurements. On m/z^+ 76 both As ($^1H^{75}As^+$) and Ti (probably $^{48}Ti^{14}N^{14}N^+$) gave an increased signal. Once again the presence of MeOH reduced the *Int* in all cases, as has been observed by other authors (Muñoz-Olivas et al., 1995; Evans and Ebdon, 1990; Hu et al., 2004; 2005).

3.2 ICP-MS analyses of soil digests

The soil digestions were measured under the different experimental conditions previously described. Procedural blanks gave soil equivalent concentrations below 0.03 mg/kg for all isotopes and all used conditions. Previous to the Se determination in volcanic soils with an unknown content, the methodology was tested in a reference volcanic soil with certified Se content (JSAC 0411, [Se]=1.32±0.27). For this certified reference material (CRM), the experimentally measured signal and the signal presumably coming from Se is shown in Figure 3. The expected Se signal was calculated using mass 78, corrected for ArAr in vented conditions.

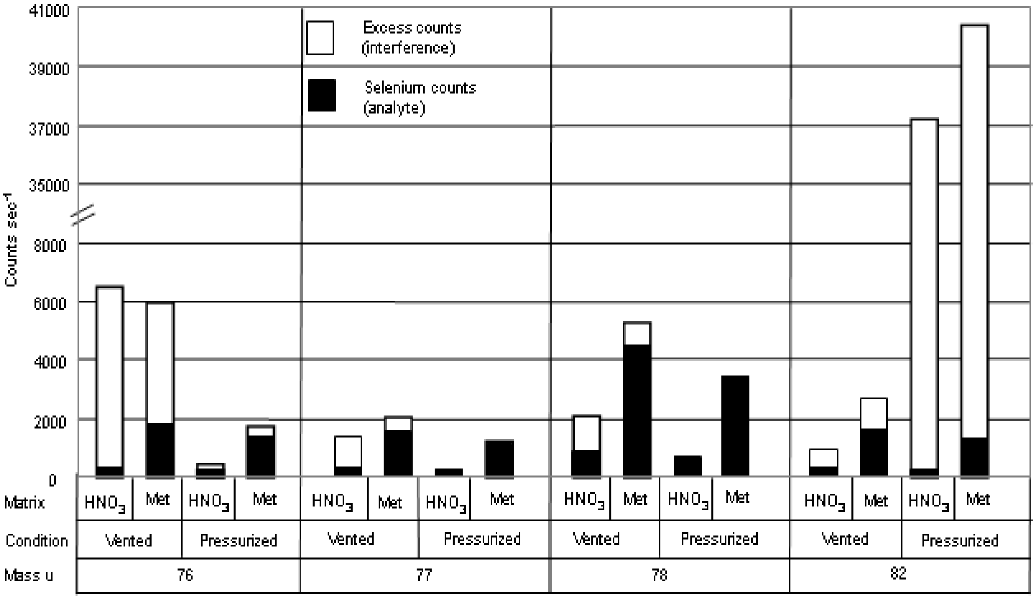


Figure 3: Counts on Se isotopes for the JSAC soil digestion for the different measurement conditions

In vented conditions all Se isotopes suffered from interferences: $ArAr^+$ on m/z^+ 76 and 78, an unknown interference on m/z^+ 77 (not observed in studied synthetic solutions) and HBr^+ and probably ZnO^+ on m/z^+ 82. MeOH addition increased the Se signal and decreased the interferences (except for m/z^+ 82), probably due to competitive carbides formation with the Ar. Only with m/z^+ 78 in a MeOH containing matrix a good result was obtained, but as ArAr is present, this method would be very sensitive for drift in the ArAr dimer. The results showed that the conventional measurements (m/z$^+$ 82, vented collision cell, no MeOH) clearly overestimates the Se content (Table 2).

Table 2: Obtained Se concentrations (mg/kg) in soils using masses 76, 77, 78 and 82 in the four different conditions. Certified Se conc. in JSAC 0411 is 1.31±0.27 mg/kg.

Sample	Cell conditions	Sample matrix	m/z$^+$ = 76	m/z$^+$ = 77	m/z$^+$ = 78	m/z$^+$ = 82
JSAC 0411	Vented	1% HNO_3	-1.2 ± *1.2*	0.73 ± *0.36*	1.53 ± *0.56*	3.19 ± *0.77*
		2% MeOH	1.20 ± *0.39*	1.47 ± *0.29*	1.38 ± *0.21*	1.87 ± *0.29*
	Pressurized	1% HNO_3	1.83 ± *0.49*	1.49 ± *0.56*	1.21 ± *0.53*	145 ± *17*
		2% MeOH	1.89 ± *0.24*	1.51 ± *0.19*	1.31 ± *0.20*	40.9 ± *2.3*
S1 Teide Tenerife Spain	Vented	1% HNO_3	1.5 ± *2.9*	1.9 ± *1.4*	0.89 ± *0.12*	1.97 ± *0.28*
		2% MeOH	0.85 ± *0.34*	0.972 ± *0.037*	0.614 ± *0.032*	0.87 ± *0.16*
	Pressurized	1% HNO_3	1.44±*0.35*	1.00 ±*0.25*	0.49 ± *0.21*	20.7 ± *7.8*
		2% MeOH	0.982 ± *0.020*	0.762 ± *0.091*	0.506 ±*0.060*	6.0 ± *2.0*
S2 Etna Sicily Italy	Vented	1% HNO_3	2.42 ± *0.71*	1.58 ±*0.21*	0.462 ±*0.010*	1.019 ± *0.050*
		2% MeOH	0.57 ± *0.41*	0.51 ± *0.17*	0.245 ± *0.054*	0.419 ± *0.060*
	Pressurized	1% HNO_3	0.64 ± *0.10*	0.440 ± *0.039*	0.150 ±*0.010*	1.27 ± *0.10*
		2% MeOH	0.421 ± *0.073*	0.307 ± *0.062*	0.159 ± *0.044*	0.511 ± *0.090*

With pressurized conditions only some Se isotopes had an interference: m/z$^+$ 76 (HAs^+ and/or $^{48}Ti^{14}N^{14}N^+$, based on synthetic solutions results) and 82 (HBr^+ and ZnO^+). Isotopes 77 and 78 did not suffer from interference because i) they followed the isotope ratios of Se in the reference soil (see Figure 3), ii) the values obtained on these masses were close to the certified value (see Table 2) and iii) similar values were obtained in the absence/presence of methanol (since MeOH suppresses interferences, lower apparent Se concentrations were obtained with methanol addition if an interference is present). The standard error was lower using methanol, related to the higher sensitivity and therefore giving improved counting statistics. Consequently, the addition of MeOH is recommended. However, aliquots without methanol addition can be measured as a control. The same value should be obtained if no interferences are present.

The results obtained for real samples differed slightly from the CRM (Table 2). Firstly, the unknown interference present at mass 77 was even present in pressurized conditions. Secondly, m/z$^+$ 78 with a methanol matrix in vented conditions could not be used, because the soils contained less Se (making the error produced by ArAr drift more significant). Nevertheless, at m/z$^+$ 78 with pressurized ORS similar results were obtained independently of the use of methanol for all soil samples. This indicates that mass 78 was interference-free and can be used with an ORS for Se determination in volcanic soil digestions.

To explore the possible application to mass limited samples, such as volcanic ash, a procedure using only about 100 mg of solid was tested. In this case for the JSAC 0411 a concentration of 1.30 ± 0.26 mg/kg (6 replicates) was obtained. Therefore, the method can be applied using lower sample mass. However, micro-homogeneity of the soil powder has to be ensured in order to achieve reliable analytical results.

3.3 TXRF analysis of soil suspensions

One of the most interesting features of TXRF in the analytical field is the possibility of quantitative direct analysis of solid samples without previous chemical treatment. In a first approximation, direct solid analysis can be reached by means of an adequate suspension followed by internal standardization (Fernández-Ruiz, 2009). In the present study, three dispersants (high-purity water and 1% Triton X-114, and 10% Triton X-114 in high-purity water) were tested for soil suspension preparation. As can be seen in Figure 4, the best sensitivity using a ratio of 20 mg soil to 1 mL suspension agent was obtained by means of high-purity water. As reported in the literature, non-ionic surfactants such as Triton X-114 could be used to adjust the viscosity of solutions and enhance the homogeneity of the analyzed samples (Stosnach, 2005). However, in this study an improvement of the results when using this reagent did not occur. On the contrary, the background of the obtained TXRF spectra increased considerably when diluted Triton X-144 solutions (1% and 10%) were used. Moreover, the sensitivity for Se determination decreased considerably. Therefore, the use of high purity water as dispersant was considered appropriate for further experiments.

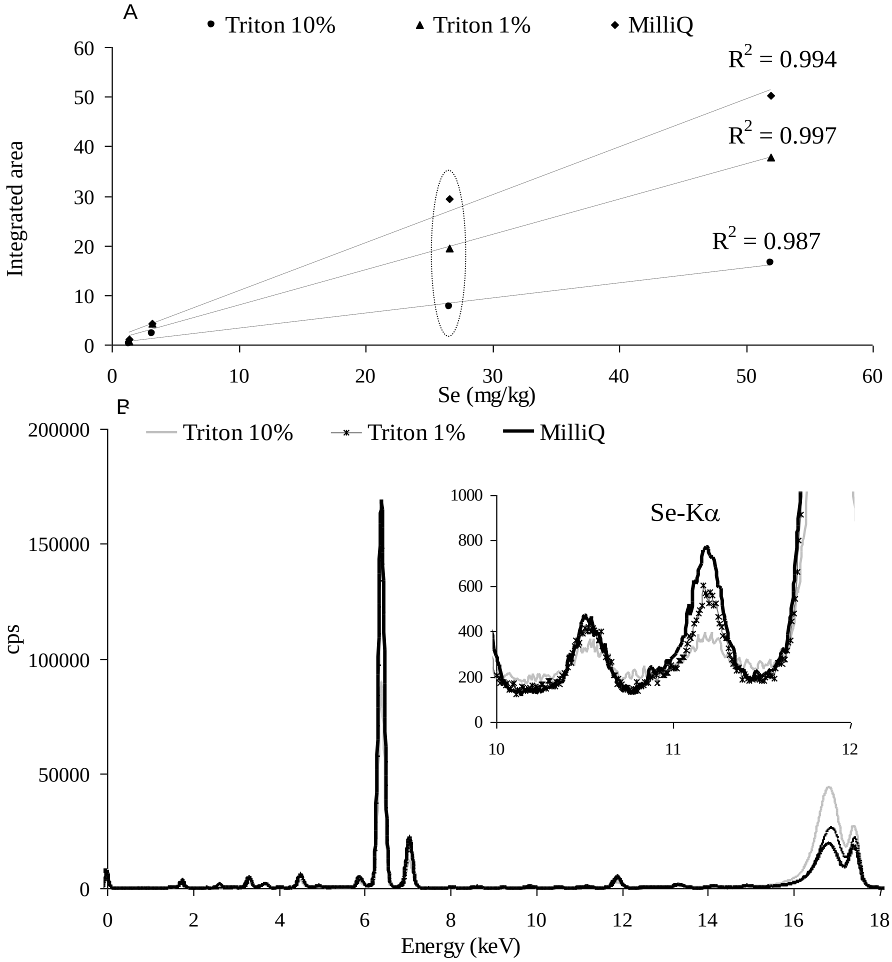


Figure 4: A: Relationship between Se signal and Se concentration in spiked soil suspensions using different suspension agents with a ratio 20mg soil/1mL (measuring conditions: 5µL, 500s. B: TXFF spectrum using spiked soil suspension. CPS= counts per second.

The influence of the slurry concentration on the background intensities and the signal-to-background ratios was also studied. For that, 20, 50, and 100 mg of the JSAC-0411 CRM was mixed with 1 mL of water. Similar results were obtained when 20 or 50 mg of sample was deposited on the reflector. However, significantly lower signal-to-background ratios were found when 100 mg of sample was deposited on the quartz disk. This demonstrates that with 100 mg of sample, the condition of thin layer was broken. In view of the obtained results, a soil amount of 20 mg was established as optimum. The calculated LOD (3 times the square root of the background, Klockenkämper, 1996) for Se when using the best analytical conditions studied to prepare the slurry (20 mg of soil per 1 mL of high-purity water) was found to be around 1.0 mg/kg.

For quantification purposes, Ge was used as internal standard. Appreciable amounts of Ga (15.0 mg/kg) and Y (38.0 mg/kg) are present in the reference soil sample. Therefore, these elements, which are commonly used in TXRF analysis as internal standards, could not be employed. By direct analysis of the slurry of the JSAC-0411, it was not possible to quantitatively determine the Se content due to the proximity of the certified Se concentration (Se = 1.32 ± 0.27 mg/kg) and the calculated Se LOD(~1.0 mg/kg Se). Nevertheless the direct measurement of soil slurries could be applied in order to get a first approximation of the concentration range for Se and other elements within the sample (multi-elemental information). This fast and simple methodology can be successfully applied to analyze seleniferous soil samples with Se concentrations in the milligram per kilogram range. It is especially suitable for mass limited samples since only 20 mg of sample is required. However, in all cases micro-homogeneity of the soil powder has to be ensured in order to achieve reliable analytical results.

3.4 TXRF analysis of soil digests.

3.4.1 Direct TXRF Analysis of Soil Digests

In a groundwater sample with low salinity and hardness (see Chapter 4), a LOD of 0.4 *μ*g/L was found when 5 *μ*L of sample, a measuring time of 500 s, and an excitation current of 47 mA were used. However, the determination of Se at a few micrograms per liter level in soil digests was not possible due to the presence of high amounts of Fe (~700 mg/L) in the matrix that increased the dead time of the detection system. Consequently, a reduction of the excitation current of the X-ray tube was necessary to decrease the detector dead time with an associated loss of emission intensity and instrumental sensitivity. The calculated Se LOD in spiked soil digests using an excitation current of 12 mA (current decreased from 47 to 12 mA) was found to be 18.4 *μ*g/L corresponding to 0.76 mg/kg of Se in the soil. For quantification purposes, Ge was used as internal standard since, as for the solid suspensions, Ga and Y are present in the soil digest. It was not possible to quantify the Se content in the direct analysis of the CRM soil digest due to the proximity of the certified Se concentration and the calculated LOD for this element. However, in order to test the capability of the direct TXRF analysis, a fortified soil extract with 115 *μ*g/L of Se (corresponding to 4.6 mg/kg of Se in the soil sample) was analyzed, and a recovery of 105% ± 14% for duplicate determinations was obtained. Therefore, direct analysis of soil digest can be used for screening of the multi-elemental composition of the soil digest or the quantification of Se in soils in the milligram per kilogram range. A further enhancement of analytical quality of TXRF results can be achieved using more sophisticated sample treatments in order to reduce the Fe content in the soil digest or to isolate Se from the soil matrix. In the present study, both analytical strategies were studied to improve the LOD for Se in soil digests by TXRF spectrometry.

3.4.2 Reduction of the Fe interference on Se determination in soil digests

In order to reduce the Fe interference on Se determination when analyzing soil digests, two different approaches were tested. Firstly, the extraction of Fe from soil digest solutions was carried out by liquid-liquid extraction using ethyl ether. In this case, it was necessary to treat the soil digest with concentrated hydrochloric acid to form the Fe-chloro complex, which was later extracted in the organic phase (ethyl ether). Since the extraction decreased the Fe content in the remaining solution around one order of magnitude, two extractions were needed to lower the Fe content from several hundreds mg/kg to several mg/kg. Secondly, a physical approach introducing a suitable absorber between the sample and the detector was adopted to decrease the Fe signal entering the detector. Taking into account the energy of the emission lines of Fe (K_α 6.403 keV; K_β 7.059 keV) and Se (K_α 11.221 keV, K_β 12.501 keV), it was found that a Cr foil was the best option to be used as absorber. The Cr absorption edge (Cr K_{abs} 5.988 keV) is suitable to decrease considerably the Fe peak without a significant reduction of Se signal. With the use of a chromium foil of 10 μm thickness, the Fe signal was reduced to 3.2%, whereas for Se the signal was only reduced to 49.7%, according to the exponential law of the attenuation photons in homogeneous matter (Van Grieken and Markowicz, 1993). In Figure 5 a comparison of the spectra is displayed for the direct analysis of the soil digest, the analysis of the extract after the application of the ether extraction procedure and the soil digestion solution with a Cr foil of 10 μm between the sample and the detector. A significant reduction of the Fe peak (>90%) was achieved in both analytical approaches with a subsequent increase of the excitation current (33 mA) and an improvement of the Se LOD (±12 μg/L corresponding to ~ 0.5 mg/kg of Se in the soil) compared with the direct analysis of the soil digest.

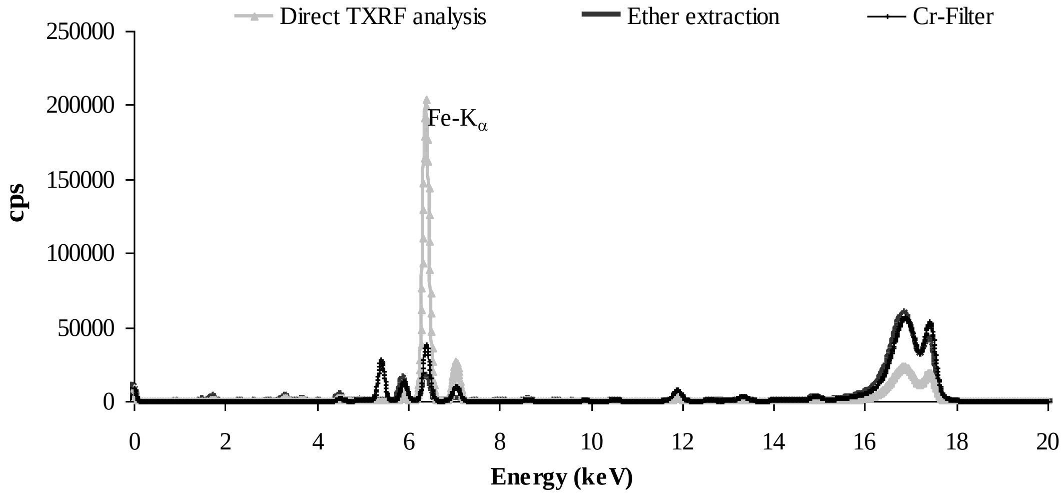


Figure 5: Comparison of TXRF spectra obtained for, direct analysis of a soil extract, after an ether liquid-liquid extraction procedure and using a Cr detector filter of 10µm. cps= counts per seconds.

To evaluate the accuracy for Se determination, three replicate analyses of the JSAC-0411 soil were performed using both methodologies. In the case of the Cr absorber approach, Ge was used as internal standard for quantification purposes. The determined Se concentration for three replicate measurements was 21.0 ± 2.1 μg/L Se corresponding to 0.87 ± 0.10 mg/kg Se in the soil. As can be seen, significant differences were obtained between the calculated Se content and the reference value. Although the Se peak was detected, the Se concentration in the sample was below the quantification level. To check the reliability of the measurements, recovery tests on a fortified soil extract containing 115 μg/L of Se (corresponding to 4.6 mg/kg of Se in the soil sample) were carried out. A quantitative recovery was obtained for duplicate analysis of soil digests with a mean value of 97.4% ± 1.6%. When the Se content in the soil extract was analyzed after the ether extraction, Ge could not be used as internal standard due to the formation of Ge volatile anionic chloro-complexes (Guo et al., 2002). In this case, a standard addition procedure was employed for quantification purposes using four Se additions in the range of 0-150 μg/L. The determined Se concentration in the JSAC-0411 soil digest following this analytical approach was 61.6 ± 3.5 μg/L Se corresponding to 2.55 ± 0.15 mg/kg Se in the soil. This shows that also in this approach Se concentrations at these levels cannot be successfully quantified. Both the introduction of a Cr absorber between the sample and the detector and the ether extraction have similar improvements of the Se LOD for samples with high Fe contents. However, the Cr adsorber is the best strategy, since no treatment of the soil digest before the TXRF analyses is needed.

3.4.3 Extraction of Se from the Soil Digest by DLLME

Taking into account the micro-analytical capability of TXRF spectrometry, the combination with a DLLME procedure to extract the Se content from the soil matrix can significantly improve the analytical performance. For the first time, the applicability of a DLLME procedure combined with TXRF spectrometry (Figure 1) was tested. This DLLME procedure uses carbon tetrachloride (0.1 mL) as extraction solvent due to the high efficiency of carbamates (organic compounds derived from carbamic acid (NH_2COOH)) to form metal complexes that are quantitatively extracted using chloride-based organic solvents (Marguí et al., 2010). Ethanol was selected as dispersant since it was miscible in both the extraction solvent and the soil digest. A volume of 0.5 mL of ethanol was used as the optimum volume in order to achieve a better and more stable cloudy solution without reducing the extraction efficiency, as has been demonstrated by Bidari et al (2007) using a similar DLLME system for Se determination in water samples. APDC (100 mg) was used as complexing agent. In this particular case of analyzing soil extracts, it was not necessary to previously acidify the sample to form the Se-APDC complexes since the matrix of the soil digest after the reduction procedure was 1 M HCl. Since better results were obtained with 2 mL of sample compared with those obtained when using 4-6 mL of sample (see Chapter 4), 2 mL of sample was used. Again Ge could not be used as internal standard due to the presence of HCl, but since DLLME removes many matrix elements, Y could be employed (see Chapter 4).

In Figure 6, a comparison of TXRF spectra obtained for the direct analysis of a soil digest and analysis after the DLLME procedure (2 mL of sample, 0.1 g of APDC, 0.1 mL of carbon tetrachloride, 0.5 mL of ethanol) is displayed. As is shown, a considerable reduction of Fe peak and a significant enhancement of Se peak were obtained after the

DLLME procedure. The calculated LOD for Se using the described sample preparation procedure was 1.1 µg/L of Se corresponding to 0.05 mg/kg of Se in the soil. Therefore, the Se LOD was improved more than one order of magnitude when the DLLME procedure was used to treat the soil extract before the TXRF analysis. Moreover, this LOD is one order of magnitude below the worldwide average of Se soil concentrations.

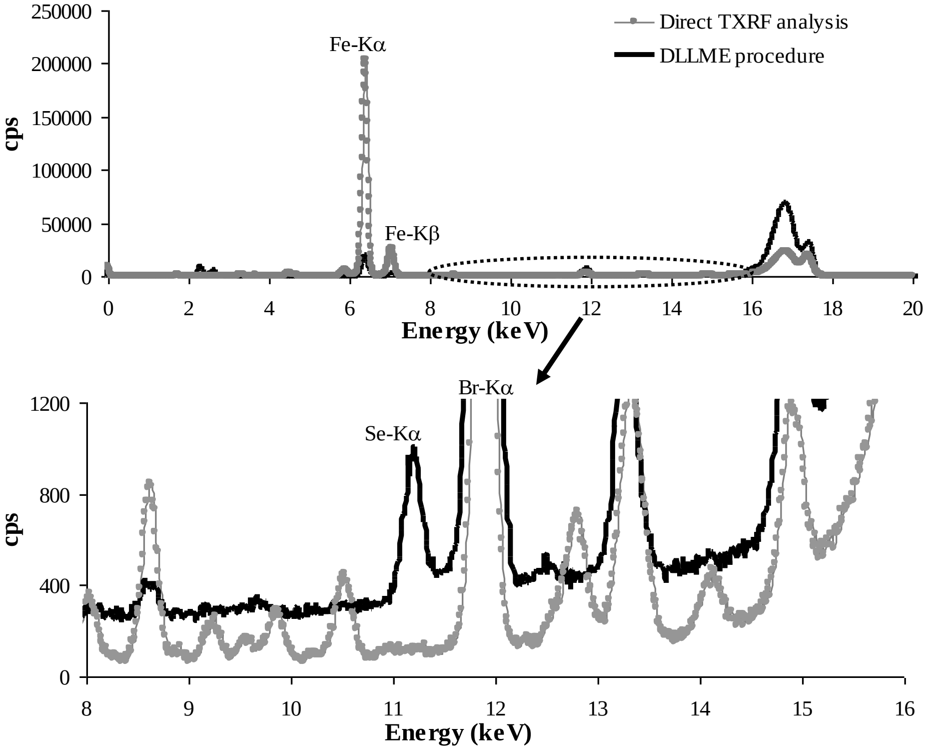


Figure 6: TXRF spectra obtained for the direct analysis of a soil extract and after the dispersive liquid-liquid microextraction procedure (experimental conditions: 2mL of sample, 100mg APDC, 0.5mL ethanol, 0.1mL carbon tetrachloride). Cps = counts per seconds.

The effect of major elements present in the soil matrix on Se extraction was tested by investigating the extraction efficiency using Se standard solutions with and without the presence of Fe (200 mg/L) in the range 25-100 µg/L of Se. It was found that the extraction efficiency for Se (~75-79%) was independent of the initial metal concentration and the Fe content present in the initial solution (Figure 7). This demonstrates the feasibility of the use of the DLLME procedure for quantification purposes, since the metal extracted in the organic phase is related to the initial Se content in the soil digest. A similar trend was observed when the same experiment was performed on spiked soil extracts in the range 25-100 µg/L of Se. However, despite the constant extraction efficiency for Se in the studied concentration range (53% ± 7%), in this case the recovery was lower than that obtained for Se standard solutions. Therefore, it was not possible to use external calibration with aqueous Se standards for quantification purposes and a standard addition procedure was necessary. To compensate for small differences in sample deposition on the reflector, the relative Se signal (Se signal/Y signal) was considered.

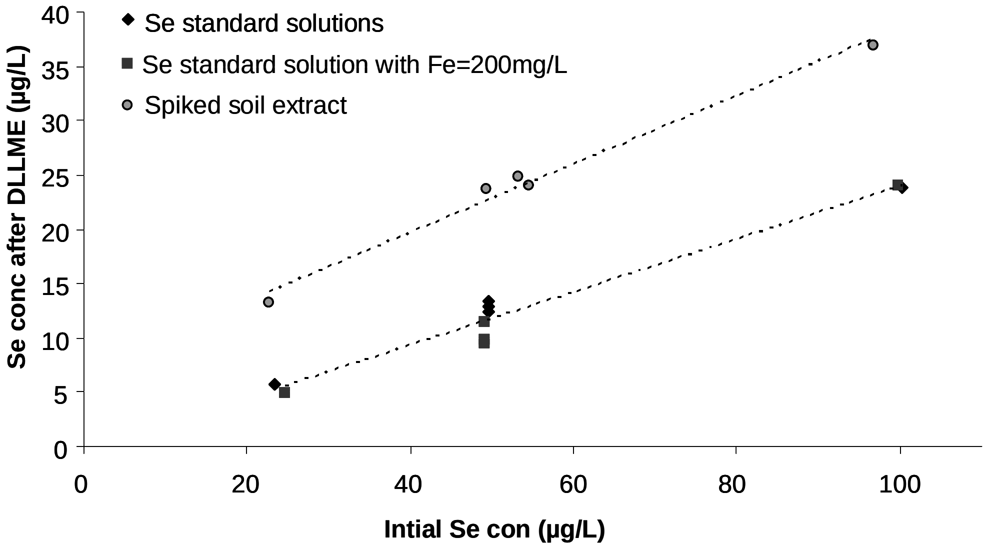


***Figure 7: Relationship between Se concentration in the initial solution and Se concentration in the solution after the DLLME procedure (sample volume: 5mL*)**

Following this analytical approach four Se additions in the range of 0-100 *µ*g/L were performed and Se determination in the CRM soil digest was 33.7 ± 5.6 *µ*g/L Se corresponding to 1.40 ± 0.23 mg/kg Se in the soil. The measured Se content was in excellent agreement with the certified value (1.32 ± 0.27 mg/kg Se) and no significant differences at the 95% confidence level were found. Thus, the accuracy of the developed DLLME procedure and its suitability for the determination of trace amounts of Se in soil digests was confirmed. A summary of the LOD and accuracy of the developed TXRF analytical methodologies are given in Table 3.

Table 3: Limits of detection and accuracy of results obtained for Se determination in soils using the developed TXRF analytical methodologies.

	Limit of detection		**Accuracy**	
	Se (µg/L)	**Se (mg/kg)**	**Se (µg/L)**	**Se (mg/kg)**
Solid sample				
20 mg/ 1 mL Milli Q	-	0.91	n.d.	n.d.
Digested sample				
Direct	18.4	0.76	n.d.	n.d.
Cr filter	12.61	0.52	21.0±2.1	0.87±0.09
Ether extraction	11.99	0.49	61.6±3.5	2.55±0.15
DDLME	1.11	0.05	33.7±5.6	1.40±0.23

4 Conclusions

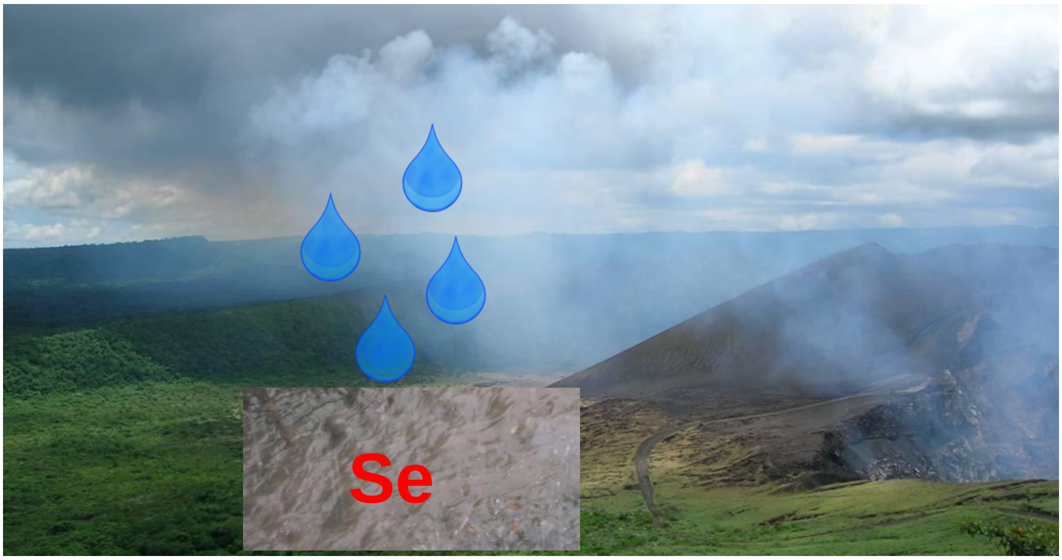
In this chapter protocols were developed for total Se determinations using ICP-MS and TXRF. Firstly, spectral interferences on Se isotopes in volcanic soil digestions using ICP-MS have been evaluated. The results show that in this matrix under vented ORS conditions all Se isotopes suffered from interferences. The isotope of the $^{82}Se^+$ isotope overestimated the Se contents, caused by the formation of HBr^+ and potentially also ZnO^+. This has additional consequences for the measurement of As when applying correction equations. With H_2 pressurized conditions in the ORS some Se isotopes can be subject to interferences, but m/z^+ 78 produced consistent interference-free determinations. The presence of methanol reduced the magnitude of the interferences further, due to an enhancement in Se sensitivity and a lower interference intensity. Since it does not influence the values for non-interfered masses, different aliquots of samples with and without methanol could be used as a control. Methanol addition decreased the confidence interval as a result of improved counting statistics. Therefore, for Se determination in (volcanic) soils it is recommended to use mass 78 with addition of methanol to the samples. Using this protocol a procedural blank was obtained with a soil equivalent concentration of <0.03 mg/kg and a Se concentration within the uncertainties of the certified value for the CRM.

Secondly, the possibilities of several analytical approaches combined with TXRF spectrometry for Se determination in soils were demonstrated (Table 3). The use of direct analysis of soil suspensions by TXRF is a fast and relatively simple methodology to get a first approximation of the multi-elemental composition of the soil. Moreover, it can be successfully applied to determine the Se content when an extremely small amount of sample is available (only 20 mg of soil is required) provided that the Se content is sufficiently high. A further enhancement of Se LOD can be achieved using more sophisticated sample treatment on the digested soil sample by the application of a liquid-liquid extraction procedure using ethyl ether or simply the introduction of a Cr absorber in the instrument configuration removing the high Fe intensity. With both approaches, the LOD for Se was reduced around 35% compared with the direct analysis of the soil digest. However, if Se content in soil samples is below the milligram per kilogram level, the applicability of a DLLME procedure to extract the Se content from the soil matrix and improve the LOD for Se by TXRF is a good alternative. By this simple and low-cost sample preparation strategy, accurate results can be obtained at the low milligram per kilogram range. The Se LOD is almost 10 times lower than the worldwide mean concentration of Se in soils, and it is also competitive with those determined using other popular spectrometric techniques such as GFAAS, ICPMS, and AFS (Chapter 2).

Although DLLME combined with TXRF analyses reveals LOD very suitable for the application to environmental samples in the lower mg/kg, the method is laborious. Therefore, ICP-MS analyses will be more practical for a large set of samples. Nevertheless, for samples with a Se higher content (several mg/kgs or higher), the TXRF analyses of solid suspension will be the fastest and cheapest method. Moreover, in this case multi-elemental information can be obtained. The described methods can also be applied to mass limited samples such as volcanic ashes. For TXRF analyses with solid suspension as little as 20 mg of solid material is needed. For ICP-MS analyses an adapted microwave program using 100 mg rather than 400 mg of material revealed the same results. However, for the DLLME procedure with TXRF analyses more solution is needed, since a standard addition approach has to be performed. In summary, the suitability and applicability of the proposed techniques strongly depends on the sample characteristics.

Chapter 4

Selenium quantification in soil extractions: total and inorganic speciation determinations



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1 Introduction

To understand the environmental implications of selenium in soils, chemical mobility must be considered as a more determining factor than total Se concentrations. In this sense, a common practice in environmental study is the application of extraction procedures to identify Se carriers or to study Se leaching under simulated field conditions (Bujdos et al., 2005; Nakamaru et al., 2005). On one hand, adsorption and desorption processes play a key role in the chemical fate of Se (Goh and Lim, 2004; Nakamaru et al., 2005; 2006, Dhillon el at., 2008). On the other hand, the mobility of Se is also strongly influenced by its speciation.

The analysis of some complex environmental samples (e.g. hydrothermal waters, soil extraction solutions) presents significant problems related to the low Se concentrations and the matrix of this type of samples. Especially in the case of soil extractions in acidic conditions, the matrix of the resulting solution can be complicated due to partial dissolution of minerals (Oelkers and Gislason. 2001). Low limits of detection (LODs) are a major concern in the study of desorption processes of natural samples or sorption experiments using realistic natural low concentrations. Moreover, in the application of lab controlled experiments to mass limited samples such as volcanic ashes, the amount of sample volume needed is a critical issue. As described in Chapter 2, different analytical methods exist for total Se determinations. The advantage of Total reflection X-ray Fluorescence (TXRF) is that multi-elemental information can be obtained with tiny sample amounts. In the previous chapter it was shown that the sensitivity strongly depends on the used matrix with orders of magnitude higher LOD for soil digestions compared to groundwaters. However, TXRF has not been much applied to Se determinations in other environmental complex matrices. Therefore, the applicability of TXRF for Se determinations in geochemical studies should be investigated in a range of different matrices.

Speciation analyses are even more demanding, since they involve the determination of individual species which are fractions of low total Se concentration (Gonzalez et al., 2009). Nowadays the commonly applied technique for Se speciation in solutions is High Performance Liquid Chromatography (HPLC) coupled to an Inductively Coupled Plasma Mass Spectrometry (ICP-MS). As described in Chapter 2, a key issue in speciation analyses is to preserve the integrity of the samples, which is particularly challenging in complex chemical matrices (Wrobel et al., 2005; Hymer and Caruso, 2006; Gonzalvez et al., 2009). Acidic environmental samples are often rich in dissolved iron and aluminium (Al) (Sanchez-Rodas et al., 2006; Oliviera et al., 2006) which can precipitate during chromatographic separation when the samples are adjusted to the mobile phase pH. In consequence, measurements can be biased and the chromatographic column can be damaged. The prevention of Fe precipitation received significant attention for arsenic speciation and several strategies have been developed, such as the addition of chemicals preventing As oxidation (Chapter 2). However, there is a lack of such studies for Se and the potential Al precipitation has not been evaluated in speciation studies. Since the solubility of Fe and Al strongly depends on solution pH, an alternative approach is the use of a mobile phase with a low pH similar to that of the samples. Nevertheless, previous work on inorganic Se speciation by HPLC-ICP-MS for non-acidic samples used buffers with pHs of 4.8 or higher (Chapter 2). If acidic Fe and Al rich samples are adapted to these pHs, precipitation of the latter phases is thermodynamically favourable.

Although TXRF in principle reveals total concentrations, most sample preparation treatments depend on the Se oxidation state in solution. This means that for total Se concentrations, a prereduction step is necessary. However, it also implies that these methods can be used to obtain information on the Se speciation. Aretaki and Kallithrakas-Kontos (2009) used the selectivity of the formation of colloidal Se on quartz reflectors combined and the comparison of the results with and without sample prereduction to obtain the inorganic Se speciation by TXRF. Bidari et al (2007) used a dispersive liquid-liquid micro-extraction (DLLME) procedure combined with graphite furnace atomic adsorption spectrometry (GFAAS) analyses for inorganic Se speciation analyses in water.

In this work I focus on analytical techniques for Se total and speciation determination in soil extractions using TXRF and HPLC-ICP-MS. Since little previous work has been performed on Se determinations by TXRF in complex liquid samples, first Se LODs for different geochemical solutions were evaluated. Afterwards, the potential of several fast and simple chemical strategies before TXRF analyses to improve the Se LOD was investigated for acid soil extractions simulating acid rain – soil interaction at Mount Etna. Moreover, the potential of such sample preparation step to obtain Se speciation information was explored. Afterwards, a new protocol for Se speciation at trace levels by HPLC-ICP-MS equipped with the octupole reaction system (ORS) technology in acidic environmental samples using a low-pH buffer is presented using the same case-study.

2 Experimental section

2.1 Reagents and materials

Standards for total determinations and spiked samples were prepared with stock solutions of 1000 ± 0.5 mg/L (Spectroscan, TECKNOLAB A/S, Norway). Selenium speciation stock solutions were made from sodium selenate and sodium selenite salts (Sigma, 99%). For ICP-AES speciation analyses 10 mg/L selenite-selenate mixtures have been used, while for ICP-MS analyses concentrations between 0.1 and 10 µg/L were prepared. High purity water used for dilution of stock solutions and samples was obtained from a Milli-Q purifier system operated at 18.2MΩ (Millipore Corp., Bedrod, MA).

Concentrated hydrochloric acid (Trace Select) was obtained from Fluka, Germany and concentrated sulfuric acid (SpA grade), sodium pyrophosphate ($Na_4P_2O_7$) and sodiumhydroxide (NaOH) were acquired from Merck, Germany. All samples have been filtered before analyses with 0.45 µm pore size filters (polypropylene, Whatman) for total Se determination and 0.22 µm pore size filters (0.22 µm, polypropylene, Tracer) for Se speciation measurements.

Cation exchange columns (Chromabond, SA polypropylene columns) were tested to improve the Se LOD by decreasing the content of cations (Zn and Ca) from the extraction solutions prior to TXRF analysis. The ethanol (absolute, >99.5%), carbon tetrachloride (>99.5%) and APDC (~99%) used to perform the DLLME procedure before the TXRF measurements were purchased from Sigma-Aldrich (Spain).

Mobile phases for HPLC were prepared from di-ammonium hydrogen citrate (Reagent Ph Eur, Panreac), methanol (chromsolv plus, >99.9%, Sigma-Aldrich) and concentrated nitric acid (Romil Suprapure, Se < 0.1 µg/L). All mobile phases have been filtered using a 0.45 µm cellulose nitrate filter (Whatman). Polypropylene sample vials (Agilent Technologies, Basel, Switzerland) were used for the HPLC analyses.

2.2 Samples

In this work, I selected different types of environmental waters (groundwater, rainwater and thermal water) and extraction solutions (acid and selective extractions) commonly used in environmental and geochemical studies. Groundwater samples analyzed were from the ARS29-32 Interlaboratory Quality Evaluation organized by the Swiss Federal Institute of Aquatic Science and Technology (Berg and Stengel, 2009). Thermal waters were collected during a geothermal exploration at the volcanic islands of Guadeloupe belonging to the Lesser Antilles arc (Millot et al., 2010a). A natural rain sample was collected 5.5 km from the craters to the craters of Mount Etna volcano by means of a bulk collector (Calabrese, 2009).

All the studied extraction solutions were obtained from the interaction of volcanic soils collected at Mount Etna. Soil extractions simulating acid rain-soil interactions were employed using diluted H_2SO_4 at pH 2 with a soil-solution ratio of 1:5 and a contact time of 4 hours (see Chapter 6 for more details). For total Se determination all solutions were filtered with a 0.45 µm pore size filter and acified with nitric acid. However, for Se speciation determinations the solutions were not acified and filtered with a 0.22 µm filter. To assess the oral bioaccessibility (i.e. release during ingestion) of the Se contained in the soils, an acidic extraction was performed in order to simulate mobilization of Se in the acid conditions of the stomach. At present, there is no standard method of estimating bioaccessibility (Oomen et al., 2002). Therefore, as a first approach an extraction using HCl at pH = 2 with a soil-solution ratio of 1:5 and a contact time of four hours was applied. Two selective extractions were carried out using standard protocols for Al and Fe dissolution techniques (García-Rodeja et al., 2007). On one hand, for the study of Se associated to organic matter present in the soil, a selective extraction with 0.1 M $Na_4P_2O_7$ was used. On the other hand, for the extraction of the so-called total free content, a selective extraction using a solution of 0.5M NaOH was performed. For both extractions, a soil-solution with a ratio of 1:100 was constantly shaked overnight.

2.3 Chemical pretreatment procedures prior to TXRF analyses

For the direct TXRF analysis of extraction solutions Y, Ga or Ge were used for internal standardization, depending on the used solution. In all cases, an appropriate amount of internal standard was added to 0.25mL of solution to give final concentration of 0.5mg/L. After homogenization (Vortex device) an aliquot of 10 µL was transferred onto a quartz glass sample carrier and left to dry at room temperature either under a laminar flow hood, under vacuum, on a hotplate of 100°C or with an IR lamp before TXRF analysis.

To decrease the Zn and Ca concentration in the extraction solutions, a cation exchange procedure was carried out before the TXRF analysis. First, cation exchange columns were preconditioned with Milli-Q water. Then, 1mL of extraction solution was passed through the column. Afterwards, the column loaded with cation species (i.e., Ca and Zn) was rinsed with Milli-Q water (3x1mL) and the collected solution (containing the Se) was evaporated at 70ºC to obtain the start volume (in this case 1 mL but other volumes can be used). Then the solution was treated in the same way as described above for direct TXRF analysis.

A dispersive liquid-liquid micro-extraction procedure (DLLME) using APDC as complexing agent was employed to separate and pre-concentrate Se from the extraction solutions as described in Chapter 3. To test the effect of sample volume on Se extraction 2, 4 and 6 mL of two standards solutions containing 10 and 30 µg/L of Se were submitted to the DLLME procedure. For selenite determination in soil extractions the DLLME was performed without any sample preparation. However, a reduction step was necessary to determine total Se in extraction solutions (Bidari et al., 2007). Prereduction has been performed as described in Chapter 3. The selenate concentration could be estimated using the difference between untreated and pre-treated samples.

2.4 Preparation of HPLC mobile phases

To evaluate the effect of different mobile phase parameters (e.g. ionic strength, pH, citric acid concentration) eluents with different compositions have been used. The mobile phase was made with 5-20 mM di-ammonium hydrogen citrate (Reagent Ph Eur, Panreac). Two percent of methanol was added to improve Se sensitivity (Bird et al., 1997; Diaz huerta et al., 2003; Bueno et al., 2007). Mobile phases were adapted to the desired pH (studied pH range 3.0 - 4.8) with concentrated nitric acid and subsequently filtered.

2.5 Instrumentation

The TXRF analyses were performed as described in Chapter 3. However, acquisition times of either 500 or 1000 seconds were used. For comparison with the TXRF analyses, Se was determined with ICP-MS using the same measurement conditions as in Chapter 3 with a hydrogen-pressurized octupole reaction system (ORS). For speciation analyses by HPLC the effects of the mobile phase parameters were evaluated with an anion-exchange chromatography column (Hamilton PRP X-100, 150 × 4.1 mm I.D., 5 *µ*m) coupled to an ICP-AES (Varian Liberty II). Standards and samples have been analyzed with HPLC-ICP-MS. For this, an anion exchange chromatography column (Agilent G3154-65001, 150 x 4.6 mm) fitted with a guard column (Agilent G3154-65002, 10x4.6 mm) was coupled to an Agilent 7500cx ICP-MS. The ORS was pressurized with 4.7 ml/min hydrogen. An injection volume of 25 µL was used. The total flow rate was 0.7 mL/min, from which 0.33 mL/min were split to waste after separation. Indium was added continuously after separation as internal standard (50 µg/L). The ICP-MS was optimized daily using a tuning solution for high sensitivity remaining low CeO/Ce ratios. The plasma was operated with 1.5 kW, 15 L/min plasma gas and 0.8 L/min carrier gas. The detected isotopes were $^{78}Se^+$, $^{79}Br^+$, $^{80}Se^+$, $^{82}Se^+$ and $^{115}In^+$ with an integration time of 0.3 sec per isotope. Peak areas were integrated with the Mass Hunter software (Agilent Technologies).

2.6 Thermodynamic calculations

The precipitation of mineral phases during pH adjustment was predicted using thermodynamic calculations by PHREEQC-2 (Parkhust and Apello, 1999). This model is based on aqueous thermodynamics and equilibrium chemistry of aqueous solutions interacting with minerals. Calculations were performed with the databases provided with the program.

3 Results and discussion

3.1 Sample preparation for TXRF analyses

3.1.1 Effect of sample dying procedure

A study was conducted to test the effect of the sample drying procedure on the Se determination. For that, aliquots of 10 µL of the ground water ARS-29 were submitted to different drying procedures including vacuum, hot plate at 100ºC, infrared lamp and room temperature under a laminar flow hood (n=3). No significant statistical differences were obtained between the different procedures and quantitative results for Se were obtained in all cases (Figure 1A).

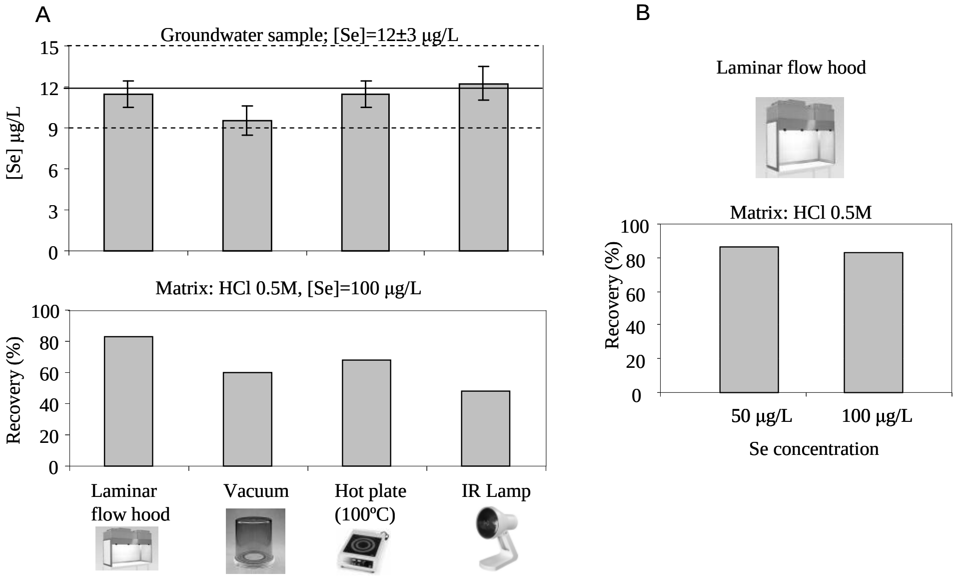


Figure 1: Effect of drying procedures on Se recovery

However, it is known that Se volatilize more easily in the presence of chloride (Cl) due to the formation of Se-Cl compounds (Bye and Lund, 1988). Volcanic waters can be enriched in Cl. Moreover, to asses the release during ingestion of solids, an oral bioaccesibility test was performed using HCl to simulate the acid conditions of the stomach (Oomen et al, 2002). Therefore, a similar study was performed to test the effect of the sample drying procedure on the Se determination using a 0.5 M HCl matrix. In this case significant variation in recovery was observed for the different drying techniques. The highest recovery (80%) has been obtained using a laminar flow hood. Although the recovery is not exhaustive, the recovery is independent from the Se concentration (Figure 1B). As a result, external calibration using a sample-matched matrix can be used to compensate for this effect. Given the fact that the laminar flow hood give best results for both matrices, all samples have been dried using this procedure.

3.1.2. Use of internal standard

Preparation of samples as thin layer exclude absorption and secondary excitation and thus, the quantification in TXRF analysis can be done simply by the addition of an internal standard to the sample (Klöckenkamper, 1996). An ideal element to be used as internal standard is one that is not present in the original sample, does not interfere with the target element (Se) and gives an adequate XRF response. Both Yttrium (Y) and Gallium (Ga) are commonly used in TXRF analyses for this purpose. For groundwaters, thermal waters and the selective extractions using $Na_4P_2O_7$ and NaOH sodium, Y was selected as internal standard. However, in the acid soil extractions appreciable amounts of Y were found (around 100 µg/L, ICP-MS results and a detectable peak in TXRF spectra, Figure 2A).

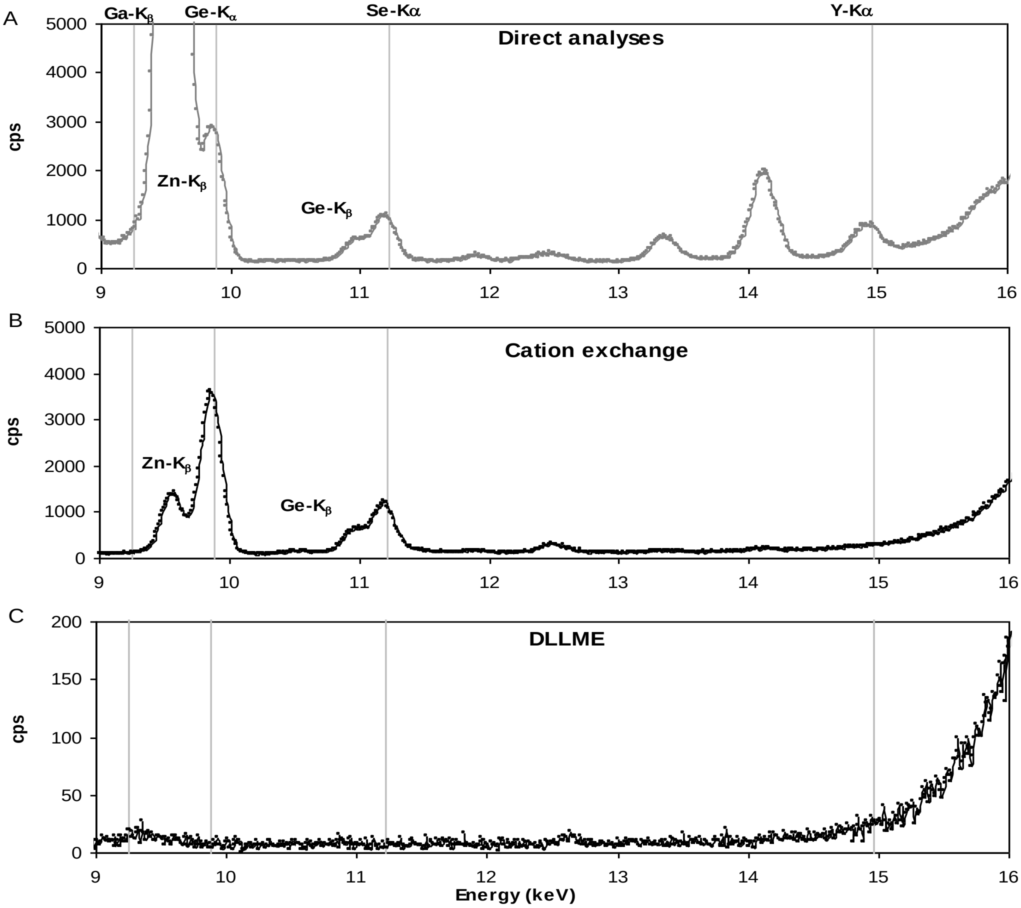


Figure 2: TXRF spectra showing the potential use of internal standards in sulphuric acid soil extraction in A: direct analyses (Ge and Se added), B: after passing a cation exchange column (Se and Ge added) and C: after DLLME procedure (without reduction procedure, nothing added). Grey vertical lines indicate K_α energy lines of Se and potential internal standards. Cps = counts per seconds.

In the extraction using sulphuric acid also noticeable amounts of Ga were detected (around 10 µg/L, ICP-MS results). Therefore, Ge was used as internal standard. Nevertheless, the Ge-K_{α} was overlapped with the Zn-K_{β} peak, which significantly hampers the fitting. Therefore, slightly discrepancies on the results can be found in Se determination at higher Zn concentrations (Figure 2B). As a result, an advantage of the removal of Zn by a cation-exchange procedure (Section 3.3.1), is the improvement of the fitting of the Ge-K_{α} peak and the related quality improvement of the obtained quantitative results. Moreover, this procedure eliminates the Y from the matrix. Using the DLLME procedure, the matrix contained HCl. It was found that even after the addition of 0.5 mg/L Ge, no Ge peak was observed. This can be explained by the formation of Ge volatile chlorocomplexes (Guo et al., 2002). Nonetheless, most matrix elements, including Y, were removed from the extraction solution in the DLLME treatment (Figure 2C). For the HCl extraction again Ge could be volatilized and Y was present in the matrix. Therefore, Ga was used as internal standard. In summary, the selection of the internal standard is critical in environmental complex matrices, due to the wide range of elements present in the matrix and potential spectral interferences between the internal standard and these elements.

3.2 Direct TXRF analysis

3.2.1 Limits of detection and accuracy

Direct TXRF analyses have been performed for a range of geochemical relevant solutions, such as natural waters (Figure 3), acid extractions (Figure 4) and specific extractions (Figure 5). Selenium limits of detection (LODs) were calculated as the concentration corresponding to three times the square root of the background area for the Se peak (Klockenkämper, 1996). For groundwaters with a low salinity and hardness, the calculated LOD was 0.1 µg/L of Se. In Table 1, the obtained concentrations and linear regression analysis parameters between TXRF data (n=3, 10µL of sample, measuring time: 1000s) and indicative values for the intercomparison samples (ARS-29, ARS-30, ARS-31 and ARS-32) are presented. There is a good agreement between the Se concentrations determined by TXRF and the indicative values. No statistical differences at the 99% confidence level exist. The results were also satisfactory for other minor and trace elements present in the sample. This demonstrates the possibility to perform quantitative multi-elemental analysis. Moreover, it shows the absence of matrix effects and the suitability of performing the direct analysis of groundwater samples by TXRF. For thermal waters high amounts of bromine (up to 50 mg/L for the selected samples) caused overlapping between the Se-K_{α} and the Br-K_{α} peak, which significantly hampered the detection and the fitting of Se peak (Figure 3). The Se LOD for thermal waters with a low bromine content (Br<1mg/L) was 3 µg/L, whereas in the samples containing high amounts of Br the LOD was almost 25 times higher. To check the reliability of the Se measurements in thermal waters, recovery tests on spiked samples at the level of 50 µg/L of Se (when Br~1mg/L) and 250 µg/L of Se (when Br~50mg/L) were performed. The recovery was quantitative for thermal waters with low Br contents with a mean value of 100.2% for duplicate analyses. However, it was not possible to get accurate results for the analysis of thermal waters enriched in bromine. Since volcanic waters are often enriched in Br (in this study natural samples were analyzed), the spectral overlap between the Se-K_{α} and the Br-K_{α} peak might hamper the use of direct TXRF analyses for low level Se determinations in natural waters.

Table 1: Concentration and values of parameters for linear regression analysis between TXRF data (n=3, 10µL of sample, measuring time: 1000s) and indicative values for the intercomparison samples (ARS-29, ARS-30, ARS-31 and ARS-32) for several elements.

Samples	**Element**		**As #**	**Se #**	**Fe***	**Mn***	**Ca***	**Cu #**	**Zn #**
ARS-29	Reference	Value	66	**52**	3.3	0.68	27	200	480
		StdDev	6.6	**6.24**	0.264	0.054	2.16	16	38.4
	TXRF	Mean	63.8	**50.1**	3.29	0.68	27.1	208	482
		Std.Dev	4.2	**2.5**	0.07	0.01	1.2	8	7
ARS-30	Reference	Value	28	**29**	1.3	0.86	68	125	200
		StdDev	2.8	**3.48**	0.104	0.07	5.44	10	20
	TXRF	Mean	23.6	**27.2**	1.43	0.86	71.4	123.6	238.9
		Std.Dev	2.6	**1.3**	0.03	0.06	5.5	1.6	73.4
ARS-31	Reference	Value	185	**70**	0.37	0.39	40	47	1150
		StdDev	14.8	**10.5**	0.037	0.03	3.2	4.7	92
	TXRF	Mean	178.9	**67.4**	0.42	0.41	40.4	46.8	1233
		Std.Dev	3.3	**4.7**	0.03	0.01	2.4	0.8	52
ARS-32	Reference	Value	330	**12**	5.9	0.17	66	100	1250
		StdDev	26.4	**3**	0.472	0.017	5.28	10	100
	TXRF	Mean	299	**10.7**	6.4	0.18	69.6	105.6	1248
		Std.Dev	8	**0.6**	0.3	0.01	1.4	3.4	15
Regression analyses	r^2		*0.9989*	***0.9999***	*0.9984*	*0.9997*	*0.9998*	*0.9987*	*0.9971*
	Slope	*Value*	*0.910*	***0.980***	*1.071*	*0.978*	*1.092*	*1.046*	*1.009*
		=1?	*Yes*	***Yes***	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*
	Intercept	*Value*	*2.71*	***1.09***	*-0.026*	*0.019*	*-2.72*	*-2.44*	*22.8*
		=0?	*Yes*	***Yes***	*Yes*	*Yes*	*Yes*	*Yes*	*Yes*

* Concentration in mg/L and # Concentration in µg/L

*Regression analysis: TXRF=Intercept + Slope * (Indicative value); 99% confidence level*

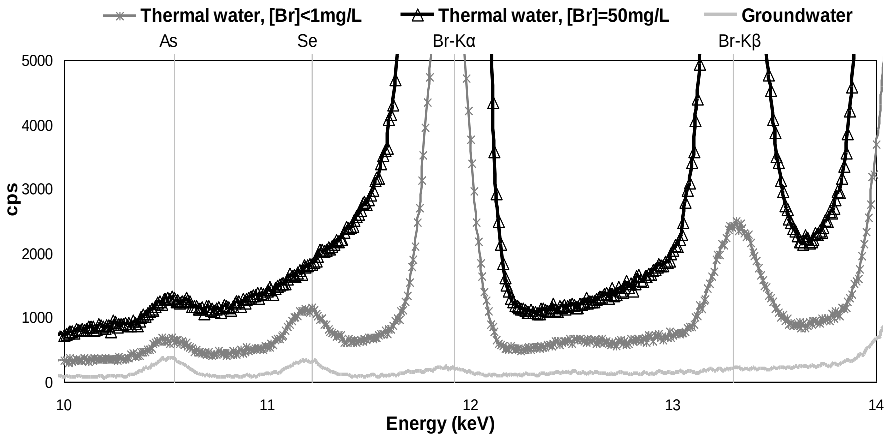


Figure 3: TXRF spectra of natural waters with different concentrations of bromine (Br) and around 50 µg/L. Sample volume: 10 µL and measuring time: 1000s. Grey vertical lines indicate energy lines As, Se and Br. Cps = counts per seconds

The TXRF spectra for two types of acid extractions are displayed in Figure 4. For comparison purposes, the spectrum of a groundwater sample (ARS29) is shown too. The first acid extraction used diluted H_2SO_4 at pH=2. Here, the presence of high amounts of Zn (~50mg/L) in the matrix hampered the determination of Se at trace levels due to an increased dead time of the detection system. Consequently, a automatic reduction of the excitation current (from 47mA to 33mA) of the X-ray tube was necessary to decrease the detector dead time with an associated loss of emission intensity and instrumental sensitivity. The calculated Se LOD in a spiked extraction solution (Spiked level= 50 µg/L Se) was 6.9 µg/L. This value is almost two orders of magnitude higher than that determined in the direct TXRF analysis of ground water samples. It was not possible to quantify the Se content in the direct analysis of the target extraction solution due to the proximity of the Se concentration (6.37±0.7 µg/L, ICP-MS) and the calculated LOD for this element (6.9 µg/L, TXRF). However, results for the direct TXRF analysis of the spiked acid rain-soil interaction solution were accurate with a mean recovery of 110%. The second acid extraction was performed with 0.5M HCl. These solution types were characterized by high amounts of Fe in the matrix (up to 250 mg/L) that increased the dead time of the detection system, reduced the excitation current and decreased the instrumental sensitivity. The Se LOD for such extraction solutions was 18µg/L. In these acid soil extractions multi-elemental information can be obtained. For example, the spectra have clear peaks for Y, Sr, Rb, Zn, Cu, Ni, Fe, Mn, Ca and V (Figure 4). The peaks above 16 keV are instrumental scatter radiations which derive from the Mo X-ray tube.

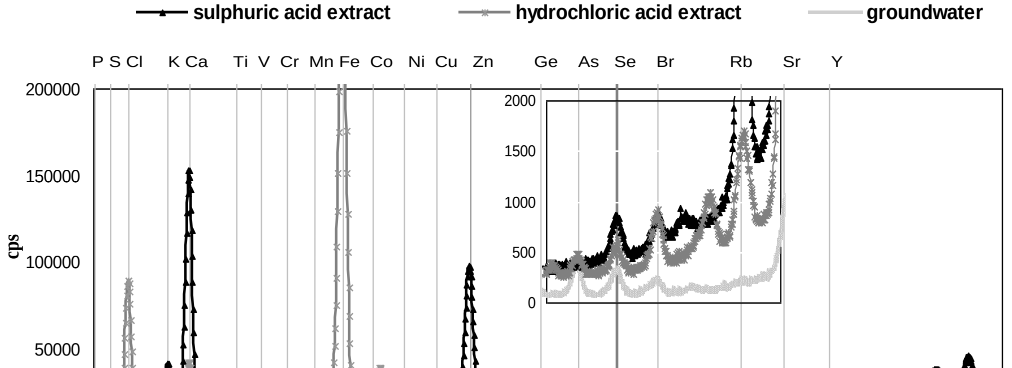


Figure 4: TXRF spectra of acid soil extractions with 50 µg/L Se added. Sample volume 10 µL and a measurement time of 1000s. A groundwater sample (ASR 29) is shown for comparison. Grey vertical lines indicate K_α energy lines of several elements. Cps = counts per seconds.

Afterwards, the detection limits and accuracy for Se determination in direct TXRF analysis were evaluated for selective extractions commonly used to evaluate elements associated to soil organic matter and the so-called total free metal content (0.1M $Na_4P_2O_7$ and 0.5 M NaOH, García-Rodeja et al., 2007). The high content of Na, P (in the case of $Na_4P_2O_7$ extraction) and organic matter present in the extracts increased the background in the spectra compared to that for groundwater samples (Figure 5).

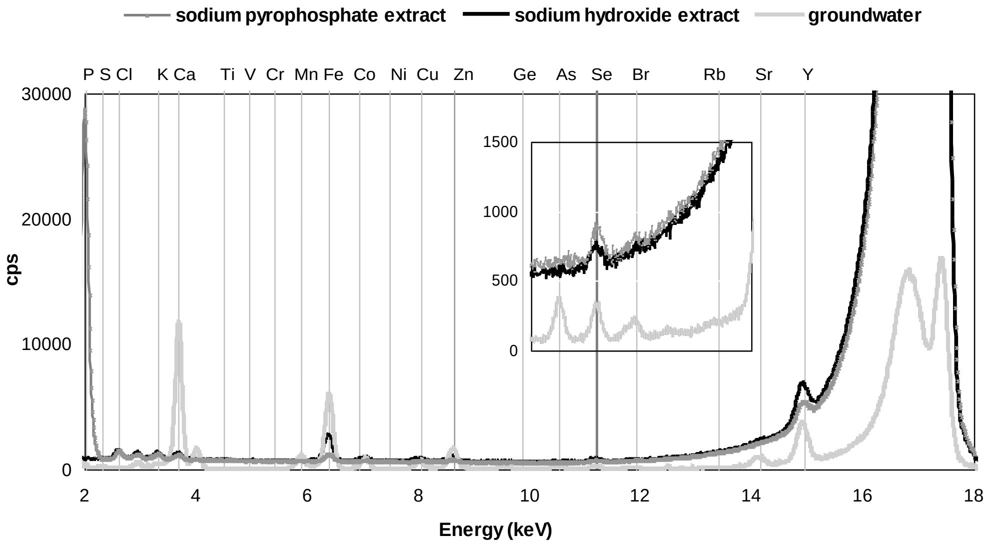


Figure 5: TXRF spectra of specific soil extractions with 50 µg/L Se added. Sample volume 10 µL and a measurement time of 1000s. A groundwater sample (ASR 29) is shown for comparison. Grey vertical lines indicate K_α energy lines of several elements.

The calculated Se LODs in these extraction solutions were 6µg/L and 11.2 µg/L for respectively the NaOH and $Na_4P_2O_7$ extractions. These values are almost two orders of magnitude higher than Se LOD previously determined for ground water samples. In a recovery study performed analyzing fortified extractions solutions (with 50 µg/L Se) mean values of 108% ($Na_4P_2O_7$ extraction) and 110% (NaOH extraction) were obtained for duplicate tests. A summary of the obtained LOD for the different solutions can be found in Table 2.

Table 2: Matrix effects on Se detection limits for TXRF analysis of environmental samples. Analytical conditions: 10µg/L of sample, measuring time: 1000s).

Sample type		LOD (µg/L)	Matrix Effects
Natural waters	Groundwaters	0.1	-
	Thermal waters	2.8	[Br]<1mg/L
		77	[Br]~50mg/L
Acid extractions	H_2SO_4 extracts	6.9	Zn
	HCl extracts	18	Fe
Selective extractions	$Na_4P_2O_7$ extracts	11.2	Na, P (↑background)
	NaOH extracts	6.0	Na (↑background)

3.2.2 Effect of major elements

The above results indicate that major elements present in the sample significantly affect the determination of trace amounts of Se. As shown above, the constituent which hinders strongly depends on the solution. In the solutions studied the elements which hamper the analyses are Br for thermal waters, Zn and Fe for acid extractions and Na for selective extractions. Therefore, the effect of Br, Zn, Fe and Na were studied (Figure 6). For that, several Se standard solutions (50 µg/L) containing increasing amounts of one of the major elements were analyzed. Moreover, a constant Ca concentration was added at realistic concentrations for each type of solution.

The Se LOD increased progressively with increasing bromine concentration. As can be seen in Figure 4 and discussed in 3.2.1, this is related to overlap between the Br-K_α and Se-K_α peaks. Moreover, at concentrations above 50 mg/L the excitation current of the source decreased (Figure 6A). Due to this lower current, there was less Se excitation and the sensitivity decreased. For bromine concentrations of 50 mg/L or higher it was not possible to calculate the limits of detection using the standard of 50 µg/L. The Se LOD also increased when augmenting the Zn content present in the Se standard solutions (Se=50 µg/L). However, in this case the excitation current remained constant. Nevertheless, an increase in background was observed. Augmenting the Fe content in the Se standard solution affected the Se LOD too (Figure 6C). In Figure 6D an experimental study on the effect of Na content (0-10000mg/L) on Se LOD is displayed. It was found that the Se LOD increases exponentially when augmenting the Na content. The importance of the background was also confirmed when comparing the obtained LOD for these synthetic solutions compared with the real solutions. For example, a spiked extraction solution rich in Fe had a 3 time higher LOD compared to a Se standard solution with realistic Fe and Ca contents. This demonstrates that not only the presence of one major element can explain the increase in LOD, but that the general matrix hampers the Se determination at trace levels. This is confirmed with the observed higher background within the TXRF spectrum for more complex solutions compared to the groundwater (Figures 3, 4 and 5).

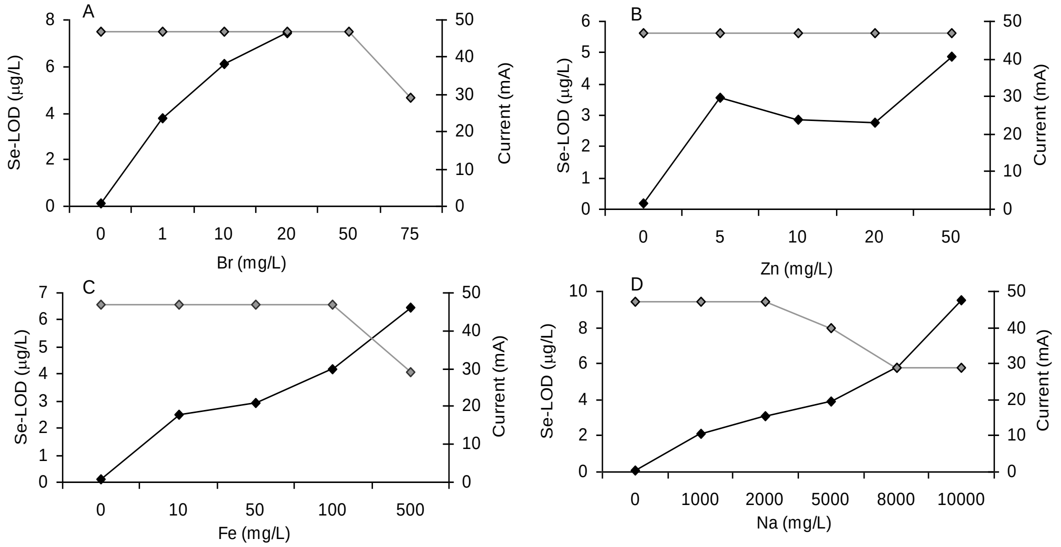


Figure 6: Effect of matrix concentration on Se detection limits (♦) and current of the excitation source (♦) using a Se standard solution of 50 µg/L and (A) Br (0-75 mg/L), Ca= 500 mg/L (B) Zn (0-50 mg/L), Ca=200 mg/L, (C) Fe (0-500 mg/L), Ca=300 mg/L and (D) Na (0-10000 mg/L).

3.3 Improvement of Se LOD by sample preparation prior to TXRF analyses

A further enhancement of the analytical quality of TXRF analyses can be achieved using more sophisticated sample treatments in order to reduce the matrix effects. This could allow trace level analysis of Se suitable for environmental samples. However, it has to be kept in mind that for sample preparation a higher sample volume is needed. Moreover, the multi-elemental character of TXRF is affected. In this section the possibilities of sample preparation to improve the LOD for the simulation of acid rain – soil interaction using diluted H_2SO_4 at pH 2 were explored. As discussed in Section 3.2, the Zn in the extraction solution significantly hampers the analysis. Therefore, the reduction of the cation content or the isolation of Se could significantly enhance the analytical capabilities of Se determination in TXRF spectrometry. In the present study both analytical strategies were studied to improve the LOD for Se in these extraction solutions.

3.3.1 Extraction of interfering ions form matrix (Cation exchange procedure)

In order to decrease the cation (Zn and Ca) concentration in the extraction solution the application of a cation exchange procedure before the TXRF analysis was carried out. Using this approach, cation species are retained in the cation exchange column whereas selenium (present as SeO_4^{2-} and $HSeO_3^-$) remains in the target solution. As can be seen in Figure 2, a significant reduction of the Ca and Zn peaks (>90%) was achieved with a subsequent increase of the excitation current (47mA) and an improvement of the Se LOD (3µg/L) compared to the direct analysis of the soil extract. However, the Se LOD was still one order of magnitude above the LOD for groundwaters. This again demonstrates that the LOD is not only influenced by one element, but by the general matrix (Section 3.2.2). To test the accuracy of the methodology, the procedure was applied for the analysis of a extraction solution containing 4.29±0.4 µg/L of Se (ICP-MS analysis). Good agreement was obtained between the Se concentrations determined by both techniques (3.9±0.4 µg/L of Se, TXRF). Thus, the accuracy of the procedure and the decrease of matrix effects were confirmed for trace Se determination (low µg/L range) in this type of solutions. A range of elements are affected by the cation exchange procedure, as can be observed in Figure 2. As a result, the TXRF analyses using this approach can be only used for anionic and neutral species.

3.3.2 Isolation of Se form the matrix (DLLME procedure)

Taking into account the micro-analytical capability of TXRF spectrometry the combination with a DLLME procedure to isolate the Se content from the extraction solution can significantly improve the analytical performance. A study was conducted to test the effect of sample volume on Se extraction to the organic phase (100µL carbon tetrachloride). For that 2, 4 and 6 mL of two standards solutions containing 10 and 30 µg/L of Se were submitted to the DLLME procedure and the amount of extracted Se in the organic phase was estimated from the difference of the initial Se concentration in the standard solution and the concentration measured in the supernatant after the sample preparation treatment by ICP-MS. Higher percentages of Se extraction were obtained when using 2mL of sample compared to 4-6 mL of sample for two Se concentration levels studied (Figure 7). Moreover, results achieved for the TXRF analysis of the sedimented organic phase showed that the Se signal-to-noise ratio improved with decreasing sample volume. To be able to compare the results with ICP-MS, the performance of DLLME for smaller volumes was not evaluated. Nevertheless, the use of lower amounts of sample to apply the DLLME procedure is feasible. For this study, 2 mL of sample solution was selected for this approach.

Using this DLLME approach the extraction was not exhaustive, as can be seen in Figure 7. As a result, internal standardization for quantification purposes cannot be used and external calibration is required. To compensate for small differences in sample deposition on the reflector, the relative Se signal (Se signal/ internal standard signal) was considered. For calibration purpose, the DLLME was applied to six aqueous standard solutions and spiked extraction solutions in the range of 0-90 µg/L Se. The calculated relative Se signals were plotted versus known concentrations of Se in the solutions and a straight line was fitted to measured points by the least-square method. Figure 8 shows the obtained calibration line, including a detailed view of the obtained Se peaks (Se-K_{α} and Se-K_{β}) in the TXRF spectra. Regressions coefficients were higher than 0.99 indicating a good linearity and a wide working range under experimental conditions. This confirms that the TXRF-determined Se in the organic phase is related with Se content in the initial solutions. Moreover, no significant statistical differences (at the 95% confidence level) between the sensitivities curves for Se standard solutions and extraction solutions spiked with Se were found. This allows the use of an aqueous standard calibration when an extraction solution is analyzed, simplifying the whole quantification process.

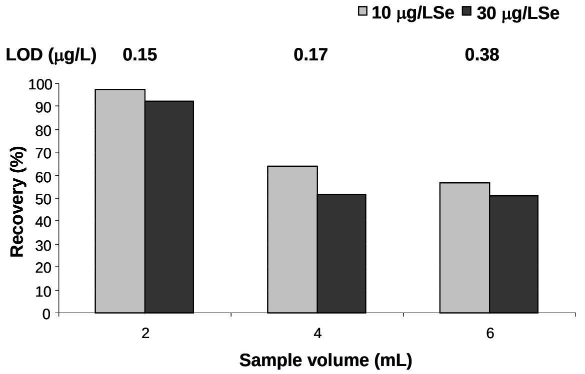


Figure 7: Effect of sample volume on the Se extraction efficiency using DLLME procedure for solutions at two Se concentration levels based on ICP-MS determination and the corresponding LODs using TXRF analyses. For comparison: the WHO guideline is 10 µg/L and natural waters have often Se contents in the low µg/L range.

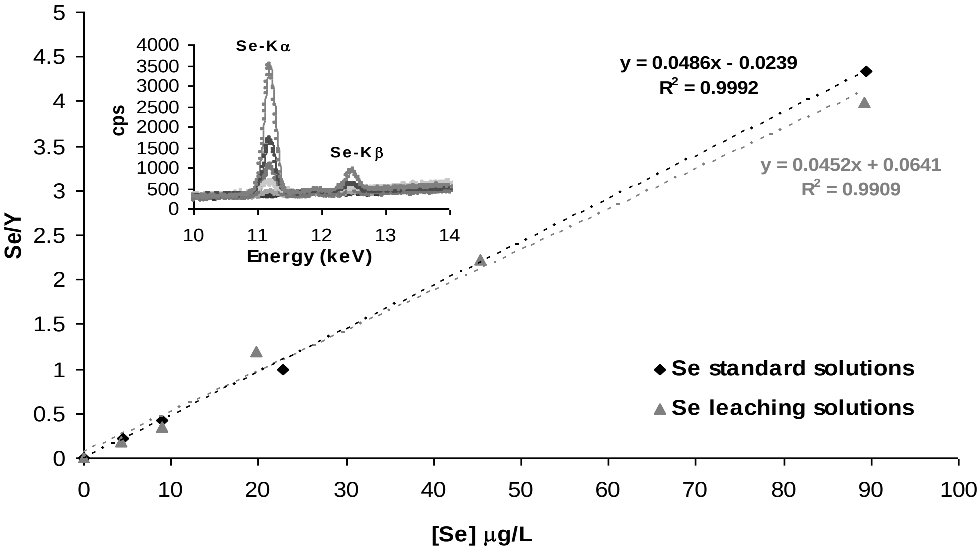


Figure 8: Relative signal intensity (Se-K_{α} / Y-K_{α}) as a function of Se concentration for Se standards and Se spiked extraction solutions.

The calculated LOD for Se using the described sample preparation procedure was 0.73 µg/L of Se in the extraction solution. Therefore, the Se LOD was improved almost one order of magnitude when using the DLLME procedure compared to direct analyses. Moreover, the LOD is suitable for the application to natural samples. To test the applicability of the proposed methodology, an extraction solution containing 6.95±0.7 µg/L of Se (ICP-MS quantification) was analyzed. First, the DLLME procedure was applied to the analysis of the untreated extraction solution (without reduction). No Se peak could be detected in the obtained TXRF spectra. In contrast, when performing the DLLME procedure to the reduced extraction solution a Se peak was detected corresponding to 7.2±1.4 µg/L of Se (TXRF quantification). In Figure 9, a comparison of TXRF spectra obtained for the analysis of the extraction solution with and without a reduction step before the DLLME procedure is displayed. Taking into account that the developed DLLME procedure is only effective for selenite, the concentration of selenate could be estimated as the difference between the concentrations of Se obtained for the analysis of the extraction solution. In this particular case it was found that the amount of selenite was almost negligible (<Se LOD) and the highest part of Se present in the extraction solution was in the form of selenate. These results agree with HPLC-ICP-MS analyses (Section 3.4) showing that 95% of the Se was present as selenate. Therefore, a first indication of the Se speciation in the extraction solution can be obtained using the DLLME procedure with TXRF detection comparing untreated and reduced solutions analysis.

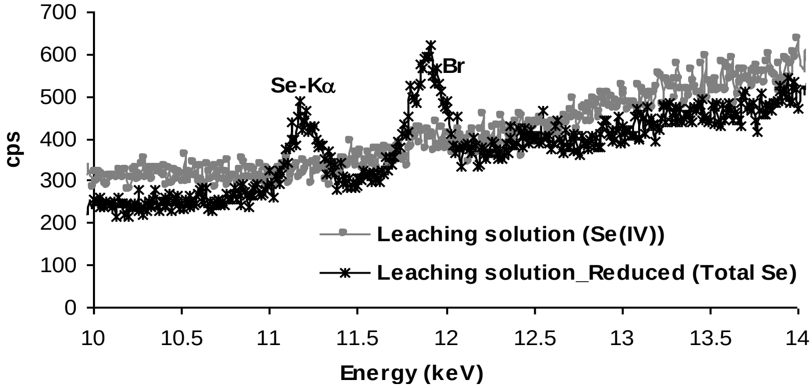


Figure 9: Comparison of the TXRF spectra obtained for the analysis of an extraction solution after the DLLME procedure with and without a prereduction step. Cps = counts per second

3.4 Selenium speciation by HPLC-ICP-MS

With the DLLME procedure prior to TXRF analyses a first indication of the Se speciation in the acid extraction can be obtained. However, for more sensitive speciation analyses HPLC-ICP-MS could be a good alternative. In this section a new protocol for Se speciation analyses by HPLC-ICP-MS using a low pH mobile phase was developed. Since the eluent matched the natural low pH of the samples, no sample pH-adjustment was needed, avoiding the risk of Se loss and species interconversion. Firstly thermodynamic modelling was used to evaluate the potential pH range appropriate for samples with elevated Fe and Al levels. Secondly, the influence of mobile phase composition on the separation of selenite and selenate at low pH was evaluated. Afterwards, the developed method was applied to a natural acid rain sample and an acid soil extraction.

3.4.1 Essentiality of the new protocol

Thermodynamic calculations predicted that gibbsite (γ-Al(OH)$_3$) is the thermodynamic stable phase at pHs above respectively 4.1 and 3.6 for the acid soil extractions, which have an Al concentration between 2 and 130 mg/L, (Figure 10A). Natural acid rain samples from Mount Etna have up to 49 mg/L Al (Calabrese, 2009), which means that at a pH > 3.7 gibbsite is the thermodynamic stable form. Amorphous aluminium (α-Al(OH)$_3$) is the thermodynamic favourable phase at a pH above 4.5-5.2, depending on the Al concentration. As a consequence, precipitation can occur when such samples are adjusted in pH for speciation analyses by conventional methods.

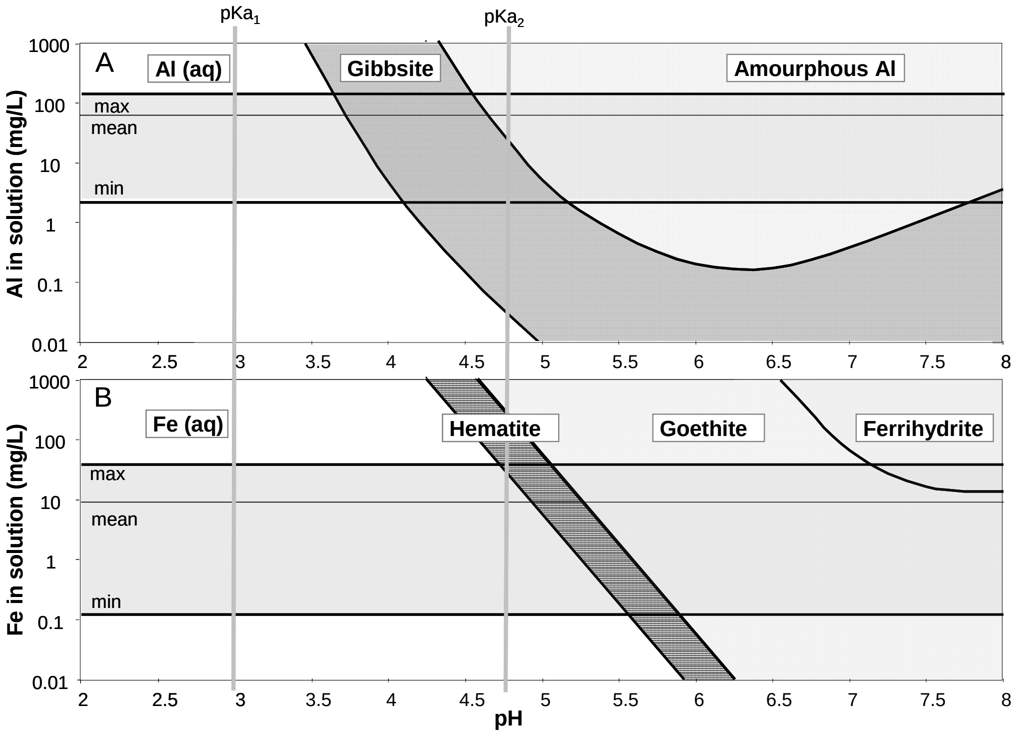


Figure 10: Solubility diagrams showing thermodynamic favourable species of A) Al and B) Fe with Fe and Al concentrations range found in acid soil extractions (grey boxes) and pKa$_1$ and pKa$_2$ of citric acid (grey bars) indicated.

However, the occurrence of precipitation does not only depend on the thermodynamic stability of minerals, but also on mineral precipitation kinetics. Hence, a solution can be oversaturated with respect to one phase, such as gibbsite (Nagy and Lasaga, 1992). Currently, no kinetic data are available for my experimental temperature. However, experiments performed at 80°C showed that some gibbsite is formed within 3 minutes (Loh et al., 2000). Due to the lower ordering compared to gibbsite, the precipitation of amorphous aluminium oxide is kinetically even faster. Thus, expected precipitation kinetics are within the frame of chromatographic separation (~10 minutes). Although hematite (Fe$_2$O$_3$) appeared as the thermodynamic stable species for the acid soil extractions with highest Fe concentrations at pH 4.8 (Figure 10B), this highly ordered mineral phase can only be formed at enhanced temperatures or by transformation from other Fe minerals (Cornell and Schwertmann, 2003). Therefore, its precipitation is not expected at the Fe levels in the samples. However, it is known that goethite (FeOOH) and ferrihydrite ($FeOOH \cdot 0.4H_2O$) can directly precipitate from solution (Cornell and Schwertmann, 2003). As a result, precipitation can occur for samples with higher Fe concentrations or when using a mobile phase with higher pH.

As explained in the introduction, the prevention of precipitation is needed for speciation analyses. This can be done with a low pH mobile phase. At pH 3, as employed in this study, soluble Fe and Al are the thermodynamic stable species for all samples (Figure 10). Even with Fe and Al concentrations up to the several weight percent, no precipitation is expected to occur.

3.4.2 Effect of mobile phase composition

A 5 mM di-ammonium hydrogen citrate buffer with a pH of 4.8 has been previously used in Se speciation studies for non-acidic samples (Ge et al., 1996; Bird et al., 1997; Diaz Huerta et al., 2003; Bueno et al., 2007). This citrate-containing mobile phase is suitable for the adaptation to a low pH since citric acid has different pKs (pKa_1=3.1, pKa_2=4.8 and pKa_3=6.4, Harris 2006), including one at a sufficient low pH to prevent Al or Fe precipitation. The experiments showed that almost no effect of pH or citrate concentration on the selenite retention time was detected. Selenite is mainly present as $HSeO_3^{-1}$ in the tested pH range (3.0-4.8) and therefore little interaction occurs between the column and this analyte. In contrast, selenate is present as SeO_4^{2-} and therefore displays more interaction with the column. In agreement with this, the retention time for selenate was observed to be strongly influenced by mobile phase composition. A decrease in pH increased exponentially the retention time of selenate (Figure 11A; power law r^2= 0.999 and 0.997 for respectively 10 and 20 mM).

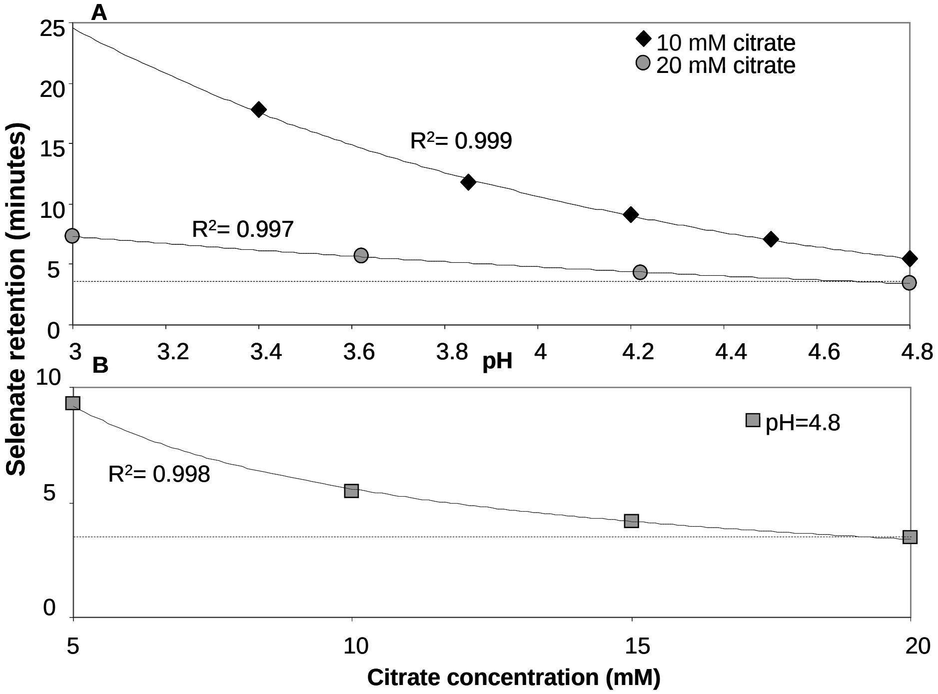


Figure 11: Effect of pH and citrate concentration of mobile phase on selenate retention time. Dashed line indicates selenite retention time.

This behaviour can be explained by the interaction between the citrate in the mobile phase and the column. At lower pH, citrate will be protonized to a higher degree and therefore interact less with the anion exchange column. As a result, selenate will be retained more and show higher retention times. Using the same citrate concentration as employed in previous Se speciation studies but at pH 3, the expected retention time is unacceptably long (>30 min). However, the effect of the pH can be compensated by more citrate (Havel et al., 1999). At higher concentrations, the citrate ion will interact stronger with the column, decreasing selenate retention. The extrapolated retention time with a citrate concentration of 10 mM at pH 3 was around 24 minutes while for a 20mM citrate buffer at the same pH the elution time was around 7 minutes. A similar trend could be observed at pH 4.8, previously employed in Se speciation studies (Figure 11B; power law r^2=0.999). Based on these preliminary tests, I propose a 20 mM citrate buffer at pH=3 with 2% methanol as the optimum mobile phase for Se speciation in acidic samples.

3.4.3 Selenium speciation of acidic environmental samples

For the first time, a mobile phase matching the acidic pH of environmental samples has been employed for Se speciation analyses by HPLC-ICP-MS. Example chromatographs of a natural acid rain sample and an acid soil extraction are given in Figure 12. The use of a hydrogen pressurized ORS allows the monitoring of the more abundant Se isotopes ^{78}Se and ^{80}Se instead of the less abundant ^{82}Se, improving the sensitivity.

The limit of detection (LOD) and limits of quantifications (LOQ) based on repetitive blank measurements (Vial and Jardy. 1999) were around 0.1 µg/L and 0.2 µg/L respectively for both selenite and selenate using either $^{78}Se^+$ or $^{80}Se^+$. Although ^{80}Se is more abundant than ^{78}Se and therefore has a higher sensitivity, obtained LODs and LOQs were similar. This is related to the higher baseline noise on m/z^+ 80 (several hundreds counts per second), probably due to $^1H^{79}Br^+$ interferences derived from bromine within the mobile phase (based on signal m/z^+ 79 and 82) and from the remains of the Ar dimer. The sample-derived bromide anion was resolved in this method, since it had a different retention time than the Se species (RT for bromide ~ 9 min, selenate ~ 7 min and selenite ~ 3 min, Figure 3A). Only in one sample with very high bromine content the bromide and selenate peaks eluted very close and small overlap might occur (Figure 12B). Due to this potential overlap at high bromine concentrations and since LODs and LOQs are similar $^{78}Se^+$ is recommended as monitoring isotope, with $^{80}Se^+$ only for quality control.

Calibration in the concentration range of interest (0.5 to 10 µg/L) was linear with a R^2 of > 0.997 (Table 3). In order to check for matrix effects, a natural and a synthetic solution (using the same sulphuric acid concentration as in the experiments and a Fe concentration of 50 mg/L) were spiked with selenite and selenate at different concentrations. In case of selenite, there were no statistical differences at the 95% confidence level (Miller et al., 2002) between the slopes for the standards, for a spiked natural sample and for a spiked synthetic sample, indicating the absence of matrix effects (Table 3). However, a statistical difference existed in the selenate slope. Since the slope for the synthetic and natural samples were the same at the 95% confidence interval, matrix-matched standards should be used. Moreover, it could also be observed that selenite and selenate have a slightly different slope. Therefore, separate calibration should be performed for both species. Triplicate measurements of some of the samples show acceptable variations in concentration below 10 %. In summary, this method is able to obtain Se speciation information in acid samples rich in Al, Fe and Br.

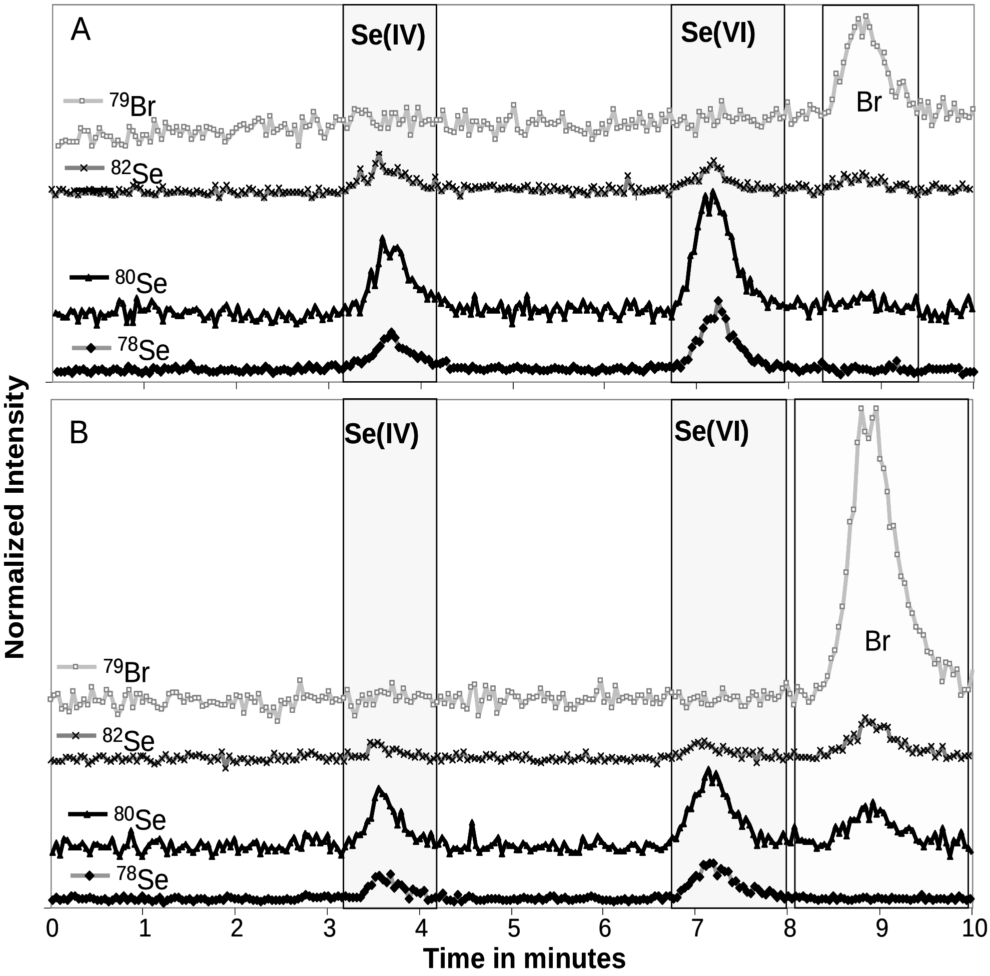


Figure 12: HPLC-ICP-MS chromatographic separation of selenite (Se(IV)) and selenate (Se(VI)) and bromine (Br) (interference with $^{80}Se^+$ and $^{82}Se^+$) in an acid soil extraction (A) and a natural rain sample (B). Baselines are separated for clarity. Normalized intensity is counts per second (cps) of the analyte mass divided by the cps of the internal standards ($^{115}In^+$).

Table 3: Comparison of slope (at the 95% confidence interval) in standards, spiked synthetic samples (450 mg/L SO_4^{2-} and 50 mg/L Fe) and spiked acid soil extractions using selenite and selenate levels up to 10 µg/L and $^{78}Se^+$ as monitoring isotope.

	Selenite		**Selenate**	
	Slope	R^2	Slope	R^2
Standards	3391 ± 39	0.9997	4305 ± 13	0.9997
Synthetic sample	3406 ± 83	0.9990	4153 ± 61	0.9997
Acid soil extraction	3318 ± 240	0.9897	4189 ± 167	0.9971

4 Conclusions

Direct TXRF analyses are a cheap and fast method to obtain multi-elemental information. For groundwaters samples with low salinity and hardness, the measured LOD (0.1 µg/L) was two orders of magnitude lower than the WHO drinking water guideline (10 µg/L Se). Moreover, it was shown that multi-elemental information can be obtained. Therefore, direct TXRF analyses are suitable for the analyses of groundwaters. However, for thermal waters the LOD can significantly increase due to the high Br content, making direct TXRF analyses less useful.

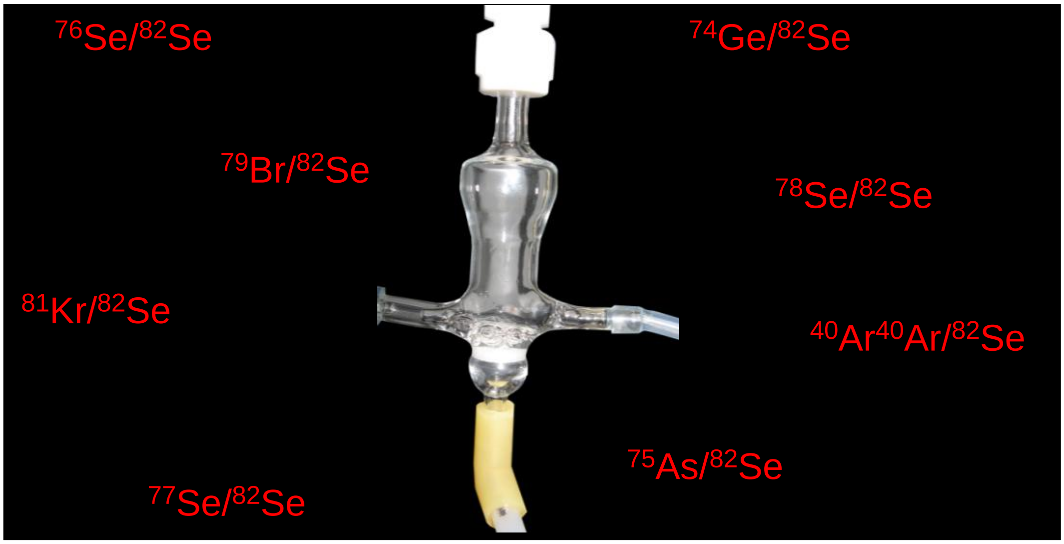
The Se LOD in soil extractions is significantly higher, due to increased background noise compared to groundwater spectra and to the presence of major elements such as Fe, Zn and Na. Therefore, only Se-rich natural samples have high enough levels for direct TXRF analyses. Even so, this approach can be very useful in lab controlled experiments using non-natural conditions, such as kinetic studies of sorption processes. The multi-element information obtained thorough the direct TXRF analysis of the extraction solution is a powerful tool for understanding the controlling factors of Se mobility. Moreover, the small sample volume required opens the possibility to perform also kinetic studies on mass limited samples such as volcanic ashes.

Sample preparation can significantly improve the LODs. The Se LOD was improved by a factor of 2 using a cation exchange procedure to eliminate the cations from the acid soil extraction matrix. However, a higher sample volume was needed compared to direct TXRF analyses and the method can only be used for anionic and neutral species. Even better LODs have been obtained using a DLLME technique to separate the Se from the matrix. A disadvantage of this approach is that no multi-elemental information can be obtained. However, the LOD was suitable for the application to environmental samples. Another advantage using this procedure is that a first insight in the inorganic Se speciation could be obtained.

For more sensitive speciation analyses, HPLC-ICP-MS should be used. Precipitation of Fe and Al phases due to pH adjustment for chromatographic analyses should be prevented, since they can bias the measurements and damage the HPLC chromatography column. Thermodynamic modelling showed that the use of mobile phase with a low pH close to that of the natural samples could eliminate the risk of precipitation. In order to remain an efficient separation, the ionic strength of the eluent should be increased. Using a mobile phase with 20 mM citrate and 2% methanol at a pH of 3, selenate and selenite could be separated in a total measurement time below 10 minutes. The utilization of an ICP-MS equipped with collision/reaction technology allowed the determination of Se trace levels with a LOD of 0.1 µg/L using $^{78}Se^+$ for detection. The application to a natural rain sample and an acid soil extraction shows the suitability of this method for acidic samples rich in Al, Fe and/or Br.

Chapter 5

Analytical improvements for selenium isotope ratio measurements



G.H. Floor, T.D. Bullen, T.M. Johnson, R. Millot. Evaluation of pseudo-high mass resolution for selenium isotope ratio measurements by hydride generator multi collector ICP-MS
To be submitted to International Journal of Mass spectrometry.

G.H. Floor, R. Millot, M. Iglesias and Ph. Négrel, 2011. Influence of methane addition on sensitivity and interferences for selenium isotope ratio measurements by Multi-Collector-ICP-MS. *Journal of Mass Spectrometry* **46**, 182-188.

1 Introduction

Selenium isotope ratio variations could be a useful tool in the understanding of Se mobility in volcanic environments, since Se isotopes can be either used as a source tracer or as an indicator for redox transformations (Chapter 2 and 3). Selenium isotope signatures are currently measured using primarily Hydride Generation Multi-Collector Inductively Coupled Plasma Mass Spectrometry (HG-MC-ICP-MS), because of its sensitivity, accuracy and sample throughput. However, the measurements are extremely challenging for a number of reasons as explained in Chapter 2. The main problem is that numerous interferences overlap selenium isotopes and that extensive sample preparation is required. The main concern for Se measurements by ICP-MS techniques are the Ar-based interferences. (Moellmer et al., 2007; Elwaer and Hintelmann, 2008a,b; Muñoz-Olivas et al., 1995). Different approaches currently exist in Se isotopic analysis by MC-ICP-MS to overcome these. A Micromass Isoprobe MC-ICP-MS contains a hexapole collision-reaction cell, which can be used to chemically attenuate the polyatomic interferences by collisions between a gas and the ion beam (Rouxel et al., 2002; 2004, Carignan and Wen, 2007). However, most MC-ICP-MS instruments are not equipped with such a device. In this case, the contributions of Ar dimers have been corrected using mathematical equations (Chapter 2; Clark and Johnson, 2008; Elwaer and Hintelmann, 2008b, Zhu et al., 2008).

Since interferences often have slightly greater masses compared to those of the analyte isotopes, high mass resolution is another potential approach to resolve interferences. High mass resolution has been used for Se concentration measurements by sector field ICP-MS (Moor and Kobler, 2001; Wildner 1998; Feldman et al., 2000; Townsend, 1999; Krachler et al., 1999; Narasaki and Cao, 1996; Elwaer and Hintelmann, 2008a). Nevertheless, MC-ICP-MS has a lower resolving power since a wide detector slit is needed to obtain flat top peak shapes which are indispensable for high precision isotopic analysis. In this configuration often called ´pseudo-high´ mass resolution analyte and interferent beams can be measured separately, but their peaks are not totally separated in mass scans. This approach has been used recently for the isotopic analyses of Fe (Weyer and Schwieters, 2003; Malinovsky et al., 2003; Poitrasson and Freydier, 2005; Schoenberg and Von Blanckenburg, 2005; Dauphas et al., 2009), Ca (Wiesser et al., 2004), Zn (Stenberg et al., 2004), Si (Georg et al., 2006; Engström et al., 2006; Van den Boorn et al., 2006), S (Craddock et al., 2008; Clough et al., 2006) and Cr (Schoenberg et al, 2008). However, the performance of pseudo-high mass resolution in MC-ICP-MS has so far not been explored for Se isotopes. The mass differences between Se isotopes and its spectral interferences are smaller compared to other isotopic system where pseudo-high mass resolution has been applied, and therefore resolving the interferences with pseudo-high mass resolution could be challenging. Nonetheless, this approach could help to simplify Se isotopic analysis.

Even if interferences cannot be (totally) resolved, the precision of Se isotope ratio measurements can still be improved by increasing Se sensitivity and analyte/interference ratios. High precision is of extreme importance in isotopic analysis, because the variations in isotopic composition are very subtle (few %, Johnson, 2004; Carignan and Wen, 2007). As discussed in Chapter 2, carbon addition to the plasma shows beneficial effects on Se determination in ICP techniques due to an improved Se sensitivity and a decrease of spectral interferences. Both effects increase the analyte/interference ratio. However, until now, carbon-loaded plasmas have not been used in isotope ratio measurements using a multi-collector ICP-MS.

The present study aims to explore two different approaches to improve Se isotope ratio measurements by MC-ICP-MS. Firstly, the suitability of pseudo-high mass resolution for the measurement of Se isotope ratios by MC-ICP-MS has been evaluated. I mainly focus on the potential to eliminate Ar-based interferences, since these interferences are the main concern and pseudo-high mass resolution could be a useful tool to resolve them. Secondly, the performance of a methane mixed plasma is assessed. For both a hydride generator and a standard introduction system, I studied Se signal intensity changes due to the presence of methane. Subsequently, the effect of methane on potential interferences, precision and mass bias have been evaluated using the hydride generation injection system. As far as I am aware, it is the first time a carbon loaded plasma has been used in multi collector ICP-MS and that a hydride generation injection system is combined with a methane mixed plasma.

2 Experimental section

2.1 Instrumentation and experimental conditions

All measurements were performed with a NEPTUNE MC-ICP-MS (Finnigan, ThermoElectron). The Neptune has three switchable entrance slits located with slit widths of 250, 30 and 16 µm resulting in ‘low’, ´medium´ and ´high´ resolution modes. The resolving power is defined as:

$$R_{power(5,95\%)} = \frac{m}{\Delta m^*} = \frac{m}{m(5\%) - m(95\%)} \tag{1}$$

where Δm is the mass difference between the points where the intensity of the peak changes from 5 (m(5%)) to 95% (m(95%)) of the maximum (Weyer and Swieters, 2003). For the evaluation of the performance of pseudo-high mass resolution the 16 µm entrance slit has been used. For the methane-mixed plasma study the low resolution slit (250 µm) was utilized. The NEPTUNE MC-ICP-MS is equipped with eight movable Faraday cups. Additionally, it contains one fixed central channel which, due to its fixed position, is used as reference in mass scans. As a result, up to nine masses can be measured simultaneous. Precise cup positioning is especially important for high mass resolution measurements to ensure a good peak overlap of several isotopes at the same time. The maximum distance between the outermost cup positions corresponds to a relative mass range of around 17% (Weyer and Swieters, 2003; Wieser and Swieters, 2005).

To introduce the sample, a hydride generator (HG) introduction system was used (Figure 1A). The sample was pumped at a flow rate of about 0.25 mL/min and merged with a reducing agent at least 40 cm before they entered a gas-liquid separator. A low-flow of argon (0.03 L/min) gas entered the gas-liquid separator in order to get efficient transport towards the plasma (indicated as Extra (Ar) in Figure 1A). The volatile selenium hydride was mixed with a carrier gas flow, sometimes mixed with a small amount of methane.

For the methane mixed plasma test also a Stable Introduction System (SIS, ThermoFinnigan) was used, which consists of a quartz glass dual spray chamber arrangement (cyclonic and standard Scott double pass) combined with a low-flow PFA microconcentric nebulizer (Weyer and Swieters, 2003). In this case, the sample was directly transferred to the plasma by self-aspiration (Figure 1B). In both set-ups the methane (CH_4 = 2.013 ± 0.040 mol% in Ar) was mixed with the carrier gas before the torch with a Y-connection part. Typical instrumental conditions for both set-ups are shown in Table 1.

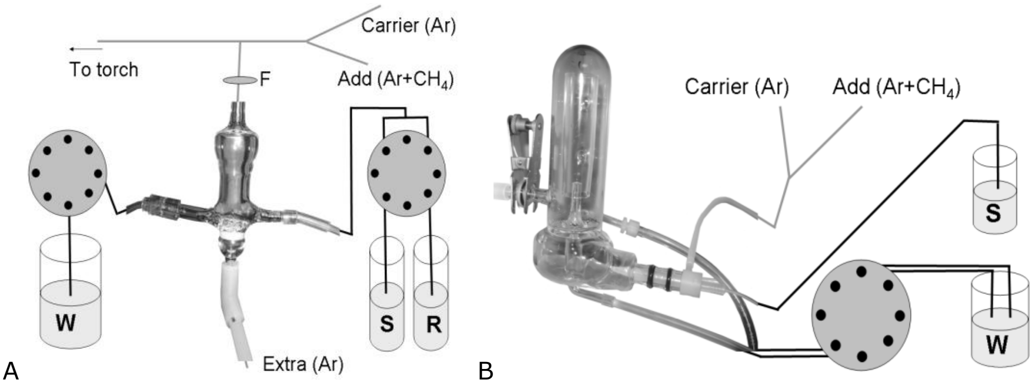


Figure 1: experimental set-up A) for a hydride generator (HG) introduction system and B) for a stable introduction system (SIS). S= sample; R= reducing agent; W= waste; F=filter.

Table 1: Typical instrumental conditions for HG and SIS injection systems.

		Hydride generator	**SIS**
RF Power (W)		1050	1100-1300
Flow rates (L/min)	Plasma	14	14
	Carrier	0.8-1.4	0.8-1.2
	Auxiliary	1.1	0.7
	Add (2% CH_4 in Ar)	0.0-0.4 (optimum 0.05)	0.0-0.4
	Extra	0.03	-
Sample matrix		2 N HCl	3% HNO_3
Reducing agent		NaBH4 (0.5% w/v) stabilized in NaOH (0.5% w/v)	
Sample input flow		0.23 mL/min (pump)	0.08 mL/min (self-aspiration)

Tuning was performed using a diluted selenium solution to obtain the best conditions for signal sensitivity and stability, peak shape and low hydride polyatomic atoms by adjusting the torch position, gas flows and lens voltages. The peak shape is an essential parameter, especially in pseudo-high mass resolution. In this approach, where measurements are performed at the edge, peak shapes determine the resolving power and the width of the flat interference plateau. Low resolution analyses were performed in the centre of the peak. For the methane-mixed plasma study the tuning was performed without methane addition. After methane addition, only the carrier gas flow and the radio frequency (RF) power were retuned for maximum sensitivity. Sampler and skimmer cones were made from nickel and a traditional H skimmer cone was used.

2.2 Reagents and materials

For the HG, standard solutions of 5, 10 and 100 µg/L Se in 2N HCl were prepared out of 1000 mg/L Se stock solution (CPI international), double distilled HCl and Milli-Q water. A blank solution consisted of 2N HCl without Se addition. HCl has a strong reducing nature favouring the selenium hydride formation (Layton-Matthews et al., 2005). With the use of a HG only part of the Cl will enter the plasma and will cause a relatively small interference on m/z$^+$ 77 (Muños-Olivas et al., 1995). The reducing agent for the hydride generation introduction system consisted of 0.5 % w/v $NaBH_4$ (Merck reagent grade) stabilized by addition of 0.5% NaOH (Merck reagent grade). For the SIS a 100 µg/L Se solution in a 3% v/v nitric acid matrix (Merck Suprapure) was used. HCl was avoided to maintain a low background level on m/z$^+$ 77, otherwise influenced by $^{40}Ar^{37}Cl^+$ (Moellmer et al., 2007).

2.3 Data acquisition

Data were acquired using the dynamic mode. In this mode, the mass in the centre cup is varied within one measurement without changing the cup positions. In the pseudo-high mass resolution study five Se isotopes (m/z$^+$ 74, 76, 77, 78 and 82), Ge (m/z$^+$ 72), Br (m/z$^+$ 79) and Kr (m/z$^+$ 83) were collected simultaneously. However, the centre cup mass (m/z$^+$ 77) was varied slightly (from 76.846-76.848 in 5 steps and 76.92) in order to evaluate the peak shape and more specifically the flatness of the Se plateau. Standards were measured using 1 block of 15 cycles and an integration time of 4 second. The masses selected (76.846-76.848) were based on the results of previous mass scans. For these mass scans, a mass range (76.83-86.99) was explored using 800 steps with an integration time of 0.1 seconds (total mass time 80 seconds).

For the evaluation of the methane-mixed plasma in the main cup configuration six Se isotopes (m/z$^+$ 74, 76, 77, 78, 80, 82), Ge (m/z$^+$ 72) and As (m/z$^+$ 75) were measured simultaneously. Subsequently m/z$^+$ 80 and 81 (ArArH/ArAr) and afterwards 83 and 84 (Kr) were measured by changing the mass in the centre cup (so called peak jumping). In this set-up all Se isotopes and masses needed for mathematical corrections were collected at the same time. Only minor interferences which are normally corrected by on-peak zero correction (blank correction using the same mass as the measurement) were measured consecutively. For the Se sensitivity test, 25 cycles of 4s integration times have been measured (total measurement time 8 minutes for the three different cup configurations). For the precision test, the main cup configuration (collecting concurrent Se, Ge and As masses) was measured during 10 minutes (150 integrations of 4 s each).

3 Results and discussion

3.1 Evaluation of interference separation by pseudo-high mass resolution

In a first step, mass scans (mass range from 76.83 to 76.99 in the centre cup) have been performed in order to evaluate the performance of high mass resolution. Schematic ion beam profiles for the different Se isotopes are given in Figure 2. The profiles are only schematic, because with an integration time of only 0.1 seconds in the total time of 80 seconds significant signal intensity variations occurs. Since interferences should have enough signal intensity to be observed, minor contributions of interferences cannot be observed.

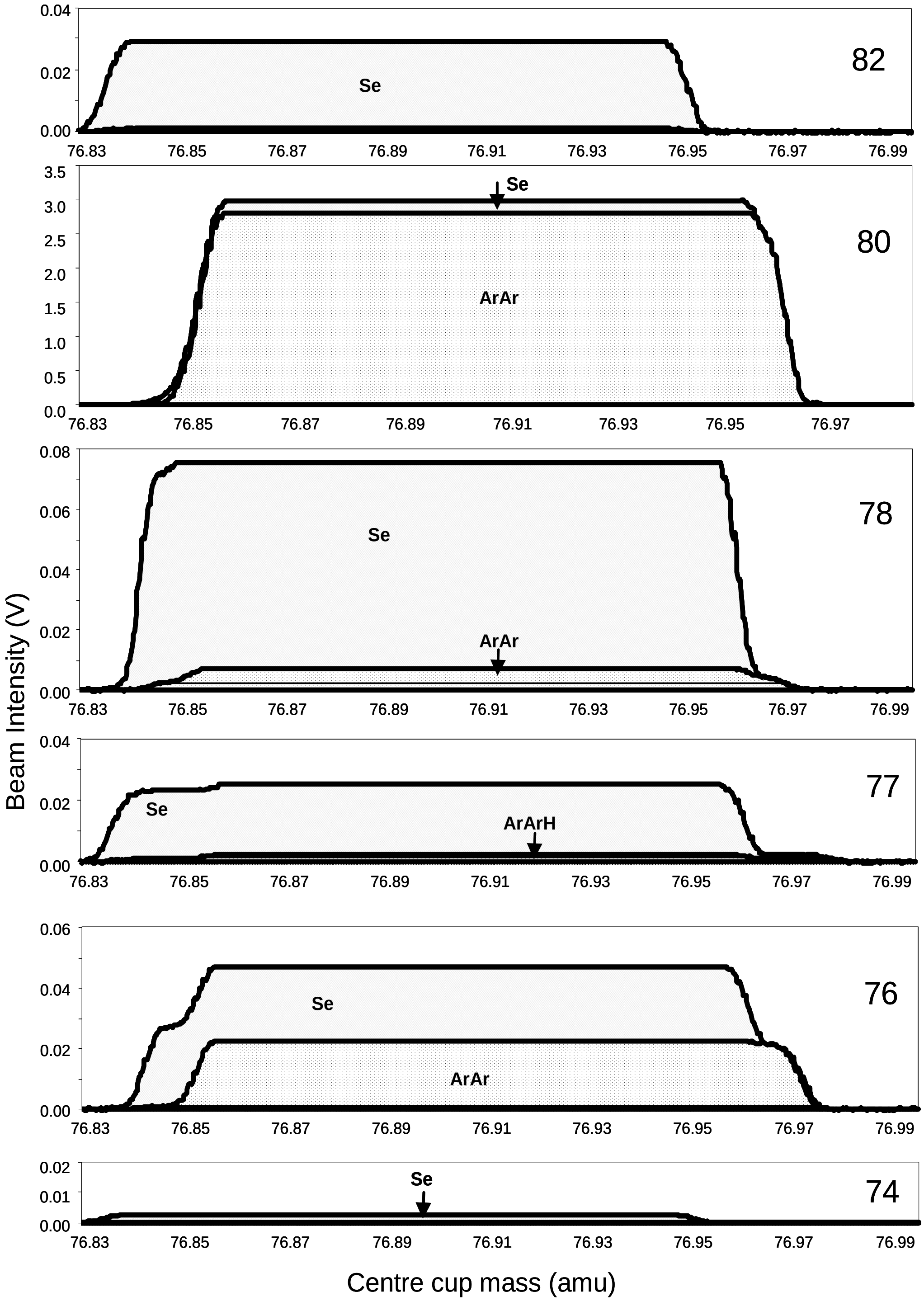


Figure 2: Schematic ion beam profiles for Se isotopes using pseudo-high mass resolution based on mass scans using a 2N HCl blank solution (dots) and a 10µg/L Se solution (stripes). The difference between the blank solution and Se solution corresponds to signal caused by Se (striped area only, not the sum). Tuning conditions: ArArH/ArAr~10% (optimum <1%).

At m/z$^+$ 82 no major interferences occured. This agrees with published studies where only minor contributions of $^{40}Ar^{40}ArHH^+$ and ^{82}Kr are reported, which can easily be corrected by an on-peak zero substraction (Layton-Matthews et al., 2005; Carignan and Wen, 2007; Clark and Johnson, 2008; Elwaer and Hintelmann, 2008b). At m/z$^+$ 80 the 10 µg/L Se solution had only a slightly higher beam intensity compared to the blank solution, related to the strong contribution of $^{40}Ar^{40}Ar^+$. Even when scanning over a narrow range of mass on the low mass side of the peak, a plateau area with only Se signal was not observed. This is as expected, since even for ´full´ high mass resolution with a single collector ICP-MS it has been shown that high mass resolution is not able to resolve this interference (Wildner, 1998; Elwaer and Hintelmann, 2008a). Therefore, in the rest of this study, mass 80 was not further investigated. At m/z$^+$ 78, the $^{38}Ar^{40}Ar^+$ contribution was relatively small compared to Se intensity with 10 µg/L. A narrow plateau area seems to be observed on the low mass side of the peak, where the signal appears to be only due to ^{78}Se. At m/z$^+$ 77 the observed pattern in the ion beam profile strongly depended on the tuning of the plasma and ion source. In the case of low ArArH/ArAr ratios (<1%, monitored using the ratio of the intensities at m/z$^+$ 81 and 80) no interferences were observed (data not shown). This indicates that the $^{40}Ar^{37}Cl^+$ interference is small compared to the Se signal, as expected with the use of a HG injection system (Muños-Olivas, 1995). In the case of a higher ArArH/ArAr ratio (~10%) an interference was observed at m/z$^+$ 77, as shown in Figure 2. The peak plateau at the left side of the peak with only ^{77}Se signal seems to be sufficiently wide to resolve this interference with pseudo-high mass resolution. However, since the mass difference between $^{36}Ar^{40}ArH^+$ and $^{77}Se^+$ is greater than for $^{40}Ar^{37}Cl^+$ and the same Se isotope, this does not mean that the $^{40}Ar^{37}Cl^+$ can also be resolved using high-resolution. At m/z$^+$ 76 the $^{36}Ar^{40}Ar^+$ and $^{76}Se^+$ had roughly the same intensity. Again, a narrow plateau area can be observed. At m/z$^+$ 74 no interferences were observed. Although $^{36}Ar^{38}Ar^+$ can arise, its occurrence is extremely low. It can also be seen that the signal intensity was low, related to the low isotopic abundance of ^{74}Se. This could cause problems in the counting statistics.

Since the different masses were collected at the same time, variation in signal intensity can be removed using normalization to a non-inferred isotope. As observed above, at m/z$^+$ 82 and 74 no major interferences were observed. However, the intensity at m/z$^+$ 74 was low, making it less suitable for normalization purposes. Therefore, for more detailed mass scans in a smaller mass range (76.83 to 76.86 in the centre cup) the intensities were normalized to $^{82}Se^+$ intensity. The normalized ion beams for a blank solution (2N HCl) and Se solutions of 10 and 100 µg/L are shown in Figure 3. At m/z$^+$ 74 similar average ratios were observed for the solutions over the whole mass range measured. However, the precision varied significantly. This can be explained by the low intensity of the ion beam at m/z$^+$ 74 (counting statistics). At m/z$^+$ 77 the signal was similar for the solutions in the centre zone of the investigated mass range. The fact that also the blank solution followed the Se ratio can be explained by memory effects. The contribution of ArArH could clearly be observed at the right-hand edge (in the case of ArArH/ArAr~10%). Its relative importance strongly depended on the Se concentration. For m/z$^+$ 76 and 78, it was observed that that even within several milli-Dalton small variations occured. No real analyte plateau was observed; this suggests that the tail of the Ar-dimer peaks still contribute small but significant intensity throughout the apparent plateaus that can be seen in Figure 2.

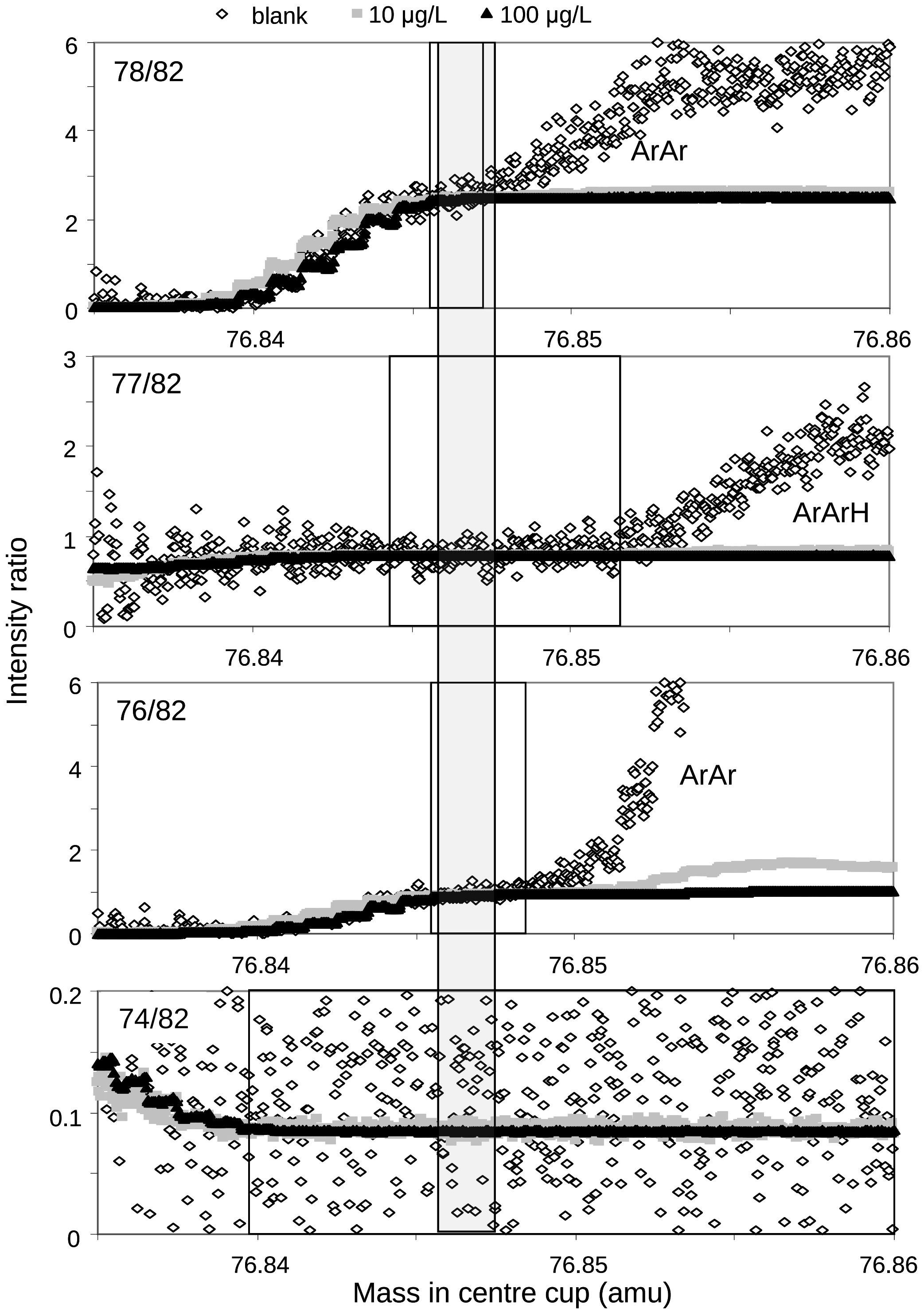


Figure 3: Normalized ion beam intensities at the left side of the peak. The range of the apparent interference- free zone (white boxes) and range of Figure 4 (grey continuous bar) is shown.

In order to better investigate these phenomena, dynamic mass scans using 15 cycles and an integration time of 4 seconds for five different masses within the ´plateau´ area were performed (Figure 4). For comparison, the ratio was also determined at the peak centre, where both Se and interference signal occurs (indicated as horizontal lines). Moreover, both blank-corrected (closed symbols, light grey line) and raw (not blank-corrected) ratios (open symbols, dark grey line) are shown within the figure.

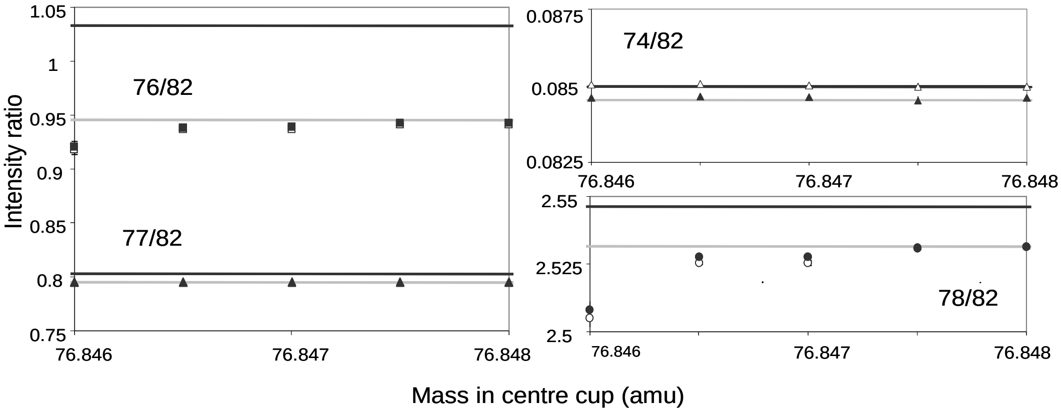


Figure 4: Isotope ratios in the plateau areas. Open symbols: raw ratios. Closed symbols: blank corrected ratios. Dark line: raw ratio at peak centre. Light line: blank corrected ratio at peak centre.

At m/z$^+$ 74 the ratios within the plateau were the same as in the peak centre (symbols plot on corresponding lines). This again demonstrates the absence of the $^{36}Ar^{38}Ar^+$ interference. However, the blank corrected and raw ratios had a small difference. This can probably be explained by memory effects of previous Se analysis with different isotope ratios. At m/z$^+$ 77 the same ratios were observed for raw and blank corrected data in the plateau area. This suggests that the $^{40}Ar^{37}Cl^+$ interference does not influence the ratios within the analyte plateau. The values also corresponded with the blank corrected ratio obtained in the peak centre. However, the raw ratio at the peak centre (black line in Figure 4) was slightly higher due to the $^{38}Ar^{40}ArH^+$ interference (and potentially $^{40}Ar^{37}Cl^+$). This indicates that an on-peak zero subtraction is enough to correct for this interference. At m/z$^+$ 76 and 78 significant variations in the ratio occur along the plateau area with an increase of the 76/82 and 78/82 ratio with increasing mass. This means that Ar-tailing occurs before a flat plateau with only Se signal occurs and that the Ar-dimers were not well resolved. In this case, tiny drifts of the magnet and the HV will reduce signal stability and poor precision, making it unsuitable for isotopic measurements.

3.2 Potential of pseudo-high mass resolution

In Section 3.1, it was found that for $^{74}Se^+$, $^{77}Se^+$ and $^{82}Se^+$ flat analyte plateaus were obtained in pseudo-high mass resolution. However, it was not possible to obtain such plateaus for $^{76}Se^+$, $^{78}Se^+$ and $^{80}Se^+$. As explained in Chapter 2 a minimum of four interference free isotopes are needed using a double-spike for instrumental mass bias correction. Using the pseudo-high mass resolution approach these cannot be obtained. For standard bracketing a minimum of two interference free isotopes are needed. In order to plot the results on the mass fractionation line two ratios are used and as a result an extra isotope is needed. Indeed three different interference-free isotopes were obtained. However, as demonstrated above, on m/z$^+$ 77 an on-peak blank correction can already solve the ArArH interference. Therefore, even with low resolution an interference free signal can easily be obtained. On m/z$^+$ 82 and 74 no major interferences were observed. This is in correspondence with literature studies, which only reports the minor interferences $^{74}Ge^+$, $^{81}BrH^+$, $^{82}Kr^+$ and $^{40}Ar^{40}ArH_2^+$. These interferences can be resolved using proper sample preparation, on-peak zero correction and/or simple mathematical equations (Chapter 2; Layton-Matthews et al., 2005; Clark and Johnson, 2008; Elwaer and Hintelmann, 2008b). Moreover, the elemental interferences $^{74}Ge^+$ and $^{82}Kr^+$ are impossible to resolve with the high mass resolution achievable using current mass spectrometry technology. Therefore, pseudo-high mass resolution does not improve the measurements of these masses. More complex are the mathematical corrections for Ar dimers (Clark and Johnson, 2008; Elwaer and Hintelmann, 2008b; Zhu et al., 2008). The elimination of these Ar-based interferences would significantly contribute to the simplification of Se isotope ratio measurements. However, with pseudo-high mass resolution these interferences were not properly resolved. A major disadvantage of the pseudo-high mass resolution approach is the loss in signal intensity (Klaue and Blum, 1999; Vanhaecke et al., 2009). Sensitivity is a major issue in Se isotopic analysis because Se has a low abundance in most geochemical matrices. With low mass resolution Se solutions with a concentration 2 and 10 µg/L can be used. However, for pseudo-high mass resolution a higher concentration is needed. In this study an internal precision of around 0.17‰ for $^{77}Se/^{82}Se$ was obtained using a 100 µg/L Se solution and a measurement time of 250s. This is similar as precisions reported using lower Se concentrations with low mass resolution and interference corrections (Clark and Johnson, 2008; Zhu et al., 2008). Additionally, the tuning for pseudo-high mass resolution is more complicated than for low mass resolution due to the importance of peak shape and a precise cup alignment (Weyer and Swieters, 2003). Therefore, pseudo-high mass resolution seems not to give any advantage over the low mass resolution approach.

3.3 Se sensitivity in a methane mixed plasma

Due to the limited success of the use of high mass resolution, the performance of a carbon loaded plasma was evaluated. Changes in Se sensitivity due to the addition of methane are shown in Figure 5 for the SIS (circle) and the HG (square) introduction systems. The results are based on the measurements on m/z$^+$ 82 in a Se solution, but other Se isotopes not (strongly) interfered (e.g. m/z$^+$ 77 and 78) show a similar pattern. All results are normalized to the Se sensitivity without any methane addition. The maximum signal enhancement was around 2.5 at a methane flow rate of 4 mL/min for the SIS. For the HG the maximum signal enhancement was lower (~1.5) and at a lower flow rate (~1 mL/min). In this case methane addition above 2 mL/min gave lower sensitivity compared to no methane addition, while for the SIS the sensitivity increased for all used methane flows (up to 8 mL/min). The sensitivity decrease for higher carbon loading with the use of organic solvents is thought to be related to the cooling of the plasma (Hu et al., 2004). However, this cannot explain the sensitivity decrease using volatile carbon compounds. Roduskhin et al (2005) explained the signal decrease by higher diffusion losses of ions from the analytical zone in the methane-mixed plasma. The enhancement factors fit within the range (between 1.5 and 9) previously reported for methane-mixed plasmas (Park et al., 2003; Roduskhin et al., 2005; Warburton and Goenage-Infante, 2007; Goenage-Infante et al., 2008).

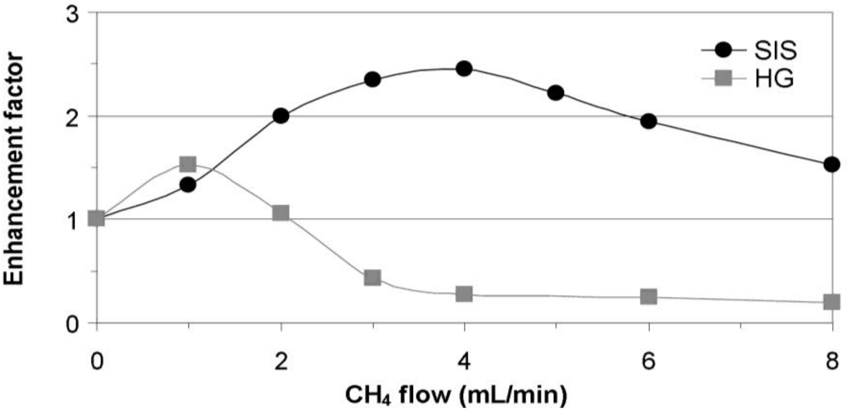


Figure 5: The effect of methane addition on Se sensitivity for SIS and HG.

The different responses of the two injector systems might be related to the different forms of Se which enters to the plasma. For the SIS, the solution arrives as an aerosol. Consequently, some plasma energy is consumed for volatilization of the matrix and to convert the aerosols to gas. As a result, Se is not efficiently ionized. For the HG, the Se enters the plasma as a gas. In this case the plasma energy is only needed for the atomization and ionization. Therefore, the ionization processes can be more efficient. The different response on the RF power for each introduction system confirms this hypothesis. The RF power is a parameter which is related to the temperature in the plasma. The optimum RF power without methane addition was higher for the SIS than for the HG. Another difference is that for the SIS the RF optimum power depended on the amount of methane present in the plasma, while for the HG the optimum RF did not change with methane addition (Figure 6). The lower RF power for a carbon loaded plasma in the SIS, suggests that the methane facilitates the ionization (Hwang et al., 1989). Another difference between the two systems concerns the sensitivity. Taking into account the different transport efficiencies and the flow rates, the Se loading towards the plasma varies about one order of magnitude between the two systems. However, about 20-30 times higher sensitivity was observed for the HG compared to the SIS. Thus, the discrepancy in sensitivity cannot be only explained by variations in the sample transfer and related Se loading within the plasma. This is an additional argument that differences in ionization efficiency occur between both systems. It also explains the dissimilarity in the enhancement factors between the two systems. Since the ionization of the SIS is less efficient, the ionization can be more improved than for the HG. Therefore, a higher enhancement factor is observed for SIS compared to HG.

3.4 Methane mixed plasma and spectral interferences on Se isotopes

Despite the fact that the use of a hydride generator eliminates potential interferences on Se isotopes, several spectral interferences can still occur (Chapter 2). In this section, I discuss the effect of a methane mixed plasma on the occurrence of argon based interferences (e.g. Ar dimers, ArCl), elements transferred to the plasma by the HG causing spectral interferences at Se isotopes (so called hydride forming elements, such as Ge and As) and other interferences (plasma and atmospheric derived Kr, sample cone derived NiO). It is essential to understand how methane influences these interferences. Even if spectral interferences can be corrected, it is advantageous to obtain the highest analyte-interference ratios possible.

3.4.1 Ar-based polyatomic ions

As mentioned before, Ar-based polyatomic ions are the main concern in Se isotopic analysis. The changes of the signal of Ar-based interferences due to the addition of methane measured in a blank solution (2N HCl) normalized to the signal without any methane addition are given in Figure 7. The results of the Ar dimers (squares) are based on the measurements on m/z^+ 80 in the blank solution (2N HCl), whilst other Ar dimer masses (e.g. m/z^+ 76) show a similar pattern. The intensity of the Ar dimer decreased with increasing methane levels. Also the $ArCl^+$ decreased due to methane addition (circles in Figure 7), investigated using the intensity at m/z^+ 77. Although $ArArH^+$ also contributed to the 77 intensity, this beam was 2 orders of magnitude smaller compared to the $ArCl^+$ with optimum tuning (ArArH/ArAr ~ 1%). Methane addition also significantly decreased the intensity of Ar_2H^+ (monitored at m/z^+ 81, diamonds in Figure 7) and therefore probably also $Ar_2H_2^+$, which cause potential interferences at m/z^+ 82. The decrease of polyatomic interferences in carbon loaded plasmas have been observed before (Evans and Ebdon, 1990; Hill et al., 1992; Evans and Giglio, 1993; Ebdon et al., 1994; Muños-Olivas et al., 1995; Roduskin et al., 2005). This has been related to the competitive formation of carbides. The $ArArH^+$ beam decreased faster than for the $ArAr^+$ ion. The difference in signal decrease might be because three instead of two atoms are involved. Another reason can be that more signal decrease is observed for smaller signals. In both cases, the signal decrease on $Ar_2H_2^+$ is expected to be more than for $ArArH^+$. Currently Ar dimers are often corrected using mathematical corrections (Clark and Johnson, 2008; Elwaer and Hintelmann, 2008b; Zhu et al., 2008). Although with the methane mixed plasma these corrections are still needed, there is an improved analyte-interference signal. The other Ar based interference (ArArH and ArCl) are currently corrected with on-peak zero correction (Rouxel et al., 2002; Clark and Johnson, 2008: Zhu et al., 2008). The drift in their abundance will have even less influence in a methane-mixed plasma because their production rate is lower.

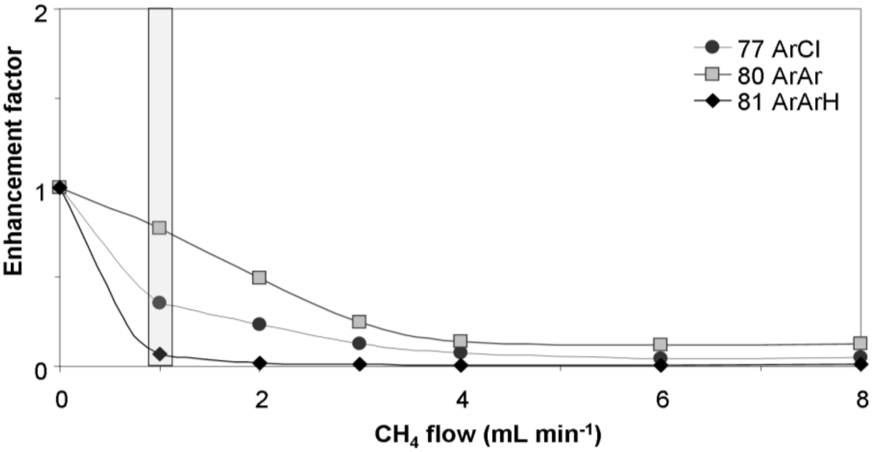


Figure 7: The response of Ar-based polyatomic interferences on methane addition. Grey bar indicated optimum methane flow (with methane in Figure 11).

3.4.2 Hydride generation transferable elements

The hydride-forming ions such as arsenic and germanium form spectral interferences which hinder the measurements of Se isotopes. Therefore, it is essential to know the effect of methane addition on the signal of As, Ge, Br and their hydride ions. The effect of methane addition on the hydride forming elements and their polyatomic ions are reported in Figure 9. It shows that the Ge signal was not enhanced, and therefore the relative influence of the Ge interference decreased.

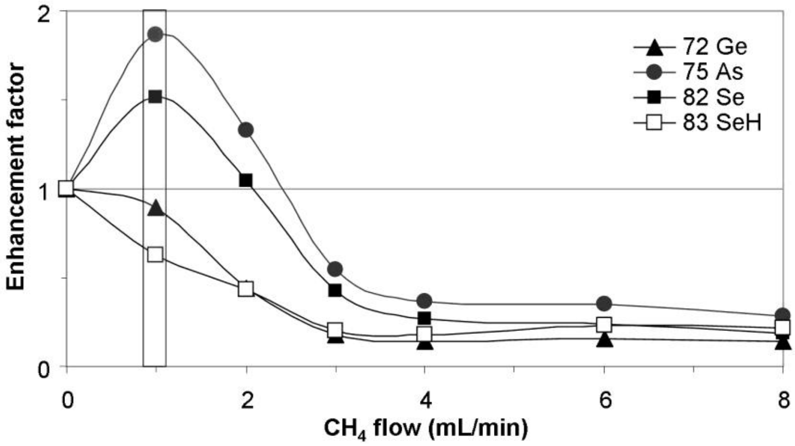


Figure 9: The responses of hydride forming elements on methane addition. Grey bar indicated optimum methane flow (with methane in Figure 11).

The optimum methane percentage for Se and As was the same, as in agreement with previous work (Allain et al., 1991; Muñas-Olivas et al., 1995; Hu et al., 2004; Roduskin et al., 2005). Although the As signal was more enhanced than the Se signal, I am only interested in AsH formation which interferes with the ^{76}Se isotope. It is difficult to assess the AsH formation, because AsH/As cannot be directly determined due to overlap with Ar dimers. However, the SeH formation can be estimated using the intensity on m/z$^+$ 82 and 83 to calculate the SeH/Se ratio. The SeH intensity on m/z$^+$ 83 decreased with methane addition (Figure 9). The SeH/Se ratio change depends on the relative change on Se intensity and SeH intensity. The hydride formation for Se decreased by a factor 0.7 at the optimum methane concentration whilst at this value As had around 1.2 times higher signal than Se. Therefore, when assuming a similar response for AsH as for SeH, the estimated relative importance of AsH$^+$ on m/z$^+$ 76 should decrease. A comparison of different bond dissociation energies are given in Table 2. It shows that the energies of SeH$^+$ and AsH$^+$ are relatively similar. Moreover, since the energy of AsH$^+$ is slightly lower, its breakdown is easier than for SeH$^+$, suggesting that AsH$^+$ will be similar or lower than SeH$^+$.

Table 2: Bond dissociation energies for different polyatomic ions

Polyatomic ion	**Bond dissociation energy**	**Reference**
ArO$^+$	0.3 – 0.6 eV	Yamada et al., 2002
ArAr$^+$	1.3 eV	
ArH$^+$	4.0 eV	
SeH$^+$	3.1 eV	Binning and Curtus, 1990
AsH$^+$	2.7 eV	

SeH$^+$ overlaps with Se isotopes at m/z$^+$ 77 and 78, but as discussed above, its formation decreased with methane addition. HBr$^+$ occurs at m/z$^+$ 80 and 82. However, since proper sample preparation can prevent this interference (Clark and Johnson, 2008; Zhu et al., 2008; Layton-Matthews et al., 2005; Carignan and Wen, 2007), the effect of methane on the HBr beam was not investigated. Other hydride-forming elements such as Te, Sb and Sn do not form spectral interferences with Se and are found not to have any adverse affect on the Se signal (Rouxel et al., 2002; Elwaer and Hintelmann, 2008b).

3.4.3 Other interferences

Kr interferences on Se isotopes occur at m/z^+ 78, 80 and 82. The $^{84}Kr^+$ beam decreased with methane addition (Figure 10). Kr has an ionization energy of 14.00 eV, which is above the ionization energy of C (11.20 eV). Previous work showed that no enhancement is observed for elements with an ionization energy above this threshold value because charge transfer reactions cannot occur (Allain et al., 1991; Hu et al., 2004). Given the lower sensitivity for Kr in a methane-mixed plasma, the measurements are less sensitive for small changes in Kr content.

Sample and skimmer cones derived NiO can overlap on especially m/z^+ 74, 76 (and with low abundance also at m/z^+ 77, 78 and 80). However, these signals are very small and probably constant. It is difficult to assess the effect of methane on NiO, because the beams are so small. Nevertheless, previous work shows that oxide levels decrease using a carbon loaded plasma (Ebdon et al., 1994; Hu et al., 2004; Rodushkin et al., 2005).

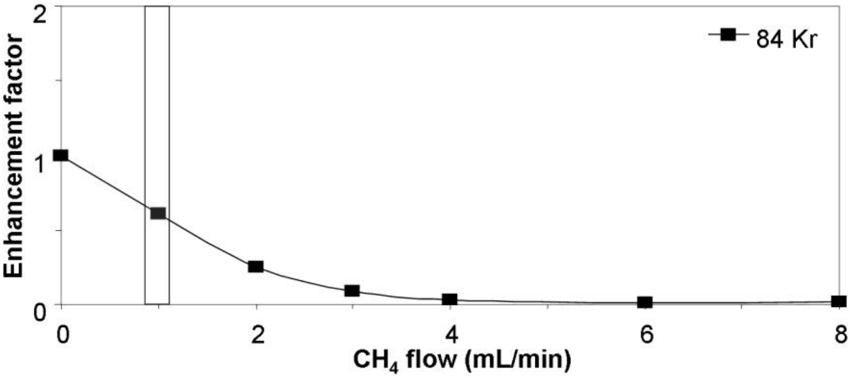


Figure 10: The response of Kr-intensity on methane addition. Grey bar indicated optimum methane flow (with methane in Figure 11).

3.5 Implications of methane mixed plasma for Se isotopic analyses

Isotope ratios corrected for the above discussed interferences are shown in Figure 11 and Table 3 for both with and without methane addition together with the theoretical mass fractionation line (exponential law). It shows that similar isotope ratios ($^{76}Se/^{82}Se$, $^{77}Se/^{82}Se$ and $^{78}Se/^{82}Se$) were obtained in both conditions. The mass discrimination is a combination of natural variations (i.e. isotopic signature of the sample) and the instrumental mass bias. Since in both cases similar mass discrimination was observed for the same Se solution, it can be concluded that methane addition does not significantly affect the instrumental mass bias.

The precision of Se isotope ratio measurements was determined using signal monitoring during ten minutes (150 integrations of 4 seconds). The stability of the signal intensity was not improved by the optimum methane addition (1 mL/min).

Although the counting statistics are improved in a methane-mixed plasma due to higher sensitivity, the variations in the low gas flow of the methane-argon mixture induces an extra error. However, variations in signal intensity are compensated since all masses are collected simultaneously (static mode). Indeed, the isotope ratios after interference correction showed a better precision for a methane mixed plasma. Using the traditional approach a standard error of ~0.2‰ was obtained. However, in the case of a methane mixed plasma the standard error was lower (~0.07‰). This means that the standard error decreased three times. The improved precision due to methane addition is related to the higher analyte-interference ratios.

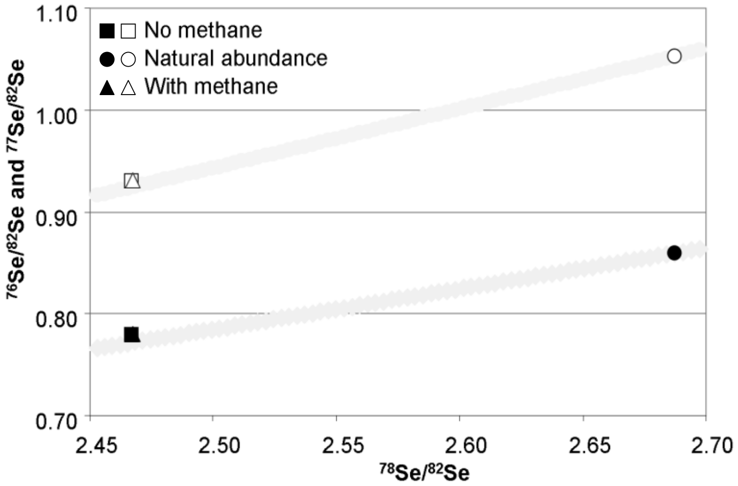


Figure 11: Interference corrected Se isotope ratios ^{76}Se/^{82}Se and ^{77}Se/^{82}Se vs. ^{78}Se/^{82}Se with and without methane addition. Open symbols: ^{76}Se/^{82}Se. Closed symbols: ^{77}Se/^{82}Se. Natural Se isotope ratio taken from Coplen et al., 2002.

Table 3: Non mass-bias corrected isotope ratios and standard errors with and without methane addition.

Ratio	No methane	With methane
76/82	0.93011 ± 0.00018	0.93092 ± 0.00006
77/82	0.77924 ± 0.00017	0.77990 ± 0.00004
78/82	2.46709 ± 0.00038	2.46729 ± 0.00010

4 Conclusions

In this work the suitability of high mass resolution HG-MC-ICP-MS for Se isotope ratio measurements was investigated. The results show that the Ar-dimers at m/z$^+$ 76, 78 and 80 cannot be resolved with the Neptune instrument and, presumably, to other instruments capable of roughly the same resolving power. Since these form the main problem in Se isotopic analysis, Se isotopes require a mass resolution beyond the capabilities of present-day instrumentation.

The use of a methane-mixed plasma does not resolve interferences, but significantly improves the analyte-interference ratio due to a higher Se sensitivity and a lower intensity of polyatomic ions. The observed increase in sensitivity differs between a standard introduction system (SIS) and a hydride generator introduction system (HG). For the SIS, the maximum enhancement factor is higher than observed at a higher carbon loading compared to HG. This result can be explained by different ionization processes in both systems related to the Se form that enters into the plasma. This is also confirmed by differences in the optimum RF power (associated with the plasma temperature) and different sensitivities that are not related to changes in Se loading.

Intensities of polyatomic interferences (such as ArAr, ArCl and several hydride containing species) decrease with methane addition, due to the competitive formation of carbides. Germanium also decreases intensity. Arsenic intensity is more enhanced than Se, however, the AsH beam is probably less enhanced than the Se signal. Corrected isotope ratios and mass bias are similar with and without methane addition. However, the precision is improved three times due to a better signal-blank ratio. This is important for the application to natural systems, since expected natural variations are relatively low. Therefore, this study suggests that methane addition has a positive effect on the determination of Se isotope ratios.

Chapter 6

Selenium mobilization in soils due to volcanic derived acid-rain

G.H. Floor, S. Calabrese, G. Román-Ross, W. D´Alessandro, A. Aiuppa, submitted. Selenium mobilization in soils due to volcanic derived acid-rain: an example from Mount Etna volcano, Sicily. *Chemical Geology*, submitted.

G.H. Floor, M. Iglesias, G. Román-Ross. P.F.X. Corvine, M. Lenz. Selenium speciation in acidic environmental samples: the case study of Mount Etna volcano. *Chemosphere,* submitted.

1 Introduction

The significant amounts of selenium (Se) emitted by volcanoes may have impact on human health due to the nutritious requirement and toxic effects upon Se exposure. Selenium is volatilized in the magmatic plumbing system and as a result several hundreds kilograms Se per day might be released by a single volcano (Chapter 1). Selenium speciation measurements in volcanic plumes are not available, but high temperature thermodynamic modelling and the comparison with coal combustion suggest the presence of H_2Se, elemental Se and SeO_2 (Suzuoki, 1964; Monahan-Pendergast et al., 2008; Symonds and Reeds, 1993). In the atmosphere oxidation and cooling will transform this Se to soluble selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) (Wen and Carignan, 2007). As a result, rainwater close to volcanoes might be significantly enriched in Se. For example, concentrations in Etnean rainwater have been reported to be up to 13 µg/kg (Calabrese, 2009). Additionally, this interaction between volcanic gases and atmospheric water causes a strong gradient in rainwater pH (from 2 to 7), both in space (km scale) and time (weeks-months). However, the environmental impact of this Se flux from the volcano towards the aquifer strongly depends on processes in the soils.

Soils formed in volcanic areas have distinctive properties that are rarely found in soils derived from other parent materials, such as a variable electrical charge and a high anion exchange capacity (Shoji et al., 1993). Moreover, soils around volcanoes are exposed to extreme conditions, including direct plume fumigation, acid rain (Delmelle et al., 2003, Bellomo et al., 2007) and fresh ash input (Agnelli et al., 2007, Egli et al., 2007), which cause strong physiochemical gradients upwind and downwind from the volcano. Although volcanic soils only occupy around 1% of the terrestrial surface, they host 10% of the worldwide population (Small and Nauman, 2001). Volcanic soils can have high Se concentrations but in contrast show low Se mobility (Byers et al., 1938, John and Saunders, 1975; Nakamaru et al., 2005). This low mobility is believed to originate from adsorption on Fe and Al minerals (John et al., 1975; Nakamaru, 2005), which have been widely reported as potential adsorption phases for Se (Balistrieri and Chao, 1990; Dynes and Huang, 1997; Parida et al., 1997; Wijnja and Schulthess, 2000; Duc et al., 2003; Peak, 2006; Fernández-Martínez and Charlet, 2009). Although soils play a key role in determining the level in food and water and thereby human health, the knowledge about the processes affecting the Se mobility in volcanic soils is limited.

Etna is the largest active volcano in Europe and has been persistently active over the past few thousand years. Mount Etna is among the most intensely monitored volcanoes of the world (Bonaccorso et al., 2003) and Se contents have been studied in the volcanic plume (Aiuppa et al., 2003b), in bulk deposition (Calabrese, 2009) and in groundwaters (Giammanco et al., 1996; Brusca et al., 2001; Aiuppa et al., 2003a), as summarized in Figure 1. However, the contents and chemical fates of Se within Etnean soils are unknown. For these reasons, Mount Etna is an excellent geochemical field site to study the behaviour of Se during soil-rainwater interaction. It has been shown that most of the rainwater rapidly infiltrates into the aquifers (Aiuppa et al., 2003a). These groundwaters, the only water resource for the about one million inhabitants around Mount Etna, are enriched in Se as concentrations up to 66 µg/L have been reported, which is above the WHO guideline of 10 µg/L. During infiltration rainwater interacts with the soils, where processes such as adsorption and desorption can occur. Although soil-rainwater interaction plays a key role in the cycling of selenium, these processes have not yet been investigated. In this study soil-rain interaction was evaluated in lab controlled experiments with samples collected from the flank of the volcano and synthetic acid-rainwater. The influence of volcanic activity induced changes in the rainwater composition (pH and sulphate concentration) on the potential of leaching and re-adsorption was investigated in controlled conditions. Differences in Se release were linked with soil characteristics, the chemical composition of the leachates and Se speciation. The Se mobility during soil-rainwater interaction has significant implications for the aquifer, and therefore on the Se intake of the population around the volcano.

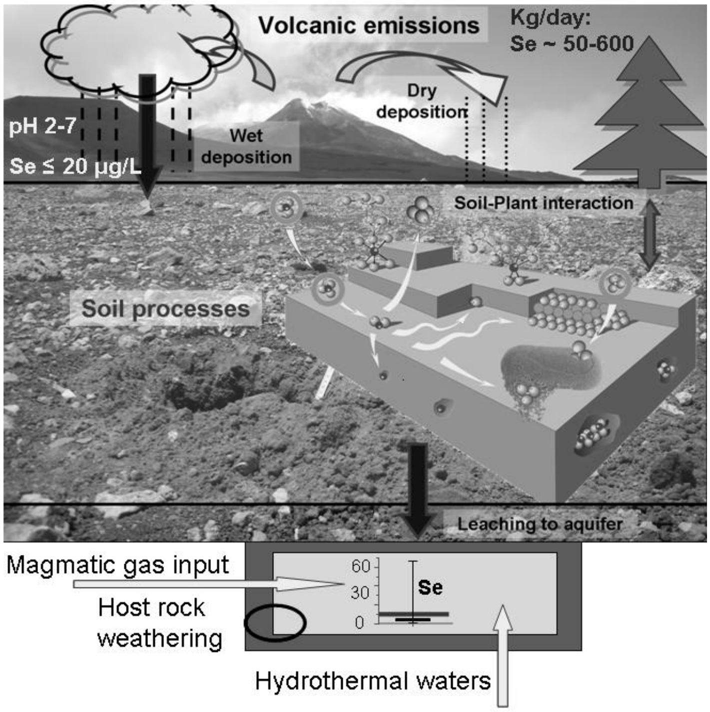


Figure 1: Schematic overview of the Se cycling around the volcano and the processes impacting Se content in the aquifer. Soil processes figure reproduced from Manceau et al., 2002.

2 Etna volcano

Mount Etna is a large (1200 km^2), 3300 m high 0.6 Ma old strato-volcano. Summit and lateral eruptions emitting lavas and pyroclastic (airborne) material with hawaiitic composition (~48% SiO_2) occasionally interrupt passive degassing (Bellomo et al., 2007; Tanguy et al., 1997). Etna volcano is considered to be at present one of the major volcanic gas emitters in the world, accounting for approximately 10% of world-wide volcanic emissions of CO_2 and SO_2 (Allard, 1997; D'Alessandro et al., 1997). It has been estimated that Mount Etna contributes to the annual atmospheric budget for alkali and heavy metals of 16-19% during eruptive activity and 2-4% in quiescent periods (Gauthier and Le Cloarec, 1998).

The climate of the Etna area is mainly controlled by its altitude, slope direction, dominant winds and geographical position. Under most atmospheric conditions, Etna's summit plume is dispersed by winds towards the SE at about the same altitude as the emission point (Bellomo et al., 2007). The altitude differences along the flanks of the volcano causes a gradual change from sub-tropical conditions at the base area to a moderate warmth in the middle and moderately cold and cold towards the higher regions. Lowest rainfall (400 mm) occurs at the lower SW flank, while maximum rainfall (1200 mm) occurs on east facing slopes at an altitude of 700-900 m due to cloud mass approaching mainly from the Ionian Sea in the east (Chester et al. 1985). Owing to the high permeability and irregularity of the lava, the edifice lacks a hydrographic network and 75% of the rain water directly infiltrates into the aquifer (Aiuppa et al., 2003a).

Table 1: Important characteristics of Etnean rainwater. Data from Calabrese, 2009. Negative distance means downwind from the craters.

Distance to craters (km)		-7.3	1.2	5.5	6.5	9.9
pH	Max	7.1	4.9	6.9	7.1	7.0
	Min	3.4	2.0	2.6	3.0	3.5
	Mean	5.6	3.7	4.2	5.0	5.2
SO_4^{2-} (mg/L)	Max	31.5	446	84.9	59.8	18.3
	Min	1.20	1.74	1.87	1.08	0.65
	Mean	6.79	81.44	12.72	9.78	7.01
Se (µg/L)	max	0.62	13.09	4.59	1.48	1.40
	Min	0.02	0.45	0.05	0.06	0.05
	Mean	0.27	3.63	0.91	0.47	0.47

The study of the chemical composition of the rainwater began in 1990 (Aiuppa et al., 2001; 2006) and included trace element analyses in 2006-2007 (Calabrese, 2009). It reveals that most of the investigated elements have higher concentrations close to the emission vent of the volcano and reflects the volcanic plume input, confirming the prevailing volcanic contribution. Some important rainwater characteristics are given in Table 1. The chemical composition of Etnean groundwaters has been extensively investigated in the past (Giammanco et al., 1996, 1998; Aiuppa et al., 2000a, 2003a; Brusca et al., 2001). The Etnean aquifers are the only water resource for drinking and agricultural purposes for around 1 million people. These studies identify three main sources for trace elements (Figure 1): (a) the leaching of the host basalt, driven by the dissolution of magma derived CO_2 which lowers the water pH and therefore enhances weathering. The variations in concentrations for several elements, including transition metals, have been explained by a variable extent of water-rock interaction; (b) mixing processes with saline brines rising from the sedimentary basement below Etna; and (c) contamination from agricultural and urban wastewaters. Furthermore rainwater has been reported to be a source of fluorine (F^-) (Bellomo et al., 2003). Rainwater could also cause a significant contribution for Se. Aiuppa et al. (2000) estimated that the aquifers discharge around 2 t/a Se. It has been estimated that around 1.6-4.4 t/a of the Se emitted by the plume is locally deposited (Calabrese, 2009). Around 75% of the rainwater is transported towards the aquifer (Aiuppa et al., 2000). This means that the potential rainwater Se flux towards the groundwater has the same order of magnitude as the aquifer Se discharge (Table 2). However, since during infiltration rainwater interacts with the soils, where adsorption and desorption processes can occur, soil-rainwater interaction will determine the magnitude of this flux. Therefore, the behaviour of Se in Etnean soils should be investigated.

Table 2: estimated Se fluxes around Mount Etna

Process	Flux (t/a)	Comment	References
Released by aquifer	**2**	Based on 0.69 m^3 discharge and average Se content	Aiuppa et al, 2000
Released by plume	200	Average for low activity	Calabrese, 2009
Local deposited	1.6-4.4	Assuming 0.8-2.2% of plume locally deposited	
Towards aquifer (if no interaction with soils)	**1.2-3.3**	Assuming all Se deposited in rain, 75% of rainwater towards aquifer	This work

Soil development in the Mount Etna area is controlled by the parental material, age, the morphology (e.g. slope) and climate. Moreover, depending on the volcanic activity winds can carry and deposit abundant pyroclastic material. The limited amount of published soil studies in the area focus on the relationship between vegetation and soil nature and show that the soils have vitric properties (Certini et al., 2001, Egli et al., 2007). Soil organic matter, imogolite-type materials, oxyhydroxides contents and weathering decrease with increasing altitude (Egli et al., 2007). The only study performed on the influence of the volcanic activity on soils focussed on fluorine and demonstrated that total fluorine contents fall within the typical range of undisturbed soils. Nevertheless, topsoils from the eastern, downwind sector of the volcano are typically richer in fluorine than the soils on the western, upwind flank (Bellomo, 2007).

Since the contribution of pyroclastic material has a strong influence on the soil properties, it is important to know when such events occurred. In recent time a considerable quantity of new pyroclastic material came from the eruptions of 2001 and 2002-03. In 2001 pyroclastic products were dispersed almost exclusively in the SE and SSE direction reaching deposition values of up to 23 kg/m^2 (corresponding to about 2 cm thickness) along the main axis (Scollo et al., 2007). During the 2002-03 eruption (Figure 2) the deposition of pyroclastic material exceeded 150 kg/m^2 (about 10 cm thickness) on a large area around the emission vent (3 km S of the summit craters). Even though ashes were deposited mainly on the southern and eastern flank of the volcano, significant deposition also took place on the western and northern flanks (Andronico et al., 2008a). Although short lived paroxysmal episodes are more frequent at Etna volcano, their single quantitative contribution is much lower. The most recent episode before the sample campaign in June 2008 (Section 3) was the SE-crater lava fountain on the 4th of September 2007. The pyroclastic material produced by this episode covered a very narrow strip in the E direction with deposition of more than 10 kg/m^2 (Andronico et al., 2008b). From October until mid November 2007, ash emissions occurred infrequently. On November 22nd, 23rd and 24th 2008 explosive activity blew a dense tephra plume NE and caused ash and lapilli falls as far as 80 km away (Andronico and Cristaldi, 2007). Shortly before the sampling the eruption that started on the 13th of May 2008 was preceded on the 10th by a lava fountain episode at the SE-crater. Much less pyroclastic material was emitted than in the September 2007 episode and dispersed over a much broader area (INGV-Ct, 2008). The impact of recent events emitting pyroclastic material close to the volcano can be observed in Figure 3.

Figure 2: Photo from October 28, 2002 taken by the Moderate Resolution Imaging Spectroradiometer (MODIS) on NASA´s Aqua satellite showing ash and smoke plume streaming southward from the volcano and out over the Mediterranean Sea.

Figure 3: Photo from June 11, 2008 taken by Geerke Floor showing ash deposits on the snow close to Punta Lucia. Ash deposits ere probably derived from the November 2007 and May 2008 events.

Besides volcanic activity, human impact is also an important environmental factor in the Etna region. Agricultural cultivation over the last centuries or even millennia has influenced substantial parts of the area. Most crops occur at altitudes of up to 900 m, but chestnut and hazelnut cultivation occurs up to 1500 m (Dazzi et al., 2007). The vegetation limit varies between 1800 to 2200 m, depending on the exposure to volcanic material and climatic conditions.

3 Experimental section

Thirty topsoils (upper 10 cm) were collected at Mount Etna between 2 to 10 km from the craters and between 900 and 3000 m altitude (Figure 4; Table 2) in June 2008. Some of the soils close to the volcano are poorly developed being more ´volcanic ash´ rather than ´soil´. Composite samples from 3 different spots at least 2 meter apart were obtained at each location. Soils were air-dried and the fine earth fraction (<2mm) was used for the experiments. A few examples of the sample sites downwind from the volcano are given in Figure 5.

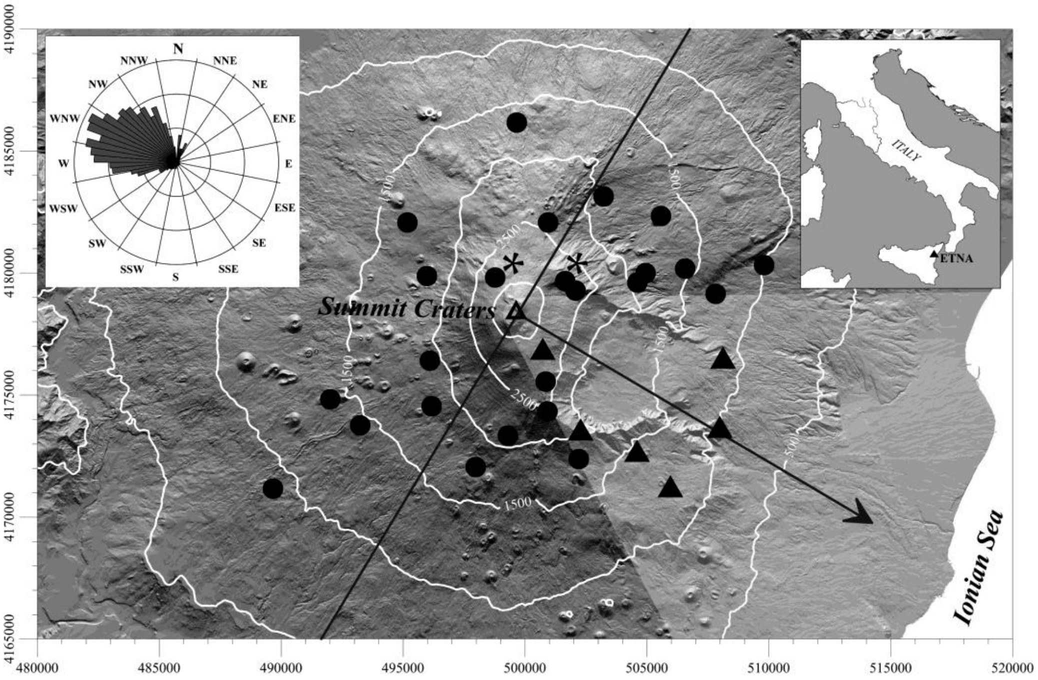


Figure 4: Soil sample locations (circles and triangles). Arrow is average direction of the volcanic plume (120°). Shaded area and triangle symbols indicated the area mostly affected by the volcanic plume (90-150°). Inset left: wind rose showing wind direction for 2001-2003 (Aiuppa et al., 2004). Inset right: location of Etna volcano. Black line shows division between upwind and downwind. *Indicates samples used for experiment with sulphate-containing neutral rain.

The major element composition was determined using Energy Dispersive X-Ray Fluorescence (ED-XRF, Actlab laboratories Canada), organic matter by a carbon combustion analyzer (Horiba EMIA-820V) and mineralogy by X-ray Diffraction (XRD, Siemens D5000). Because significant amounts of amorphous compounds were present, oxalate and pyrophosphate Selective Dissolution Techniques (STD, García-Rodeja et al., 2007), targeting respectively amorphous and organic-bounded Al and Fe compounds, were performed with a soil:solution ratio of 1:100, overnight shaking and using Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES, Varian Liberty II) for Fe, Al and Si detection. Fourier transform infrared spectroscopy (FTIR, BRUKER Equinox IFS55) was additionally applied for some selected samples to characterize the compounds present in the soils.

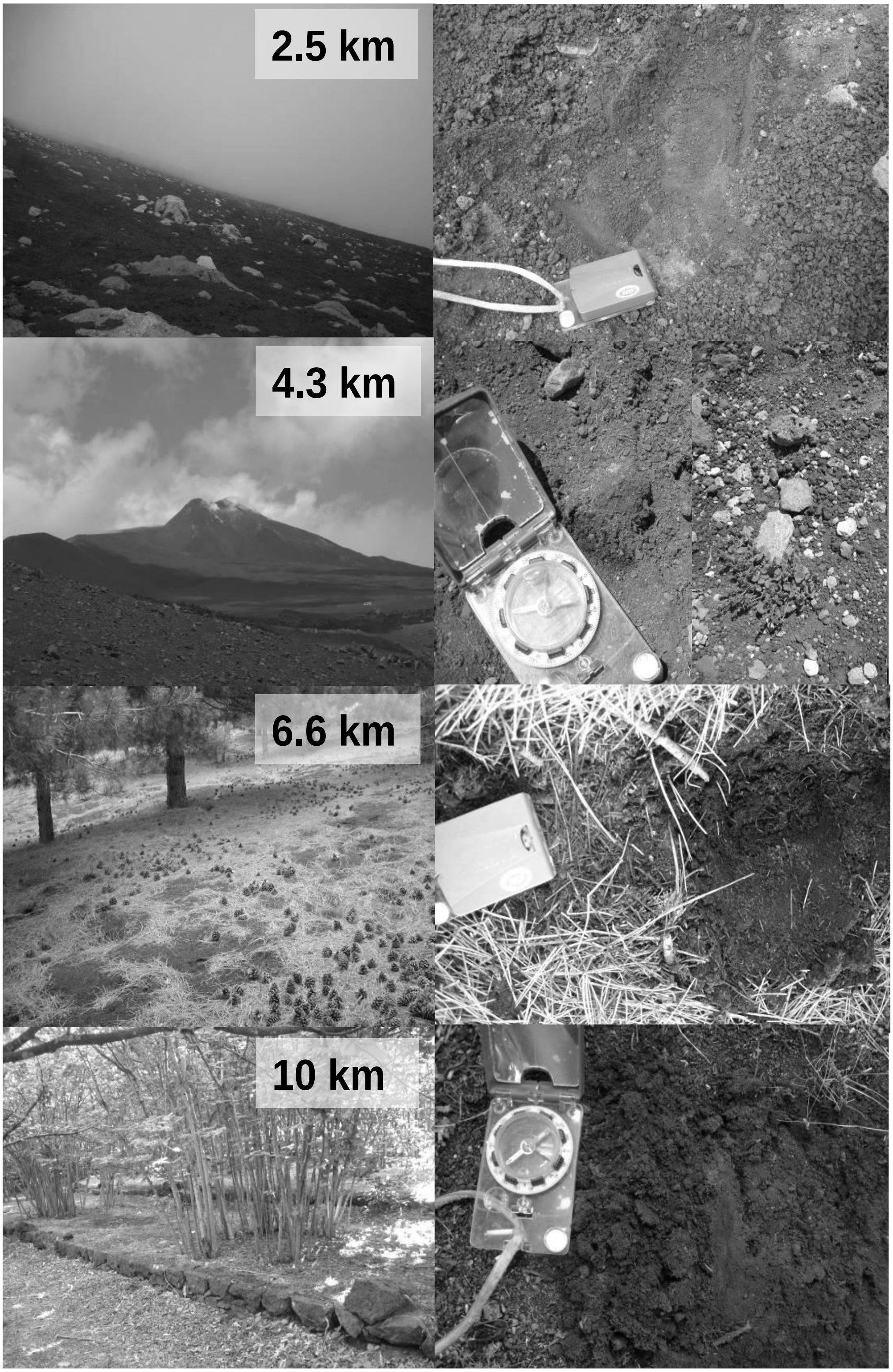


Figure 5: Photos of different locations downwind from the Etna craters indicating the diversity of the soils.

Table 2: Location parameters and field description of soils. Negative distance is downwind from the craters.

	Location			**Short site description**
#	**Altitude (m asl)**	**Distance crater (km)**	**Direction plume (°)**	
1	927	-12.41	113	Agricultural soil used for vegetables
2	1293	-8.47	124	Fine-grained low density soil with lot of organic matter
3	1439	-7.98	113	Pine forest soil, fine-grained material
4	1642	-7.77	119	Grass field, sampled within ferns. Well developed soil, fine-grained.
5	1714	-5.69	170	Forest soil, highly developed, high organic matter, lots of roots
6	1819	-5.11	101	Pine forest soil, highly developed.
7	1951	-3.97	120	Fine-grained soil, grass covered area in between in lava flows
8	2401	-3.93	99	Close to 2003 eruption, much of ash + pyroclastic fragments, vegetation
9	1777	-3.84	172	Pine forest, developed fine-grained soil
10	2913	-1.60	148	Older rim surrounded by recent lava flow, little vegetation, ash input
11	2858	1.93	21	No vegetation, ash and pyroclastic fragments
12	2825	2.46	61	Lot of fresh ashes, intensively affected by plume.
13	2735	2.57	46	Fine material covered with lot of pyroclastic fragments.
14	2639	3.15	35	Little vegetation, lot of ash and pyroclastic fragments.
15	2494	4.31	41	18th century crater, almost no vegetation, many pyroclastic fragments
16	2167	5.08	63	50% vegetation, close to recent lava flow, lot of pyroclastic fragments
17	1828	5.21	43	High slope (20%), birch and grass, small amount of rock fragments
18	2052	5.55	30	70% vegetation cover, lot of pyroclastic fragments
19	1727	5.65	46	Close to 1929 lava flow, slope 10°
20	1800	6.00	82	Fine-grained soil but covered with layer of pyroclastic fragments.
21	1725	6.54	74	Abundant vegetation, low abundance of coarser pyroclastic fragments
22	1719	6.60	36	Pine forest, very wet soil, no rock fragments
23	1564	7.21	63	Pine forest, fine-grained soils, very few rock fragments.
24	1525	7.26	44	Highly vegetated (grass and trees), no rock fragments
25	1395	7.61	18	Abundant vegetation (forest), no coarse rock fragments
26	1199	8.32	35	Chesnutt forest close to lava flow, soil covered with leaves, fine-grained
27	1112	8.79	18	Fine-grained soil, low density, quit dry, lots of vegetation
28	1160	9.62	18	Abundant vegetation (field), quit flat but close to hills.
29	916	9.71	0	Forest close to lava flow
30	975	10.46	41	Agricultural sources, terraces used for hazelnut trees

For the rainwater-soil interaction leaching experiments, three different synthetic rainwaters were prepared. The composition of two of them was based on a rainwater dataset collected around the volcano in 2006-2007 (Calabrese, 2009):

1) A neutral-rain containing pure water only (Millipore corp., Bedford, MA, USA) with a pH around 6. This pH corresponds to the average upwind rain and to downwind rain during low volcanic activity at distance from the craters (Calabrese, 2009, Table 1).
2) An acid-rain, prepared using 450 mg/kg of sulphate (out of H_2SO_4, SpA grade MERCK) with a pH around 2. The pH and sulphate concentration are based on the extreme values measured in rainwater samples collected in the period 2006-2007 close to the crater during increased volcanic activity (Calabrese, 2009).

The third rainwater contained 450 mg/kg SO_4 at neutral pH (out of Na_2SO_4, 99.99% Alfa Aesar) in order to investigate the role of sulphate competition. This solution was only used for two soil samples, each at one site of the volcano (Figure 4).

Batch leaching experiments were performed at room temperature with a soil – rainwater ratio of 1:5 and a contact time of 4 hours. A ratio of 1:5 was selected to release sufficient Se for adequate analytical determinations. Preliminary kinetic experiments showed that major element concentrations did not obtain equilibrium even after one week (data not shown), while rainwater – soil is expected to be a fast process, due to the high permeability of the soils. Selenium sorption has been reported to occur within several hours (Fernández-Martínez and Charlet, 2009). Therefore, a contact time of 4 hours was selected. Although batch experiments are a simplification of the field setting, this approach allowed the determination of Se desorption at natural levels for these uncontaminated soils. To estimate the error a couple of experiments were performed in triplicates. After the 4 hours, pH and Eh values were measured in the leachates. Subsequently, the solutions were centrifuged, filtered (Whatman, 0.45 µm polypropylene media) and acidified with nitric acid (Romil suprapure, Se< 0.1 µg/kg).

For speciation analyses some soil samples were selected at both side of the volcano and different distances. In this case, solutions were filtered with a 0.22 µm polypropylene media (Tracer) and stored directly in the dark at 4°C without acidification.

To obtain a better understanding of the potential for re-adsorption, experiments were performed with one soil collected close to the craters and initial solutions containing 200 µg/L selenite (out of Na_2SeO_3, Sigma, 99%) or selenate (Sigma, 99%) and diluted H_2SO_4 (pH=2 and pH=4), HCl (pH=2) or HF (pH=2). For kinetic experiments 3 gram soil in 30 mL solution was used. At selected times the suspension was centrifuged and an aliquot of 0.5 mL was taken, which was diluted prior to analyses. For equilibrium sorption experiments 2 grams of soils were put in contact with 20 mL solution for 24 hours.

Selenium and arsenic (As) concentrations were determined by ICP-MS as described in Chapter 3. Selenium speciation of some selected acid rain experiments was analyzed following the HPLC-ICP-MS protocol developed in Chapter 4. Major elements in solution were measured by ICP-AES.

4 Results

4.1 Soil Properties

Total Se concentrations varied between 0.12 and 2.25 mg/kg with a median value of 0.39. Half of the samples had concentrations above the worldwide average total Se soil concentration of 0.4 mg/kg (Fordyce, 2005). No relationships were observed between total Se concentrations and location parameters, such as the distance to crater and the direction compared to the main direction of the plume (Figure 6, Table 3). The soil pH varied between 4.6 and 7.0 with an average value of 6.1. Soils close to the volcano showed a lower pH, both upwind and downwind from the summit craters (Figure 6).

Table 3: Selenium, pH data and selected trace elements data.

	Selenium			pH				Other trace elements acid leaching (µg/L)		
	Total soil (mg/kg)	Leaching (µg/L)		Acid		Neutral				
#		**Acid**	**Neutral**	**Final**	**Buffer**	**Final**	**Buffer**	**As**	**Tl**	**Cd**
1	0.17	0.44	0.81	3.2	1.3	7.0	0.9	1.1	0.4	3.6
2	1.22	0.42	0.59	4.1	2.2	7.0	0.8	2.3	0.5	0.8
3	0.18	0.97	0.54	2.8	1.0	6.5	0.3	2.6	1.1	5.9
4	0.74	0.29	0.37	4.2	2.3	6.5	0.3	0.4	1.6	1.2
5	0.78	0.52	1.08	2.8	0.9	6.5	0.3	1.2	1.2	1.6
6	0.78	0.66	0.71	3.0	1.1	6.6	0.4	1.2	1.0	9.1
7	0.39	1.18	0.54	4.4	2.5	6.2	0.0	4.7	2.4	7.2
8	0.75	2.39	0.17	2.4	0.6	5.4	-0.8	7.0	7.0	4.7
9	0.20	0.95	0.72	2.6	0.7	6.8	0.6	2.5	1.9	5.9
10	1.04	4.68	0.13	n.a.	n.a.	4.7	-1.5	8.5	14.5	1.9
11	0.25	2.04	0.09	2.7	0.9	5.5	-0.7	5.1	10.8	1.1
12	1.31	7.70	0.32	3.1	1.2	4.6	-1.6	2.7	4.8	2.5
13	1.21	5.67	n.a.	3.0	1.1	n.a.	n.a.	8.2	2.7	n.a.
14	0.77	3.24	0.16	2.8	0.9	5.1	-1.1	5.2	4.9	4.1
15	0.38	3.26	0.11	2.8	0.9	5.1	-1.1	6.1	2.1	4.1
16	2.25	1.79	0.15	2.5	0.6	5.8	-0.4	5.0	3.5	14.3
17	0.58	1.67	0.22	2.8	0.9	6.0	-0.2	5.0	18.21	3.6
18	0.46	2.04	0.13	2.4	0.5	5.9	-0.3	9.7	6.8	3.4
19	0.24	1.13	0.19	2.4	0.5	5.5	-0.7	3.1	14.5	7.5
20	0.23	1.78	0.08	3.0	1.1	6.0	-0.2	8.3	4.3	3.9
21	0.31	1.24	0.18	2.8	0.9	6.6	0.4	2.7	1.8	9.2
22	0.12	0.77	0.06	2.7	0.8	6.4	0.2	3.1	4.5	3.4
23	n.a.	1.30	0.17	3.3	1.4	5.8	-0.4	3.1	4.6	8.7
24	0.23	0.89	0.14	3.0	1.1	6.3	0.1	2.3	7.2	7.4
25	0.45	0.88	0.10	2.4	0.5	6.7	0.5	1.9	2.3	5.5
26	0.22	0.63	0.09	3.6	1.7	6.6	0.4	1.8	4.5	4.2
27	0.21	0.54	0.07	3.2	1.3	6.8	0.6	1.9	2.7	6.1
28	0.24	1.54	0.03	3.3	1.4	5.8	-0.4	6.2	4.9	2.6
29	0.25	0.54	0.52	2.2	0.3	6.7	0.5	1.2	2.1	2.5
30	0.88	0.54	0.19	2.9	1.1	6.9	0.7	0.9	0.9	1.8

n.a. = not analyzed

Since adsorption processes play a key role in the Se mobility, Al and Fe compounds have been specifically characterized in the soils. Nevertheless, even using the combination of XRD, FTIR and STD to extract amorphous and organic matter associated Fe and Al, not all soil minerals could be identified. XRD analyses indicated the presence of plagioclase, augite, olivine, magnetite and hematite, but showed that a significant part of the soil compounds are amorphous. Allophane was detected with XRD in only some of the samples. Volcanic glass was one of the amorphous compounds, as confirmed by FTIR and the Fe and Al contents in the oxalate SDT (Buurman et al., 1996). The presence of volcanic glass was also reported in previous work (Certini et al., 2001; Egli et al., 2007). However, the variations in oxalate extractable Al/Si ratios (0.6-1.6) showed that numerous amorphous compounds are present (Table 4). Moreover, amorphous (oxalate extractable) Al and Fe contents showed a great variability, while total Fe and Al concentrations were very similar in all soils (standard deviation < 10%).

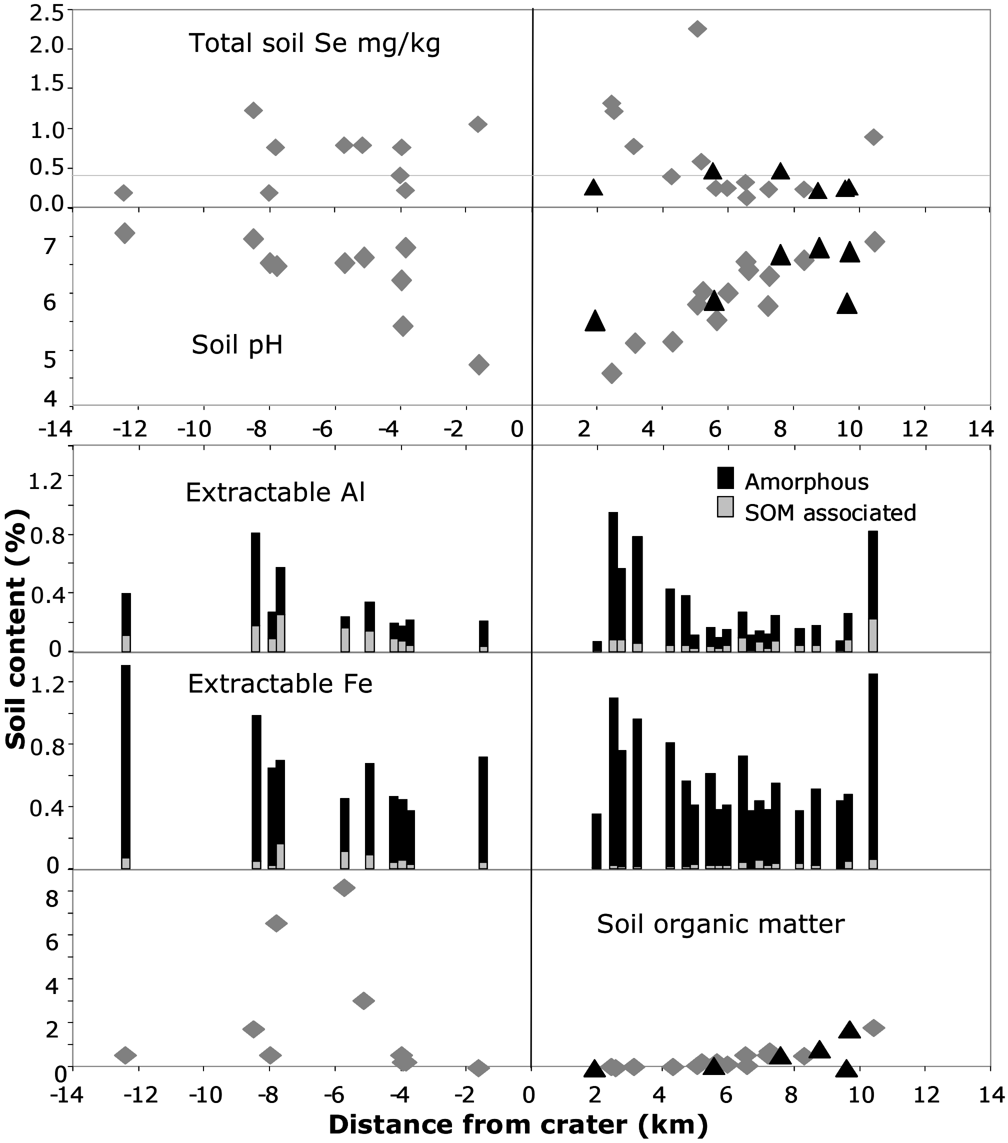


Figure 6: Total Se concentrations, soil pH, oxalate and pyrophosphate extractable Fe and Al. Distance from the summit craters. Positive distance: downwind. Negative distance: upwind. Triangles: in volcanic plume (90-150°). Diamonds: out volcanic plume. Grey line = worldwide average soil Se concentration (Fordyce, 2005).

Soil organic matter (SOM) increased with distance downwind of the summit vents from absent up to almost 2% at around 10 km distance. Upwind from the volcano SOM contents were higher (up to 8%) and did not show a specific pattern with distance. SOM strongly influences the soil Al behaviour due to the formation of metal-humus complexes (Wang and Mulligan, 2006). Indeed, samples rich in SOM showed higher percentages of Al and Fe associated with organic matter (pyrophosphate-extractable, Figure 6, Table 4), although amorphous Al was dominant in almost all soils. Even if previous works attribute a key role for SOM to behaviour of Se within the soils, (Gustafsson and Johnsson, 1992), there was no correlation between total Se content and SOM.

Table 4: Soil organic matter, silica, iron and aluminium data for soils and leachates

	SOM (%)	**Silica**		**Aluminium**					**Iron**				
		SiO_2 (%)	**Al_{ox}/Si_{ox}**	**Al_2O_3 (%)**	**Selective E (%)**		**Leaching (mg/L)**		**Fe_2O_3 (%)**	**Selective E. (%)**		**Leaching (mg/L)**	
#					**Ox**	**Pyr**	**A**	**N**		**Ox**	**Pyr**	**A**	**N**
1	0.57	50.8	1.28	18.9	0.40	0.11	23.1	0.43	10.3	1.31	0.07	0.2	0.27
2	1.76	45.2	1.82	17.8	0.80	0.18	4.0	0.58	9.5	0.99	0.05	0.1	0.38
3	0.60	n.a.	1.32	**n.a.**	0.27	0.09	72.5	0.15	n.a.	0.65	0.02	4.6	0.06
4	6.53	50.3	2.18	17.9	0.57	0.25	2.2	0.56	10.5	0.69	0.16	0.2	0.31
5	8.13	48.1	1.92	17.3	0.24	0.16	4.3	0.96	11.2	0.45	0.12	0.5	0.59
6	3.03	48.8	1.65	18.2	0.34	0.14	37.5	0.75	10.8	0.68	0.09	2.2	0.48
7	0.60	47.3	1.35	18.0	0.19	0.09	91.1	0.19	10.1	0.46	0.04	9.1	0.07
8	0.29	49.0	1.17	18.3	0.17	0.07	94.9	0.90	10.4	0.44	0.06	12.8	0.01
9	0.27	48.7	1.23	17.5	0.22	0.04	75.1	1.13	10.2	0.37	0.03	4.1	0.61
10	<0.05	49.2	1.26	17.5	0.21	0.03	87.1	1.35	10.3	0.72	0.04	11.9	<0.01
11	<0.05	46.7	0.72	14.9	0.07	0.01	60.1	0.45	12.2	0.35	0.01	36.5	<0.01
12	0.05	48.6	1.67	18.9	0.94	0.08	127	4.16	11.1	1.10	0.02	1.8	<0.01
13	<0.05	47.5	1.66	19.2	0.56	0.08	n.a.	n.a.	9.9	0.76	0.02	n.a.	n.a.
14	0.05	47.3	1.68	17.7	0.79	0.06	105	1.30	11.0	0.96	0.02	6.8	<0.01
15	0.07	46.8	1.40	16.9	0.42	0.05	114	1.25	11.4	0.81	0.01	8.2	<0.01
16	0.10	47.2	1.28	17.9	0.38	0.05	108	0.24	10.8	0.56	0.01	3.0	<0.01
17	0.29	47.4	0.96	16.5	0.11	0.03	76.6	0.33	11.7	0.41	0.03	21.5	0.14
18	0.10	47.4	1.00	15.8	0.17	0.04	74.9	0.13	11.8	0.61	0.02	10.8	0.01
19	0.27	46.3	0.88	16.2	0.10	0.02	80.3	0.29	11.4	0.38	0.02	17.3	0.06
20	0.15	47.8	1.19	17.9	0.15	0.05	76.9	0.31	10.6	0.41	0.02	12.4	0.10
21	0.59	46.8	1.24	17.6	0.27	0.10	75.7	0.29	10.6	0.73	0.04	4.2	0.14
22	0.12	46.1	0.76	15.4	0.11	0.01	69.9	0.12	12.1	0.37	0.01	23.2	0.08
23	0.61	46.3	1.22	17.1	0.14	0.07	77.6	0.41	10.8	0.44	0.06	13.5	0.22
24	0.74	45.7	0.87	16.0	0.12	0.02	66.2	0.29	11.2	0.38	0.02	12.6	0.15
25	0.60	47.7	1.14	17.3	0.25	0.07	53.4	0.29	11.5	0.55	0.04	3.6	0.14
26	0.52	45.9	0.97	16.4	0.15	0.04	59.3	0.31	11.2	0.37	0.03	9.7	0.19
27	0.85	47.6	1.00	17.1	0.18	0.04	57.5	0.18	11.4	0.51	0.02	5.2	0.27
28	<0.05	47.2	0.70	16.0	0.07	0.01	48.3	0.12	11.9	0.43	0.01	16.1	0.02
29	1.74	47.4	1.20	17.1	0.26	0.08	24.2	0.68	11.4	0.48	0.05	1.4	0.36
30	1.80	48.4	1.75	18.7	0.82	0.23	10.9	0.23	10.8	1.25	0.06	0.3	0.03

n.a. = not analyzed
Selective E = selective extractions. Ox= oxalate (amorphous compounds) Pyr = pyrophosphate (SOM associated).
Leaching = rainwater interaction experiments: A=acid leaching. N=neutral leaching

4.2 Leaching experiments

The experiments performed with the soils collected on the flanks of Mount Etna and synthetic Se-free acid rain (pH=2) showed a trend between the leached Se and the distance of soil location with respect to the craters (Figure 7). The fraction of the total Se concentration mobilized during acid-rain interaction ranged from 0.2 to 4.3%. The important differences in mobilized Se expressed in percentage showed that leaching is not controlled by total Se concentrations. The trends displayed in Se leachate concentration (Figure 7) were not observed for total soil Se (Figure 6). The highest Se leachate concentrations (up to 8 µg/kg) were detected during acid rain-soil experiments performed on two downwind sites close to the craters (Figure 7).

Elemental Se and/or selenite (as $HSeO_3^{-1}$) were the thermodynamically stable species at the resulting pH-Eh conditions after 4 hours of soil – rainwater interaction (Figure 8). Since elemental Se is insoluble, the expected species in the leachates based on thermodynamics is selenite. However, speciation analyses reveal that selenate was present in the solutions (Figure 9). For samples within 2 km from the craters, similar amount of selenite and selenate were found. For the leaching solutions with high Se concentration selenate was the main species in the solutions. Soils at more than 5 km distance downwind from the volcanoes contained more selenite than selenate in the leachates. Samples collected upwind from the volcano at more than 2 km distance from the crater did not show any systematics in the selenite-selenate ratio, but leached Se concentrations were low for these samples. For leachates of soils collected within 5 km of the craters and > 2100 m altitude selenate concentrations were above 0.5 µg/L, while for the other samples the selenate concentrations were < 0.5 µg/L.

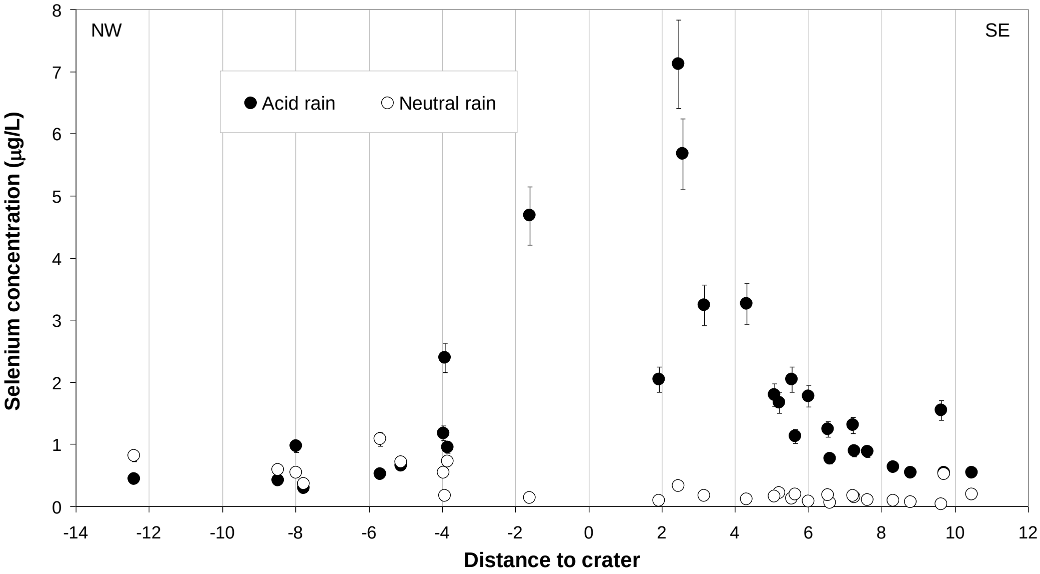


***Figure 7: Selenium concentrations in leachates versus distance to the crater. Positive distance: downwind. Negative distance: upwind*.**

In contrast to acid-rain experiments, neutral-rain experiments (pH=6) displayed no apparent trends with the distance from the craters, but did show a difference between downwind and upwind samples (Figure 7). Under neutral conditions a lower percentage of the total soil Se was mobilized compared with acid-rain interaction. For neutral rain between 0.05 and 2.3% Se was released and as a consequence leaching concentrations are < 2 µg/kg in all cases. However, with reference to previous work on the vertical displacement of dissolved Se due to rainwater infiltration in non-volcanic seleniferous soils (Dhillon et al., 2008) more Se mobilization occurred in the Etnean samples. Comparing the difference between acid and neutral conditions a very different Se behaviour was observed for soil samples collected downwind close to the craters relative to samples taken upwind, or downwind at greater distance from the volcano. Samples close to the crater presented significantly higher Se mobilization during acid conditions compared to neutral conditions. However, for the other samples Se mobilization was less pH-dependent and sometimes showed higher Se leaching at neutral pH. As a result, leachate concentrations were higher upwind than downwind from the volcano after neutral-rain interaction (Figure 7).

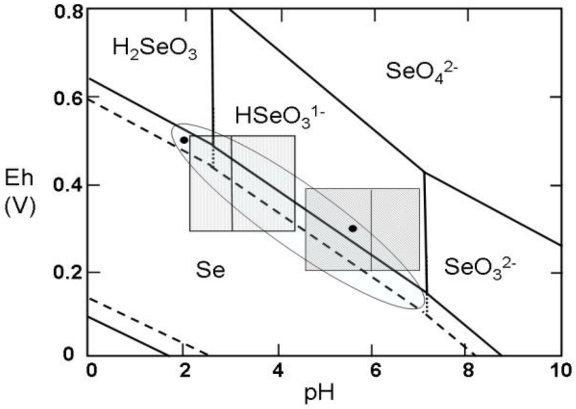


Figure 8: Part of the Eh-pH diagram of Se-O-H system at 25°C and 1 bar pressure (Brookins, 1988). Solid lines: for 10^{-6} M selenium (~0.1 µg/kg). Dashed lines indicate changes in fields for lower Se concentrations. Oval indicates expected Eh-pH field for the rainwater (Liotta et al., 2006), squares show the field of the experiments after 4 hours of rain interaction.

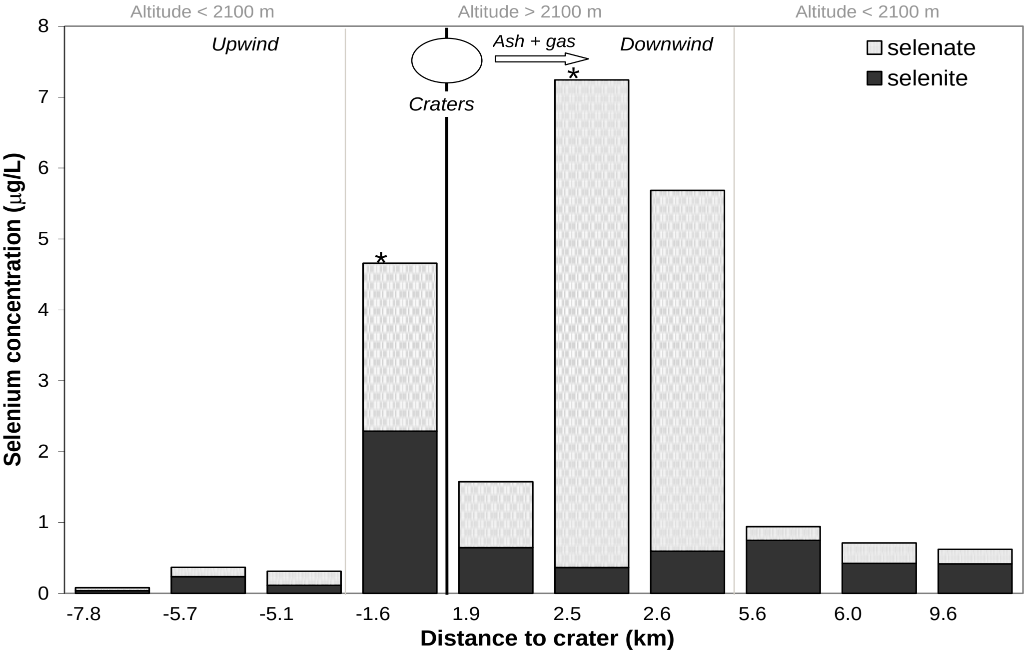


Figure 9: Inorganic selenium speciation in acid soil extractions from Etna volcano. Selenite and selenate concentrations are stacked and form together total detected Se. X-axis (distance to crater) is not in scale. * indicate samples for SO_4-containing neutral rain (location indicated in Figure 4).

Although total Al and Fe concentrations were very similar (Table 3), Al and Fe in leachates showed huge variations (Figure 10). High concentrations of dissolved Al and Fe in the acid leachates were observed (up to 127 and 36 mg/kg respectively). In general samples from high altitudes (>2100 m) had high Al concentrations in acid leachates (>85 mg/kg), while most samples from below 2100 m had Al concentrations below 85 mg/kg. Thermodynamic calculation predicts that almost all final solutions were undersaturated with respect to amorphous Al minerals. Only three of the downwind samples were oversaturated with respect to gibbsite. Even if the highest Al concentration in the leaching solution (Figure 10) corresponded with the sample rich in amorphous compounds (Figure 6), there was no correlation between the Fe and Al concentrations in acid leachates and SDT. There was a positive correlation between aluminium (Al) and Se in the acid leachates (exp law R^2 = 0.73: Figure 10), while no trend between iron (Fe) and Se (power law R^2 = 0.32) was detected. No link was observed between major element composition and Se concentration during neutral rain experiments. The resulting pH values after soil-rain interaction lacked any trend with Se mobilization in both acid and neutral conditions. However, a relationship was observed between soil pH and acid leachable Se (R^2=0.84, Figure 11). There was also a negative correlation between SOM and leached Se under acid conditions (power R^2=0.7, Figure 11).

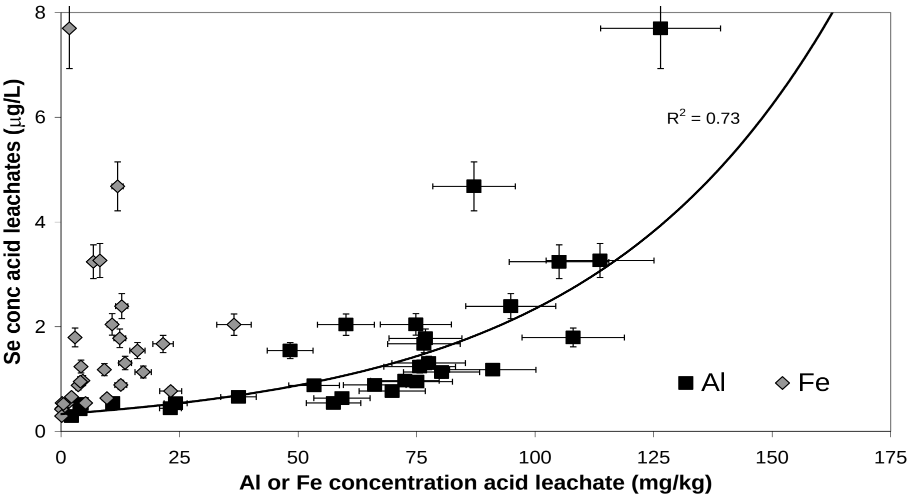


Figure 10: Relation between acid Se leaching concentration and respectively Al and Fe leaching concentrations

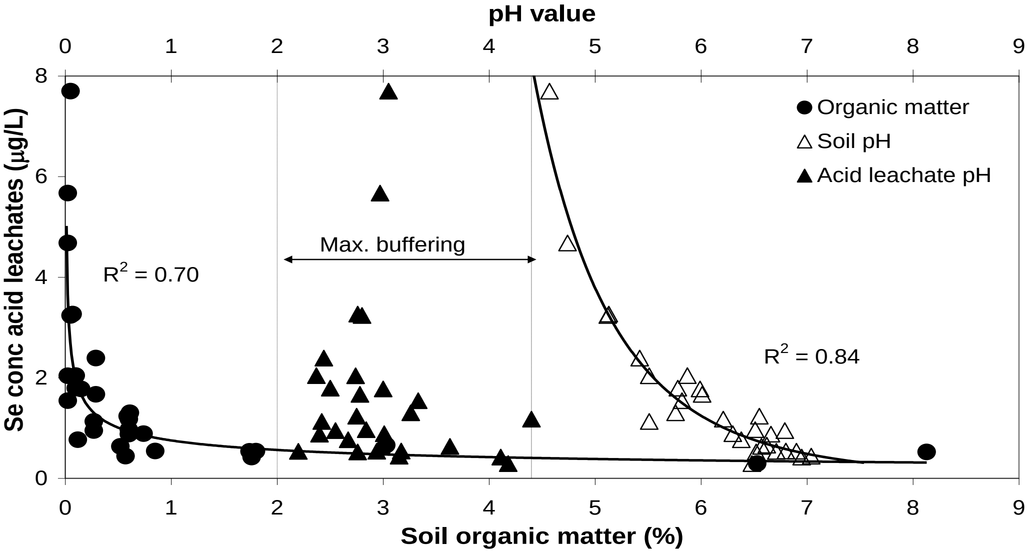


Figure 11: Relationship between acid leachable Se versus SOM, soil pH and final pH after acid rainwater interaction. The maximum buffering capacity during acid interaction is also indicated. (Start synthetic acid rain has pH=2).

The behaviour of Se is often compared with arsenic (As). For all acid leachates no correlation was observed between the two elements (R^2=0.14). However, as observed in Figure 12, taking into account the experiments with samples from below 2100 meter a good correlation between As and Se is observed (R^2=0.84).

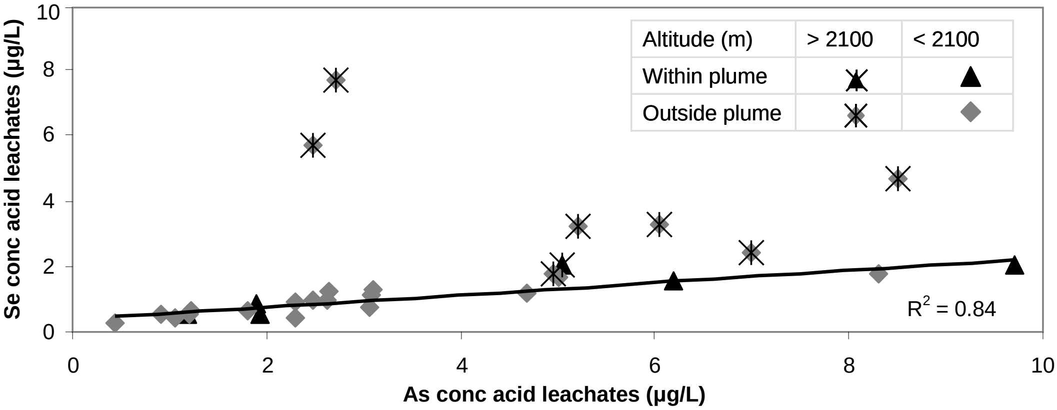


Figure 12: Comparison between Se and As concentrations in acid soil leachates.

4.3 Adsorption experiments

The kinetics of selenite adsorption using Se containing diluted H_2SO_4 solutions (pH=4 and pH=2) is shown in Figure 13. At pH 2 it was observed that about 30% of the total selenite was adsorbed within half an hour. Afterwards, the speed of adsorption decreased. After 18 hours almost no adsorption occurred anymore with a total adsorption of almost 90% of the initial Se concentration. At pH 4 about 45% of the initial Se was adsorbed at 23 hours. The kinetics were faster with equilibrium after 4 hours and 35% adsorption within half an hour.

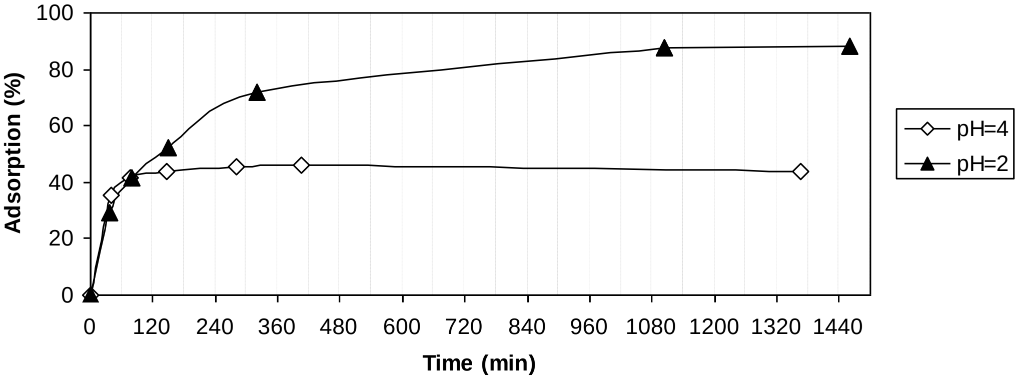


Figure 13: Kinetics of selenite adsorption with initial solutions of pH=2 and pH=4 using H_2SO_4 and 200 µg/L selenite out of sodium selenite.

Since equilibrium was obtained within 24 hours, several equilibrium experiments were performed to investigate the influence of rainwater composition and Se speciation (Figure 14). For selenite similar adsorption percentages of almost 90% were obtained in the presence of SO_4^{2-} (~450 mg/L), F^- (~200 mg/L) or Cl^- (350 mg/L). For selenate the adsorption was much lower, and moreover different in the presence of SO_4^{2-} (~5%), compared to Cl^- (10%).

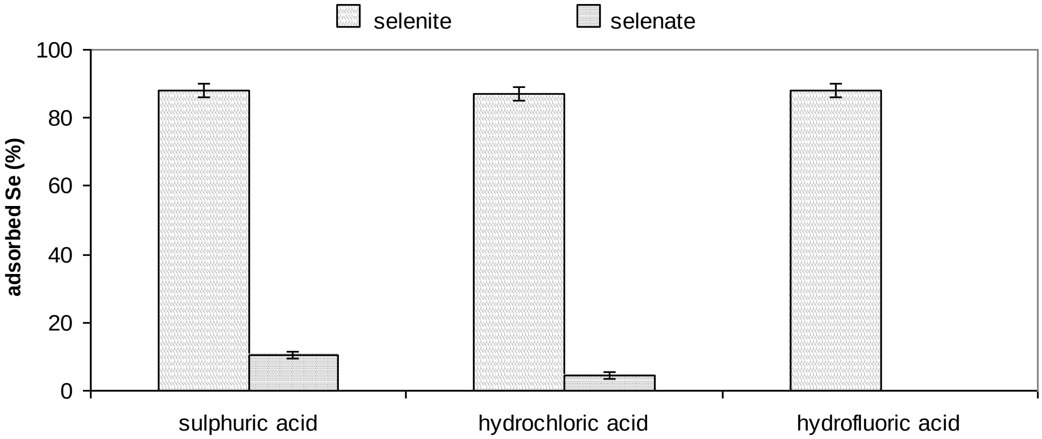


Figure 14: Percentage of adsorbed Se after 24 hours with different input solutions. All the initial solutions have 0.01 M of acid and as a result a pH of ~2.

5 Discussion

5.1 Plume trace element deposition

Volcanic emissions are a main geogenic point source for Se. It has been shown that both dry and wet deposition can have a significant influence on soils exposed to a volcanic plume (Delmelle et al., 2001; 2003, Delfosse et al., 2005; 2006, Bellomo et al., 2007). However, in the Etnean case trace element deposition from the plume can be excluded as the main process controlling the Se concentrations in the leachates. The volcanic plume is normally dispersed towards the southeast due to the dominant NW wind direction (Figure 4). Neverthless, the quantity of mobilized Se in lab controlled experiments is independent of the radial angle of the soil sample location with the main direction of the plume. For example similar Se distribution patterns are observed upwind and downwind from the crater in acid-rain experiments (Figure 6). Moreover, total soil Se concentrations show a scattering pattern (Figure 6) without any trends due to the influence of the plume. Additionally, there is no correlation in the leachates between Se and other elements strongly enriched in the plume (Calabrese, 2009) and in plant leaves (Martin et al., 2009a; Quayle et al., 2010), such as Thallium (Tl) and Cadmium (Cd) (Table 3). The influence of the volcanic Se emissions has been clearly demonstrated in the rainwater Se concentrations (Calabrese, 2009). On the contrary the Se mobilized during acid rain-soil interaction does not correspond with the deposited Se from the volcanic plume. This shows the importance of soils as reactive interfaces. However, since the plume affects the pH of the precipitation it still indirectly controls the Se mobility in the soils.

In the case of soil pH a similar distribution pattern is observed independent from the radial angle with the main direction of the plume (Figure 6). This is in contrast with previous work at Masaya volcano (Nicaragua) where soil pHs are consistently lower for sites directly exposed to the volcanic acid emissions as compared to the site located on the plume margin (Parnell, 1986, Delmelle et al., 2003). This could be explained by differences in parental material homogeneity or the plume dispersion characteristics.

Soil sites at Masaya correspond to two series each developed on homogenous parental material. The samples at Mount Etna have variable parental material. Moreover, wind directions are more variable around Etna than at Masaya (Allen et al., 2000; Martin et al., 2009a). Additional, the sites at Masaya are at approximately the same altitude of the plume vent, so direct plume fumigation occurs often increasing enormously the deposition of acidic compounds (Delmelle et al., 2001). In contrast Mount Etna has a conical form with the plume vents at the top. This geometry does not allow frequent direct fumigation of its flanks significantly reducing the deposition of acidic compounds. Although volcanic environments are often generalized, the results indicate that local dynamics play a key role in the geochemical cycle and that dominating process should be evaluated for different volcanoes.

5.2 Influence of pH

The pH controls surface charges of soil compounds (Yu et al., 1997; Barrow and Whelan, 1989), mineral dissolution (Oelkers and Gislason, 2001) and Se speciation and protonization (Figure 8). These parameters play a determining role in Se sorption processes. The adsorption experiments showed that more Se adsorption occurred at low pH (Section 4.3). This can be explained by the increased positive surface charge of the soil compounds, increasing anion adsorption (Yu et al., 1997; Barrow and Whelan, 1989).

As discussed in Section 4.2, the rainwater pH determined the Se release (Figure 7). However, the resulting pH during soil-rain interaction is strongly influenced by the soil characteristics. The soil pH is controlled by the protonation of organic matter and variable charge minerals (Herre et al., 2007). The buffering capacity of a soil also depends on the dissolution of allophane, iron oxides, primary silicate minerals and volcanic glass (Herre et al., 2007). Since dissolution only occurs under acid conditions, the buffering capacity of Etnean soils was higher in the case of acid rain interaction (Figure 11). There was no correlation between mobilized Se and the resulting pH after acid rain - soil interaction (Figure 11). This shows that pH is not the controlling parameter in the Se behaviour in the leachates. Nevertheless, a correlation between soil pH and Se content in acid leachates was observed. This can be explained by the control of SOM and variable-charge Fe and Al minerals on both soil pH and Se release (see discussion below).

5.3 Role of organic matter

Soil organic matter has been shown to play a fundamental role in soil Se availability (Gustafsson and Johnsson, 1992). Climate has a strong influence on SOM (Egli et al., 2007) which on Mount Etna is controlled by altitude, slope direction and dominant winds (Chester, 1985). However, the biggest differences in SOM depend on the location with respect to the craters, with higher SOM concentrations upwind from the volcano (Table 3; Figure 6). This can be explained by the fresh ash input downwind from the volcano that dilutes SOM and prevents soil development. Several mechanisms might be responsible for the decreased Se mobility under acidic conditions in SOM-rich samples. Firstly, there is less mineral dissolution occurring due to the stabilization by SOM (Wang and Mulligan, 2006) as confirmed by lower Al and Fe leachate concentrations. Secondly, new adsorption sites can be formed on humic acid or metal-humus complexes (Kamei-Ishikawa et al., 2007). Lastly, the presence of organic matter decreases the redox potential in the solutions (Wang and Mulligan,

2006) and therefore Se may be transformed into the immobile elemental Se (Figure 8). The kinetics of the transformation from selenite to elemental Se is reported to be fast (Bruggeman et al., 2007). Higher mobilized Se concentrations during neutral compared to acid-rain leaching in distal and upwind samples can be explained by Se redox transformations and surface charge changes. At neutral-rain experiment conditions even in the presence of SOM selenite is the thermodynamically stable species (Figure 8) and the formation of immobile elemental Se is not expected. Due to the presence of SOM the Al-phases are stable and the Se adsorption will increase at lower pH due to a higher positive surface charge.

5.4 Role of Fe and Al phases

Although there is no clear trend in the Fe and Al amorphous compound abundance with location, generally the amount of amorphous compounds decreases with increasing distance downwind from the craters. In contrast upwind from the volcano their amount increases with increasing distance (Table 3; Figure 6). Downwind samples are strongly influenced by fresh ash input and therefore have a low weathering state as evidenced by the higher content of amorphous compounds in the subsoil (Egli et al., 2007). However, upwind from the volcano weathering is mainly controlled by climate and follows Alpine characteristics with most intense weathering at higher elevated sites (Mirabella and Egli, 2003). The deviation from these trends can be explained by differences in parental materials, since the sampling strategy focused on the spatial distribution rather than on homogenous lithology. The higher content of amorphous material at the far distance downwind site (Figure 6) might be related to the agricultural activity on this site. This sample has been taken from a terraced soil. This might help to retain most of the new ash, whereas in natural sites the slope is > 0° and as a result some of the fresh ash could be mechanically removed. A comparison of the Fe and Al concentrations in the acid soil leachates compared with total and oxalate-extractable Fe and Al (Table 3) indicated that only a small percentage of the Fe is dissolved during the experiment (respectively below 1 and 5% for total and oxalate-extractable Fe). However, a significant percentage of the amorphous Al is dissolved (up to 43%, average value 18%). This cannot be related to volcanic glass dissolution, since volcanic glass with a similar composition as the bulk soils showed low dissolution (<0.5%) under the same experimental conditions.

As mentioned above, Fe and Al phases can present selective adsorption sites, particularly selenite. Anion adsorption is favourable in acid rain conditions for adsorption sites due to an increasing positive charge of the mineral surface with decreasing pH (Yu et al., 1997). In contrast, higher Se leaching is observed in acid rain conditions (Figure 7). This can be explained by dissolution of the Al compounds, during which the adsorbed Se is released too (Figure 15). Rainwater pH controls the dissolution of such minerals (Oelkers and Gislason, 2001), and thus the selenite release. The high concentrations of dissolved Al and Fe in the acid leachates indicate that some soil compounds containing Al, and to a lesser extent Fe, are unstable at low pH. In previous works, Fe oxides are recognized as the main carrier phase of Se in non-volcanic soils. However, the results confirm an important role of Al compounds, in correspondence with Se studies in Japanese volcanic soils (Nakamaru et al., 2005). The acidic leachates rich in dissolved Al are those who do not follow the relation between As and Se. As can be observed in Figure 12, these samples are relatively enriched in Se. This also indicates a role of Al phases for the Se behaviour.

Another release mechanism for adsorbed Se during acid rain–soil interaction is the competition for adsorption sites with sulphate (SO_4^{2-}, Figure 15). The acid rain in the experiments has 450 mg kg^{-1} of SO_4^{2-}, corresponding to the maximum SO_4^{2-} concentration measured in rainwater samples in the 2006-2007 period (Calabrese, 2009). Sulphate is especially competitive with selenate for adsorption sites (Wu et al., 2000). Indeed for selenite similar adsorption percentages are observed for solutions with different anions. However, for selenate lower adsorption occurs in the presence of sulphate compared to with the occurrence of chloride (Figure 14). This would suggest that sulphate adsorption is stronger than selenate adsorption and, as a consequence, sulphate containing rain might release Se. Therefore, in this case rain SO_4^{2-} concentration will be a key parameter controlling desorption of selenate. For this reason speciation can be used to obtain a better insight in the mobilization mechanism.

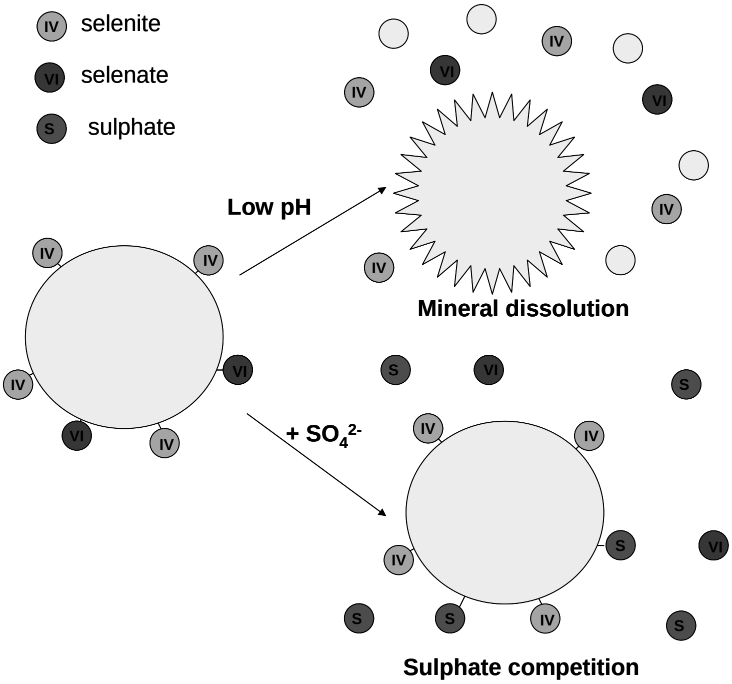


Figure 15: Desorption mechanisms for selenite and selenate. Mineral dissolution will desorb mainly selenite and some selenate. Sulphate competition will only release selenate.

5.5 Role of Se speciation

The domination of selenate in the selenium enriched acid soil extractions indicates that sulphate competition is a more significant release process than dissolution of the amorphous Al compounds. As a result, the rainwater sulphate concentration rather than the rainwater pH controls the Se release. It was observed that As and Se have different mobility for the soils within 5 km of the craters and > 2100 m altitude. These are also the samples which were rich in selenate. This indicates that sulphate does not compete with As anions for adsorption sites. As a result, Se and As do behave differently in samples collected at high altitudes during acid rain – soil interaction (Figure 12).

To check if indeed SO_4^{2-}-containing neutral-rain can mobilize selenate, additional experiments were performed for two selected samples (indicated in Figure 9). The selected sample downwind from the crater indeed releases similar amounts of Se in both conditions. In the selected sample upwind from the crater only about half of the Se amount is mobilized. This corresponds well with the observed speciation in the solutions. It shows that as expected the selenate release depends on the SO_4 concentration and the selenite mobilization on the mineral dissolution caused by low rainwater pH.

The dominance of selenate indicates the presence of thermodynamic unstable conditions, as selenite is the thermodynamically stable species in solution at the resulting pH-Eh conditions after 4 hours of soil – rainwater interaction (Figure 8). This points out that selenate is present as a metastable form in solutions. This agrees with previous work, where it has been shown that selenate is kinetically inert (Bruggeman, 2007). The presence of selenate cannot be explained by redox transformations on solid phases during sample preparation steps and/or chromatographic analyses, since the low pH mobile phase used prevented the precipitation of Al and Fe mineral phases. Additionally, oxidation by air during the experiment or storage are not expected, since the experiments mimic the natural conditions and samples were directly stored at dark and cool conditions.

The amount of selenate is higher for samples within 3 km from the craters compared to the samples further away from the volcano (Figure 9). Nevertheless, in all cases only a small percentage (0.2-4.3%) of the total Se is released. Therefore, although selenate is prevailing in the acid soil extractions, soils might be dominated by the remaining sorbed selenite and/or insoluble Se species. The higher abundance of selenate in the soils close to the craters can be explained by different processes. Firstly, the soil pH of these samples is lower (Figure 6), which favours anion adsorption (Yu et al., 1997; Barrow and Whelan, 1989). Secondly, soils close to the crater are frequently exposed to selenate-containing rainwater. Since Se concentrations rapidly decrease with increasing distance (Calabrese, 2009), the soils further from the volcano will lack this Se source.

The speciation also plays a key role in re-adsorption processes. Adsorption experiments show that high amounts of selenite can be retained in the soil, depending on the pH. However, in accordance with previous works (Wu et al., 2000; Duc et al., 2003; Bruggeman et al., 2007), selenate adsorption is much lower. As a consequence, most selenate will be retained within the solution.

5.6 Se mobility towards the groundwater

Previous studies on the chemical composition of the Etnean aquifer have emphasized the key role of magmatic derived CO_2 which lowers the pH of the water and therefore increases the leaching of the host rock (Aiuppa et al., 2000a, 2003a, Brusca et al., 2001). However, this mechanism fails to describe the Se distribution within the aquifer, because Se concentrations lack correlation with weathering indicators (e.g. Li, HCO3, Na, Mg, and Ca). This cannot be explained by redox changes, since there is no trend between Se correlations and redox potential within the groundwater. The thermal saline brines from the sedimentary basin are a Se source within some locations of the aquifer, producing anomalous Se concentrations (Aiuppa et al., 2000a). However, this source cannot clarify the enrichment of Se in all groundwaters. In this study it was showed that acid rain can mobilize Se within the volcanic soils. The prevalence of selenate implies that it is more likely that the Se is transported towards the aquifer, since adsorption experiments confirm that only a small amount of selenate can be re-adsorbed, especially in the presence of SO_4^{2-}. Taking into account that acid rain normally contains Se (Calabrese, 2009), this effect can be amplified. This has important implications for the composition of the aquifer. In Figure 16, a schematic overview of the main results and the controlling processes is given. The results indicate that three different mechanisms control Se mobilization towards the aquifer; rainwater composition (influenced by the volcanic activity), the soil characteristics (especially the Al-phases and SOM) and speciation.

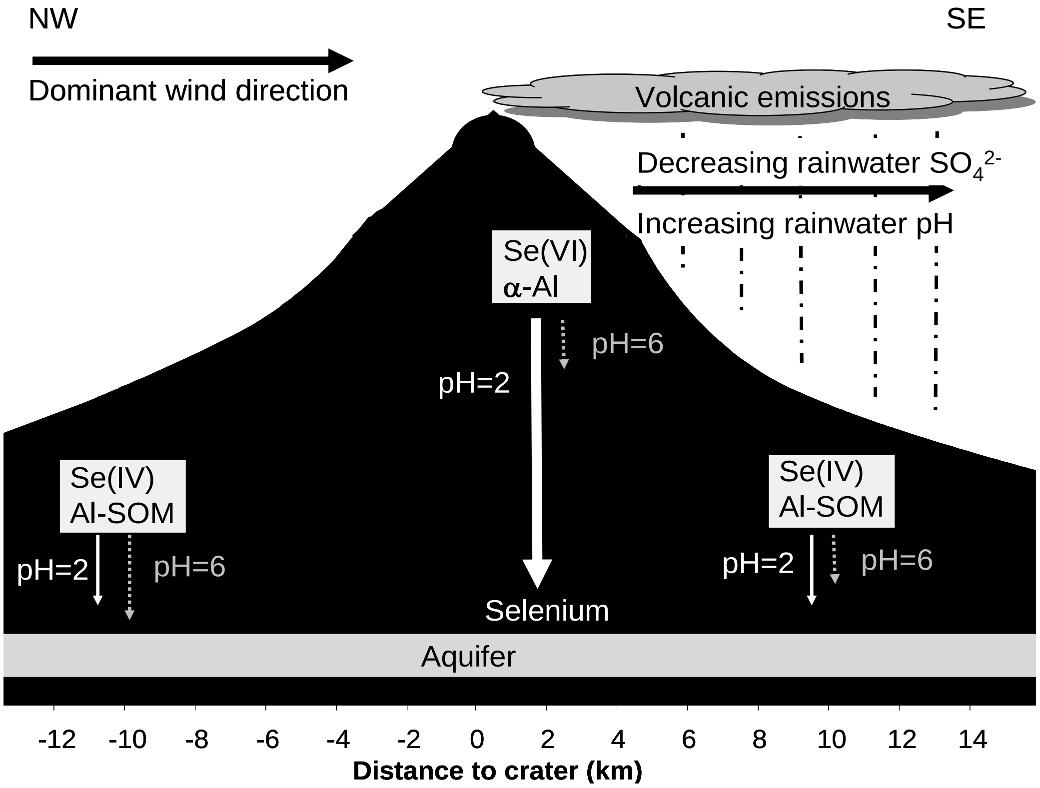


Figure 16: Schematic overview for Se mobilization towards the aquifer at Mount Etna. Se(VI)=selenate, Se(IV) = selenite. Al-SOM is areas were Al associated with SOM is present, while α-Al indicates the high content of amorphous Al phases.

I propose that Se is most likely leached into the aquifer during increased volcanic activity at sites downwind and close to the craters for three reasons (Figure 16). Firstly, the interaction of rain with the volcanic plume results in sulphate rich rain close to the crater, but the SO_4-concentration decreases with increasing distances (Calabrese, 2009). Secondly, the soils close to the crater release high levels of Se during acid rain events, which is related to the Al phases present in the soil. Thirdly, the dominance of selenate will favour the transportation towards the aquifers. Upwind and downwind further away from the crater only a small amount of Se will be leached, because at these locations rainwater will be neutral, sulphate-poor and soil properties prevent significant Se mobilization.

6 Conclusions

Acid rain-soil interaction was identified as a geogenic process which can release Se and therefore might produce natural leaching from volcanic sources to aquifers. This can have significant impact on human health, since 10% of the world populations lives within 100 km of an active volcano (Small and Naumann, 2001). Similarly, anthropogenic acid-rain could trigger large scale mobilization in contaminated soils with even more dramatic consequences for water quality and human health.

In the case of Etna volcano, fluxes of trace element deposition from the plume do not directly correlate with Se mobilization during soil-rain interaction. This shows the importance of soils as reactive interfaces. Soil composition and mineralogy, especially the presence of Al compounds, control the quantity of Se mobilized. Selenium adsorbed onto these phases can be released by competition of adsorption sites with sulphate in the case of selenate, or by mineral dissolution enhanced by the low rainwater pH for selenite. Although thermodynamics predict the presence of selenite, the soil extractions with relative high Se contents are dominated by the presence of selenate. This indicates sulphate competition as the main mobilization mechanism (Figure 15 and 16). Soil organic matter (SOM) also plays a role since it stabilizes Al compounds, can form Se adsorption sites and allows redox transformations to elemental Se. As a result, less Se is mobilized under acid conditions in SOM-rich soils.

The Etnean aquifer has been shown to be enriched in Se. Although leaching of the host rock and the input of thermal saline waters from the sedimentary basin have been previously proposed as the processes controlling the chemical composition of the groundwater, it fails to explain all Se data. In this study it was demonstrated that acid rain can produce mobilization of Se within volcanic soils and as a result might represent an additional source of Se to the aquifer. The results show that Se is most likely mobilized towards the aquifer close to the craters when volcanic-derived acid sulphate-containing rain interacts with the poorly developed soils rich in amorphous Al (Figure 16). Moreover, since these solutions are dominated by the presence of selenate, Se is likely to remain in solution and reach the aquifer, because adsorption processes within the soil profile are expected to be low. These findings have thus implications for groundwater composition in the area.

Chapter 7

Effect of weathering and climatic conditions on selenium behaviour in soils of a volcanic island

G.H. Floor, R. Millot, C. Arbelo, Ph. Négrel, G. Pardini, A. Rodríguez, G. Román-Ross. Effect of weathering and climatic conditions on selenium behaviour in soils of a volcanic island. In preparation. *To be submitted to Geochimica et cosmochimica acta.*

1 Introduction

Selenium behaves differently in volcanic soils compared to soils formed from other parental materials (Byers, 1935; 1936, Byers et al., 1936). This has been often correlated with the soil mineralogy (John and Saunders, 1975; Nakamaru et al., 2005). Since volcanic soils are widely used as agricultural resources and host almost 10% of the worldwide population (Small and Nauman, 2001), a profound understanding on the Se behaviour in volcanic soils is essential. Even so, it is poorly constrained how processes such as weathering affect the Se content and mobility. Tenerife Island, Spain, has an extraordinary variation of soils and weathering regimes depending on the location related to a strong climate gradient (Tejedor et al., 2007; Rodriguez et al., 2010). Therefore, in this work, topsoils from Tenerife, the biggest of the Canary Islands, were sampled from different locations crossing different climate zones in order to investigate the effect of weathering on Se behaviour in volcanic soils.

Weathering is an extremely important process that controls elemental transport, soil formation and earth morphology. Volcanic areas play key role in elemental transport towards the oceans since about 45% of the suspended river material delivered to the ocean comes from volcanic islands (Milliman and Syvitski, 1992; Dessert et al., 2003). Normally, suspended material originates from topsoils which are transported exclusively during storm events in these environments (Rodriguez, 2002). Water erosion has been shown to be significant at Tenerife, since 37% of the land area has slopes of > 30% (Hernández-Moreno et al., 2007). Weathering of volcanic rocks and the presence of volcanic soils also have an important role in the global carbon cycle. Silicate weathering is associated with atmospheric CO_2 consumption and basalts are the silicate rocks with the highest weathering rates (Louvat and Allègre, 1997; Dessert et al., 2003). As a result, around 30% of the long term sequestration of carbon fixed by chemical weathering of silicates in the terrestrial environment of Earth occurs on basaltic rocks (Milliman and Syvitski, 1992; Dessert et al., 2003). Moreover, about 5% of the Earths carbon is stored in volcanic soils (Eswaran et al., 1993). Volcanic rocks are also locally significant as a source of nutrients (Chesworth et al., 2004) and form agricultural important soils in densely populated areas. For these reasons, weathering processes in basalt and the resulting soils have received significant attention (Nanzyo et al., 2007; Egli et al., 2008).

Even so, it has not been evaluated how weathering and climate conditions can affect the Se content and its mobility within volcanic soils. Nevertheless, Se bioavailability will have implications for human health. During weathering, mineralogical changes occur in the soils. Volcanic glass will form allophane, imogolite and ferrihydrite (so called short range order clays (SROCs)) and organic content will increase. During more intense weathering, halloysite and gibbsite will be formed in favour of the SROCs (Shoji et al., 1993). Since Fe and Al minerals form common adsorption sites for Se but the affinity depends on the structural form (Balistrie and Chao, 1990; Duc et al., 2003; Fernández-Martínez and Charlet, 2009), the mobility of Se is expected to change. There are different tools to assess weathering. Chemical weathering indexes convert major element concentrations into a single value which varies with an increase or decrease in weathering. The chemical index of alteration (CIA) is based on a group of mobile oxides (CaO, Na_2O, K_2O) compared to the relative immobile Al_2O_3 (Nesbitt and Young, 1982; Taboada et al., 2007). A more innovative tool to investigate weathering processes is the use of Li isotopes. Lithium has two stable isotopes which produce significant isotopic fractionation in terrestrial systems due to their large relative mass difference (Tomascak 2004). Both field and experimental studies have shown that light Li (^{6}Li) is preferentially retained by secondary minerals during weathering (Pistiner and Henderson 2003, Kisakürek et al. 2004, Pogge von Strandmann et al. 2006, Vigier et al. 2009). The fractionation of Li isotopes is thus dependent upon the extent of weathering. Large fractionation seems to occur during superficial weathering while little fractionation is observed during more intense or prolonged weathering in stable environments (Huh et al. 1998; 2001; Pogge von Strandmann et al. 2006; Millot et al. 2010b).

Weathering is not the only process affecting soil properties and Se behavior. Anthropogenic Se sources comprise combustion (coal, oil, wood, biomass, and incineration), nonferrous metal melting and utilization of agriculture products (Wen and Carignan, 2007). Tenerife lacks major industrial pollution sources, but agricultural production is important for its local economics. The parental material has been mentioned as an important control on Se content of soils (Fordyce, 2005). However, due to its volcanic origin, the geological materials on Tenerife are relatively uniform in their composition (mainly basaltic or phonolitic). Tenerife's location within the North Atlantic Ocean and close to the Sahara allows regular marine aerosol and eolian dust input in the environment (Mizota and Matsuhisa, 1995; Viana et al., 2002; Alastuey et al., 2005; Kandler et al., 2007). Isotopic tracers, such as Sr isotope ratios, can be used to characterize these input sources (Mizota and Matsuhisa, 1995; Capo and Chadwick, 1999; Vitousek et al., 1999). However, the main control for the soil characteristics in this volcanic island setting is expected to be the strong climate gradient and the related differences in weathering regime (Tejedor et al., 2007; Rodriguez et al., 2010). Therefore, Tenerife is a perfect field site to study how climate-induced weathering variations affect the chemical fate of Se within soils from a volcanic island setting. Nevertheless, the other processes that impact Se content and mobility should be constrained to isolate the effect of weathering. To my knowledge, no previous works exist on the evaluation of a range of natural processes affecting Se behaviour in soils from a volcanic island.

2 Tenerife Island

2.1 Geography and geology

The Canary Islands are an island group located west of the northwest African mainland, belonging to Spain. Tenerife, located about 300 km from the African coast, is with around 2036 km^2 and a maximum altitude of 3718 meter the largest and highest island of the archipelago. With most land usable for agriculture it has been traditionally (<1970) the most populated of the island. Tenerife has almost 890 thousand inhabitants (in 2008, Instituto Canaria de Estadistica, 2010). The location close to the Sahara allows regular eolian dust input in the environment (Mizota and Matsuhisa, 1995; Viana et al., 2002; Alastuey et al., 2005; Kandler et al., 2007).

The Canary intraplate oceanic-islands formed related to an upwelling mantle plume or hotspot. There is an age progression from east to west for the shield building stage, with Fuerteventura having the oldest rocks and El Hierro the youngest. However, more recent activity is distributed throughout the archipelago with only La Gomera lacking Holocene eruptions. Tenerife is the most complex island of the Canaries from a volcanological point of view. Nevertheless, the evolution of Tenerife can be divided in three main stages, which are rather characteristics for oceanic-islands (Carracedo and Day, 2002):

1) The formation of a basaltic field with ages ranging from 12 to about 4 Ma which constitutes about 90% of the total volume of the island. Some felsic differentiates occur as dykes and domes, but the series is dominated by basaltic lavas and pyroclastics.
2) After an interval of quiescence and intensive erosion the construction of a large volcanic complex in the central part of the island started about 3 Ma, containing both basaltic and felsic (mainly in the form of pyroclastics) volcanism.
3) The formation of the current active volcanic complex; represented by many, mostly basaltic, volcanoes scattered throughout the island and by the central Teide-Pico Viejo edifice with both basaltic and felsic emissions.

Due to this volcanic origin of the island, the soil parental materials are mainly basaltic at the northern flank. However, at the southern side acid materials cover basaltic formations (Tejedor et al., 2007).

2.2 Climate

Tenerife Islands was selected as study site because of its strong climate gradient, making it a perfect location to study the effect of weathering regimes on the Se behaviour. Tenerife has seven micro-climates. The climate of Tenerife is influenced by the humid and cool trade winds coming from the northeast, the cold marine current around the Canary Islands, a thermic inversion layer at about 1500 m altitude and orography. On the windward side of the island the wind is forced to rise giving orographic precipitation on the island’s northern side and rain shadow on the leeward. Therefore, the annual precipitation increases from about 300 mm close to the coast to a maximum value at 1000 m around 850 mm. Above 1000 m the precipitation decreases to values below 600 mm at the water divide. This decrease continues on the leeside with annual precipitations below 100 mm close to sea level, whereas evaporation increases. On the northern side on altitudes between 800 and 1400 m the condensation arising from the moisture carried by the clouds can be twice the precipitation and is therefore extremely important in the water budget of the area (Figure 1, Jonsson et al., 2002; Tejedor et al., 2007; Rodriguez et al., 2010). Most rainfall occurs between October and April. As a result of the climatic varieties on a small scale, Tenerife Island is a common field site to study the effect of environmental gradients on a range of topics, such as beetles (De los Santos et al., 2002; 2004), mechanical rock weathering (Jenkins and Smith, 1990) and vegetation (Fernández-Palacios and De Nicolás, 1995; Jonsson et al., 2002; Villa et al., 2003).

2.3 Soils

Previous works also prove a strong effect of the climatic conditions on the soil properties. Tejedor et al (2007) showed that the soil type depends on the altitudinal climate variations. On the northern side two climosequences have been defined depending on the age of materials. On old basaltic lava flows Vertisols, Alfisols, Ultisols and Inceptisols corresponding to aridic/ustic, ustic, udic and xeric moisture regime are found. On recent pyroclastic materials, at these same climatic levels, Inceptisols, allophanic Andisols and vitric Andisols are present. On the southern side fewer climatic variations are present and moreover the surface contains acid materials, causing a soil climosequence of Aridisols, Vertisols and Inceptisols. Rodriguez et al (2010) indentified seven of the nine soil temperature regimes considered by Soil Taxonomy (hyperthermic, thermic, mesic, isohyperthermic, isothermic, isomesic, and cryic) on Tenerife island. The observed soil temperature regimes variations could be explained by elevation and orientation. Other soil parameters studied with respect to climatic variations are micro-morphological properties (Fernández-Caldas et al., 1975), soil organic matter (González-Pérez et al., 2007), the clay fraction (Fernández-Caldas et al., 1975) and the availability of nutrients (Köhler et al., 2006).

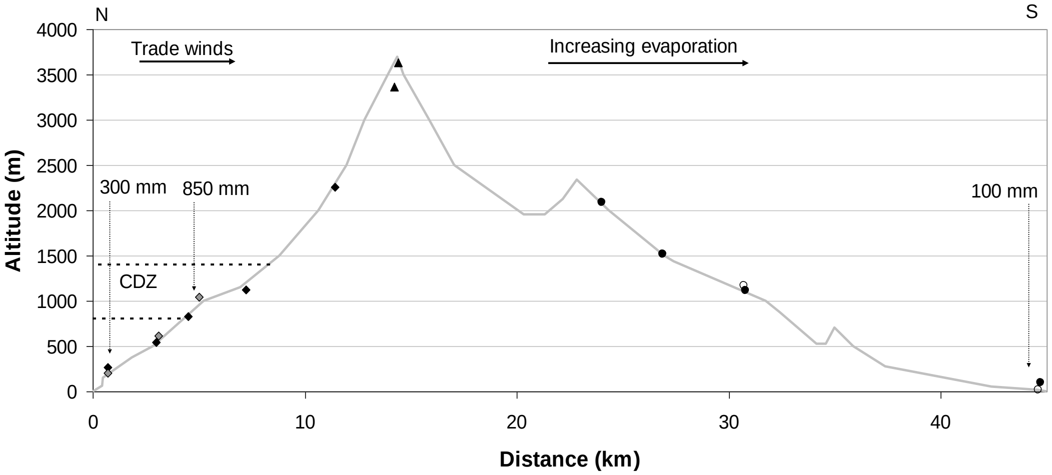


Figure 1: Climatic conditions along a north south profile indicating in which zone the samples have been collected. CDZ= condensation zone, which is the area where condensation significantly contributes to the water budget.

2.4 Vegetation and landuse

On the northern side cloud forest and tree heath woodland form the natural vegetation. From the period of the Spanish conquest in the 15th Century until recently the need for timber for fuel and construction and the growing need for farmland caused much of the vegetation to be replaced by pine and eucalyptus forest and agricultural crops (Jimínez et al., 2007). On the southern side, the climate is semi-arid and has coastal or succulent scrub as natural vegetation. Landuse changed little over the centuries, consisting mainly of goat grazing and pluvial agriculture. However, the past 40 years the landscape has been transformed dramatically by modern irrigation-based agriculture and increasing urbanization and infrastructure related to mass tourism (Otto et al., 2007). Agricultural crops are mainly located close to the coast and include bananas, tomatoes, fruits, vineyards, potatoes and orchards (Diaz-Diaz et al., 1999; Figure 2). Due to the extensive agricultural activity, most soil studies focus on the properties of these farming soils (Garcia et al., 1981; Arevalo Morales et al., 1987; Alvarez et al., 1988; Diaz-Diaz et al., 1999; Ríos-Mesa et al., 2006) and the abundance of nutrients with agricultural interest (Borges-Perez et al., 1994; Fernández-Falcon et al., 1994; Kohler et al., 2006) or pesticides (Diaz-Diaz et al., 1999). An important agricultural practice is the use of ´sorribas´, in which fertile soils (often from the middle altitudes on the northern flank) are imported to other areas with suitable climatic conditions but limiting soil characteristics (Armas-Espinel et al., 2003; Hernández-Moreno et al., 2007). Surface mulching is applied in the south and

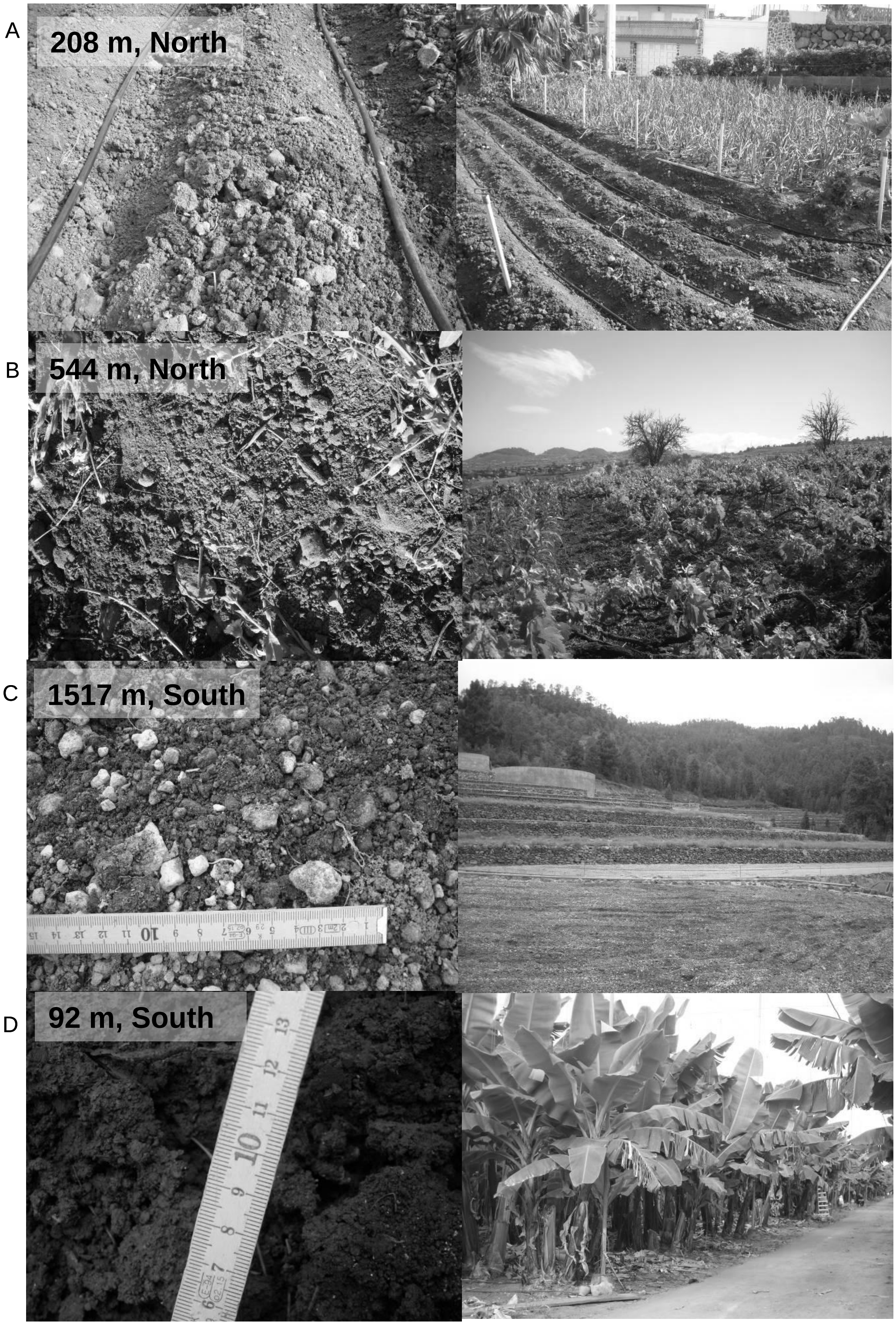


Figure 2: Examples of agricultural practices for sites within this study. A: ´Sorriba´ (imported soil) and irrigation for vegetables. B: Vineyards. C: Terraces and mixing with pumice for potatoes. D: ´Sorriba´ and covered area for bananas.

southeast of Tenerife by covering the soil with a layer (20-60 cm) of pumice pyroclasts in order to prevent evaporation (Hernández-Moreno et al., 2007; Figure 2). The use of terraces is also common. Landuse strongly affects the soil characteristics and its vulnerability for erosion (Rodríguez-Rodríguez et al., 1993; Hernández-Moreno et al., 2007; Jimínez et al., 2007).

3 Experimental Section

3.1 Sample collection

Topsoil samples (upper 10 cm) have been collected along a profile from NE close to Mesa del Mar, Tacoronte towards the SE close to Rasca, Arona crossing different climate zones (Figure 3, 4; Table 1). At the lower altitudes two samples have been collected in each climate zone: one ´natural´ soil and one ´agricultural´ soil. Since human activity is concentrated relatively close to the coast, this was not possible in the higher altitudes (> 1600 m). At each location, a composite sample has been obtained (3 different spots, minimum distance between them 2m). Soils were air-dried and then sieved (fine earth fraction, <2mm). Basalt and phonolite rock samples were collected at the Southern part of the Island (Figure 3) for normalization purposes.

Figure 3: Sample locations. Diamonds, circles and triangles indicate soil sample locations (same symbols as in other graphs). Black symbols: natural soils. White and grey symbols: agricultural soils. Map obtained from Google Earth.

3.2 General soil parameters

Most total element concentrations have been determined using a combination of Instrumental Neutral Activation Analysis (INAA), total digestion Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and lithium metaborate/tetraborate fusion ICP-MS at Activation Laboratories Ltd in Canada. Based on these data the Chemical Index of Alteration (CIA) was calculated according to Nesbitt and Young (1982) following:

$$CIA = 100*Al_2O_3/(Al_2O_3+CaO+Na_2O+K_2O) \qquad (1)$$

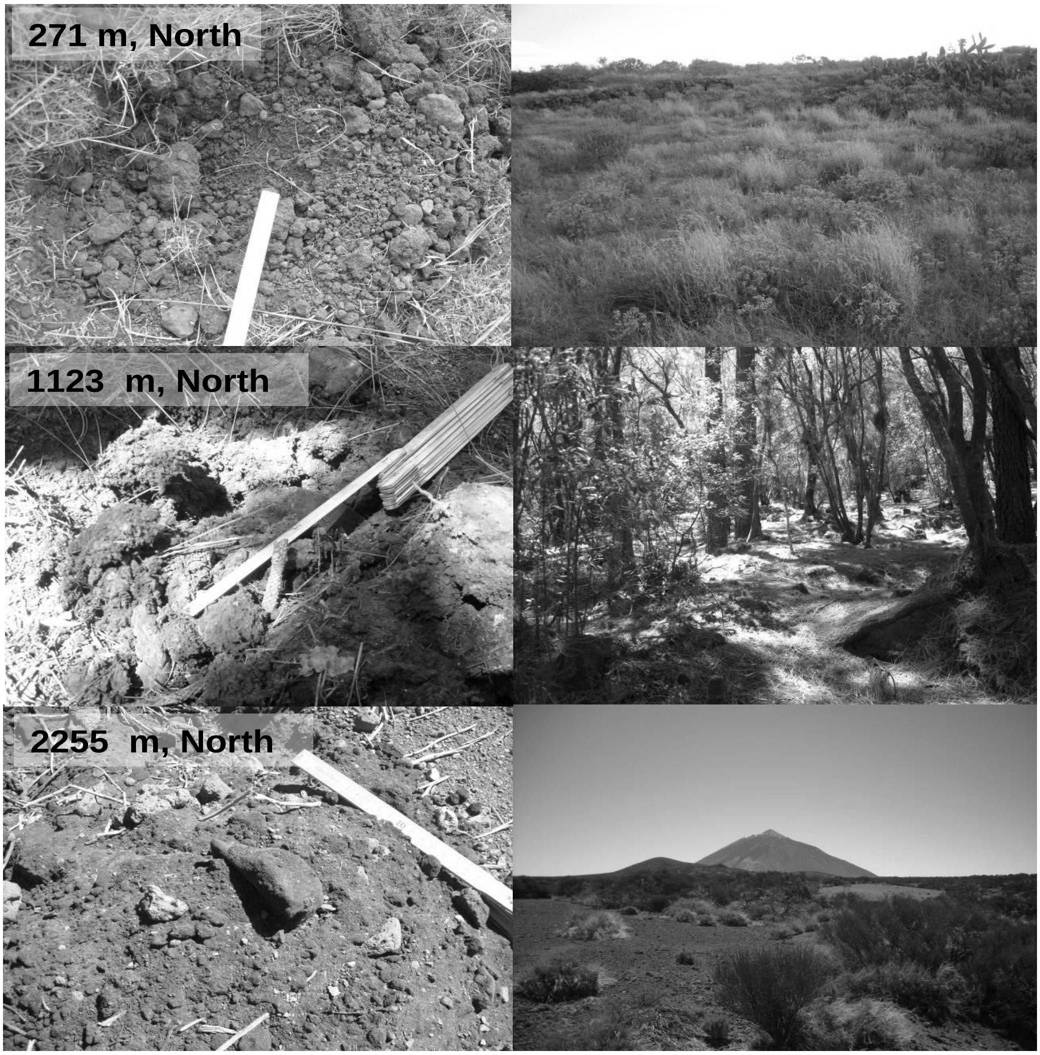
Total Se contents have been determined by ICP-MS as described in Chapter 3. Total Li concentrations were measured by ICP-MS (Element 2, Thermo) after total digestion of the sample. For that, 50 mg of crushed sample was dissolved in a closed beaker with an ultrapure mixture of three acids for 4 days at 100 °C: 4 ml of HF (23 N), 1 ml of HNO_3 (14 N) and 0.1 ml of $HClO_4$ (12 N). Four days later, 4 ml of HCl acid (6 N) was added and heated for 4 days at 100 °C. Procedural blanks for the total digestion of the solid samples by acids (HF, HNO_3, $HClO_4$ and HCl) contain < 300 pg of Li, which is less than 0.1% of the sample. The first step of the BCR sequential extraction (Rauret et al., 1999; Hernández-Moreno et al., 2007) was used to determine the exchangeable Se concentrations (Nobbs et al., 1997; Peters et al., 1997; 1999). For that, 1 gram of sample was shaken for 16 hours in 40 ml of 0.11 acetic acid solution. After centrifugation and filtration (Whatman, 0.45 μm polypropylene media) Se concentrations were determined by ICP-MS (Agilent, 7500c) using a pressurized collision-reaction cell (3.5 mL/min H_2) with matrix-matched standards and ^{103}Rh as internal standard.

The pH-H_2O was determined with a soil-solution ratio of 1:2.5. Grain size distribution was investigated using wet sieving of the sand fraction and suspension in sodiumpolyphosphate for the fine fractions after removal of organic matter by H_2O_2 (Buurman et al., 1996). Organic matter content has been assessed using the Walkley-Black method, in which organic carbon in the sample is oxidized with a mixture of potassium dichromate and sulphuric acid without external heating. The excess potassium dichromate is titrated with ferrous sulphate (Buurman et al., 1996). The mineralogy was determined in soil powder (ground <2 mm fraction) and the clay fraction (using titration of the suspension in sodiumpolyphosphate) by X-ray Diffraction (XRD; Siemens D5000). Because significant amounts of amorphous compounds were present, ´amorphous´ Al, Fe and Si were extracted with a 0.2 M ammonium oxalate – oxalic acid mixture at pH=3 (Buurman et al., 1996; García-Rodeja et al., 2007). The Fe, Al and Si detection was performed using Atomic Adsorption Spectrometry (AAS).

3.3 Li and Sr Isotopes

Lithium isotopic compositions were measured using a Neptune Multi Collector ICP-MS (Thermo Fischer Scientific). $^7Li/^6Li$ ratios were normalized to the L-SVEC standard solution (NIST SRM 8545, Flesch et al., 1973) following the standard-sample bracketing method (see Millot et al. (2004) for more details). The analytical protocol involved the acquisition of 15 ratios with 16 s integration time per ratio, and yielded in-run precision better than 0.4‰ ($2\sigma_m$). The samples were prepared beforehand through a process of chemical separation/purification by ion chromatography (James and Palmer, 2000), as required to produce a pure mono-elemental solution. A sample aliquot (30 ng of Li) of the acid dissolution residue was dissolved in 0.5 ml of HCl (0.2 N) before being placed in a column containing cationic resin (BioRad AG® 50W-X12 resin, 200–400 mesh) for Li separation (Millot et al., 2004). Accuracy and reproducibility of the entire method (digestion + purification procedure + spectrometric analysis) was tested by repeated measurement of the JB-2 basalt standard (Geological Survey of Japan). This yielded a mean value of δ^7Li = +4.58‰ ± 0.14 (2σ, $n = 5$), which is in good agreement with published values (Carignan et al., 2007; Tomascak, 2004).

Chemical separation of Sr from the digestions was done with an ion-exchange column (Sr-Spec, Pin and Bassin 1992), with a total blank <0.5 ng Sr for the entire chemical procedure. A part of the treated sample was loaded onto a tungsten filament and analysed with a Finnigan MAT 262 multiple collector mass spectrometer (TIMS). The ^{87}Sr/^{86}Sr ratios were normalized to a ^{86}Sr/^{88}Sr ratio of 0.1194. An average internal precision of $\pm 10\times10^{-6}$ (2σ) was obtained during this study. The reproducibility of ^{87}Sr/^{86}Sr ratio measurements was tested through multiple analyses of the NBS 987 standard and the mean value was 0.710230 ± 0.000009 (2σ; $n = 14$).



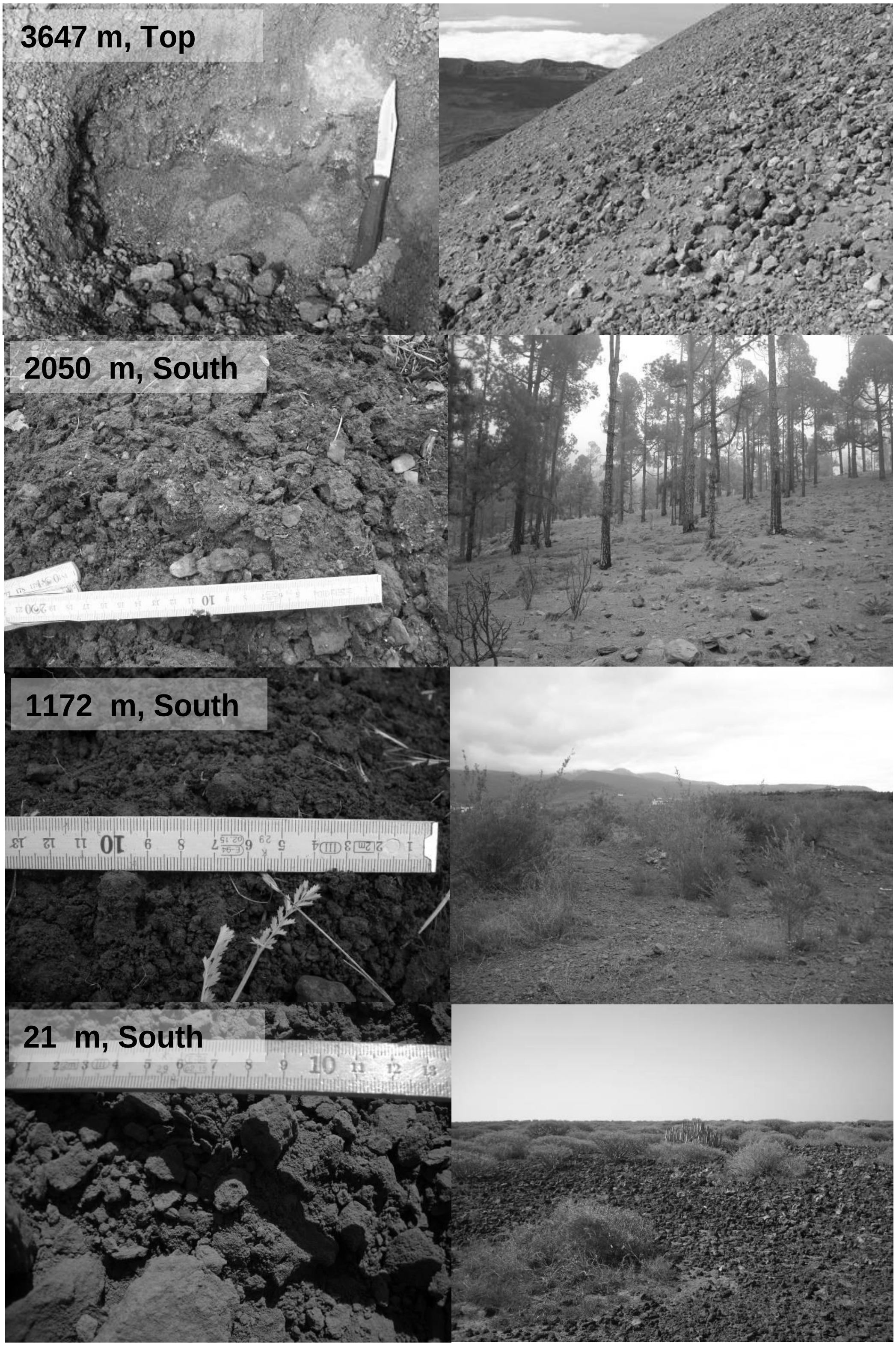


Figure 4: Examples of soil sample location in this study along the climatic gradient without anthropogenic influences

4 Results

4.1 Selenium concentrations and mobility

Selenium concentrations in Tenerife soils varied between 0.03 and 1.23 mg/kg with an average of 0.38±0.3 (1σ, n=17) (Table 2). This corresponds with the worldwide average soil content of 0.4 mg/kg (Fordyce, 2005). In Figure 5A the Se concentration is reported as a function of the distance to the sample collected close to Mesa del Mar (NE). The highest Se levels were at the north side of the island. Especially the soils collected in the condensation zone (800-1400 m) were enriched in Se. The lowest concentrations were found for the samples collected at the SW point of the island. The exchangeable Se (extracted in 0.11 M acetic acid, Nobbs et al., 1997; Peters et al., 1997; 1999) varied between 0.2 and 3.2% of the total Se content with an average of 0.8% (Figure 5B; Table 2). This low Se mobility corresponds with previous work on volcanic soils (Byers, 1935; 1936, Byers et al., 1936; John and Saunders, 1975; Nakamaru et al., 2005; 2006; Nakamaru and Sekine, 2008). The highest mobility was observed for the natural sample collected at the SW (Malpaís of Rasca) and in the Teide natural park, while the lowest percentages were observed for the samples from the condensation zone.

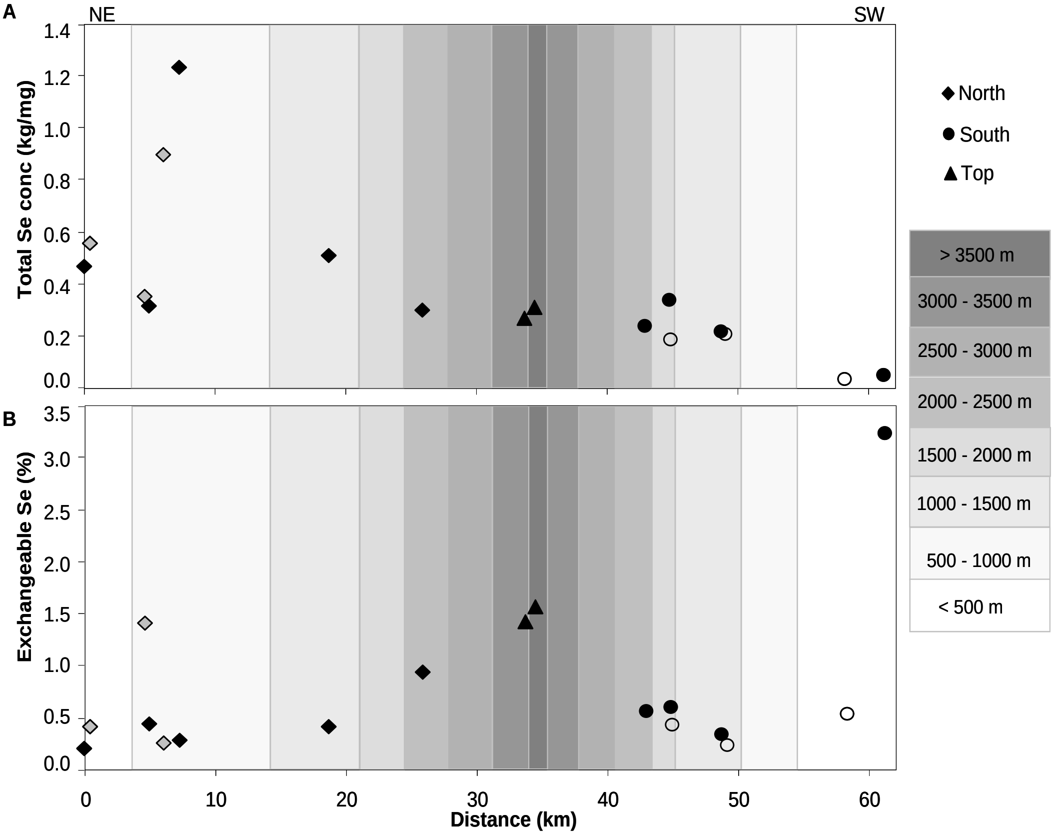


Figure 5: Spatial distribution of A: total Se concentration and B: leachable Se (0.11 acetic acid solution). Distance in km is compared to location most NE on the Island (see Figure 2). Grey tints indicate altitude. Black symbols: natural soils. White and grey symbols: agricultural soils.

4.2 Other soil parameters

The important soil parameters used in this study are given in Table 1. Therefore, in this section I only discuss some key parameters. A high variation existed in most of the soil parameters. For example, the soil pH varied between 4.4 and 8.2 and the clay fraction between 2.7 and 48.9%. Some of the soils contained high percentages of amorphous Al and Fe (Al_{ox}/Al_T and Fe_{ox}/Fe_T up to 17.8 and 22.6% respectively, Table 1). The highest content of amorphous Al and Fe compounds were found in the condensation zone at the northern side of the island (800-1400 m). These soils also had a high content of soil organic matter (SOM, up to 17.8%, Table 1). In contrast the soils from high altitudes (>3000) had a SOM below 1%.

4.3 Weathering intensity

The primary aim of this study is to asses the effect of weathering on the Se contents and mobility within volcanic soils. The Chemical Index of Alteration (CIA) is an often used proxy in the assessment of weathering intensity. Values below 50 indicate no weathering while 100 corresponds to very intensive weathered material (Nesbitt and Young, 1982). The soils from Tenerife Island had a wide variation in the CIA between 56 and 90, indicating the high weathering contrast along the island (Figure 6; Table 1). The samples collected at altitudes >1500 m and the most southwestern sample had CIA below 70. The soil samples from <1500 m altitude (except the most southwestern sample) had a CIA above 70. The highest CIAs were found in the condensation zone and the sample from the banana plantage. The δ^7Li values, also often used to assess weathering (Huh et al. 1998, 2001, Pistiner and Henderson 2003, Kisakürek et al. 2004, Pogge von Strandmann et al. 2006, Vigier et al. 2009, Millot et al. 2010b), varied between +1.2 and +9.1 ‰. This is in agreement with reported δ^7Li values between -0.4 and +13.7 ‰ for volcanic soils from Hawaii and Iceland and variations between 4 and 12 ‰ within one soil profile (Pistiner and Henderson, 2003; Huh et al., 2004).

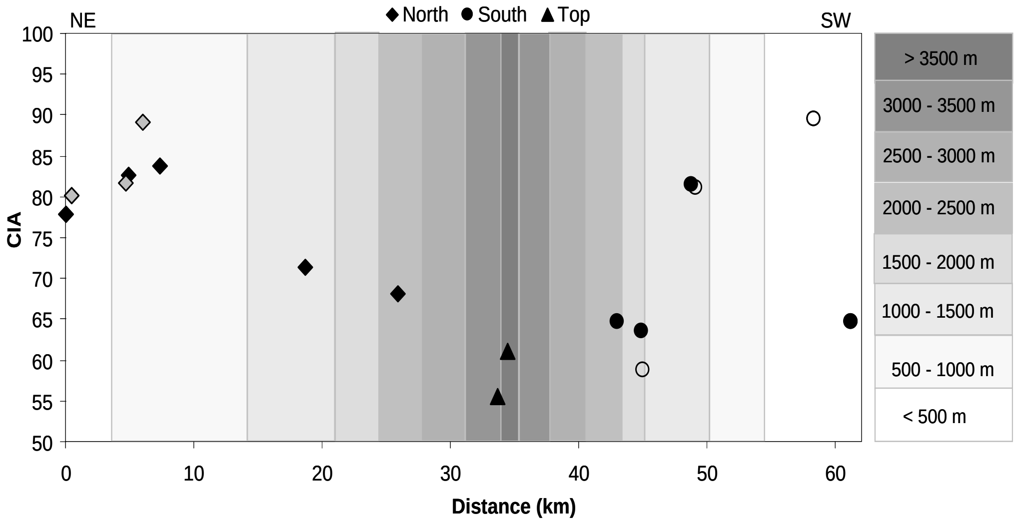


Figure 6: Spatial distribution of CIA. Distance in km is compared to location most NE on the Island (see Figure 3). Grey tints indicate altitude. Black symbols: natural soils. White and grey symbols: agricultural soils.

Table 1: Soil locations, characteristics and process tracers

	Soil sample location						Soil characteristics						Process tracers				
	Coordinates		Alt (m)	Cat	Landuse / vegetation	Δ dis (km)	pH-H_2O (1:2.5)	Clay fraction (%)	SOM (%)	Al_{ox}/Al_T (%)	Al_{ox}/Si_{ox}	Fe_{ox}/Fe_T (%)	CIA	Conc (mg/kg)		Isotopes	
	x_{utm}	y_{utm}												Sr	Li	$^{87}Sr/^{86}Sr$	δ7Li (‰)
A1	360996	3154800	271	N1	Abandoned field?	0.0	6.8	41.2	2.7	1.7	0.7	5.2	78	239	25	0.70660	+9.1
B1	360556	3149908	544	N1	Abandoned vineyard?	4.9	6.3	35.3	4.8	2.4	2.3	13.5	83	148	36	n.a.	+6.5
C1	362528	3147670	827	N1	Lauriselva forest	7.3	6.1	13.8	14.9	3.3	0.3	20.0	84	103	20	0.70722	+2.8
D1	353001	3137955	1123	N1	Pine forest	18.6	6.3	22.4	16.1	17.8	1.8	22.6	71	211	13	n.a.	+3.0
E1	349889	3131458	2255	N1	Retamar	25.9	4.8	12.3	5.4	7.3	1.6	14.2	68	332	13	n.a.	+4.3
A2	361426	3154640	208	N2	horticulture (sorriba)	0.5	6.3	48.9	2.4	1.5	2.1	7.5	80	296	22	n.a.	+5.7
B2	360493	3150188	616	N2	vineyard	4.6	4.4	36.9		1.9	0.7	11.1	82	176	26	n.a.	+5.8
C2	361173	3148776	1041	N2	Pine forest (replanted)	6.0	5.6	19.9	17.8	16.1	1.3	21.8	89	81	24	n.a.	+1.3
F1	332483	3100706	94	S1	´Malpaís´	61.2	8.2	17.9	0.8	1.6	0.2	4.5	65	484	24	0.70523	+6.8
G1	337248	3112305	1118	S1	matorral	48.7	7.3	32.9	1.5	4.0	2.6	6.5	82	316	16	n.a.	+4.8
H1	338464	3116108	1517	S1	Pine forest	44.8	7.9	12.6	3.7	1.3	0.3	8.0	64	325	9	n.a.	+1.6
I1	336900	3119317	2090	S1	Pine forest	42.9	6.4	17.6	10.7	5.0	4.2	10.0	65	176	12	0.70515	+1.8
F2	334788	3102843	21	S2	Banana plantation (sorriba)	58.2	7.1	42.0	3.0	6.2	1.8	12.7	90	195	14	n.a.	+1.2
G2	336731	3112177	1172	S2	Vineyards	49.0	6.9	29.1	2.8	1.6	0.2	6.1	81	321	20	n.a.	+4.0
H2	338410	3116024	1517	S2	Potatoes	44.9	5.9	12.5	8.9	4.7	4.1	6.3	59	192	10	n.a.	+1.9
T2	338970	3128347	3635	T	National Park	34.4	7.9	6.3	0.7	n.a.	n.a.	n.a.	61	198	14	0.70322	+3.7
T4	339889	3128655	3365	T	National Park	33.6	6.6	2.7	0.9	n.a.	n.a.	n.a.	56	181	16	n.a.	+3.0
RB				R	x	x	x	x	x	x	x	x	45	1037	6	0.70325	+4.9
RP				R	x	x	x	x	x	x	x	x	56	159	11	0.70367	+1.5

Alt= altitude

Cat= Category. N: North, S: South, T: Top, R: Rock, 1=natural, 2=agricultural. RB: Basalt. RP: Phonolite

Δdis = distance relative to soil location A1. n.a. = not analyzed. X = parameter not relevant

Table 2: Soil elemental composition

	Selenium behaviour		**Major element composition (%)**								**Immobile trace elements (mg/kg)**						**Oxy-anion forming elements (mg/kg)**				
	Se conc (mg/kg)	Exch Se (%)	SiO_2	Al_2O_3	FeO_T	MgO	CaO	Na_2O	K_2O	TiO_2	Hf	Ni	Ta	Y	Zr	La/Yb	As	Cr	Sb	U	V
A1	0.46	0.21	45	17	12	2.49	1.49	1.40	2.03	3.22	10	144	6.1	30	531	26	11	354	0.7	3.1	258
B1	0.31	0.44	43	18	10	1.41	0.70	1.09	2.25	2.47	12	104	5.8	31	520	30	11	238	0.8	4.7	193
C1	1.2	0.29	21	15	8	2.21	1.72	0.48	0.71	2.14	9	136	4.8	19	408	22	7	282	0.7	3.7	168
D1	0.51	0.42	25	13	8	3.22	3.30	1.01	0.88	2.12	7	114	5.4	26	332	32	5	232	1	2.6	140
E1	0.30	0.94	37	16	11	6.71	3.74	2.15	1.54	2.88	8	180	5.2	23	366	21	4	288	3.8	2.7	212
A2	0.56	0.42	45	18	11	1.83	1.65	1.17	1.65	2.99	11	78	6.8	34	407	29	10	204	0.7	3.8	239
B2	0.35	1.41	40	19	11	1.97	1.16	1.07	1.75	3.26	12	111	7.4	29	503	29	15	252	0.9	5.1	246
C2	0.90	0.26	20	15	7	0.86	0.75	0.44	0.68	1.80	9	127	3.4	20	339	29	11	261	0.5	4.7	159
F1	0.05	3.22	49	17	7	3.77	2.99	3.30	2.84	1.76	9	51	4.7	29	401	30	4	111	3.1	1.8	117
G1	0.21	0.34	40	21	11	1.54	1.50	1.40	1.77	3.06	11	58	6.6	41	671	28	9	122	1.8	4	227
H1	0.33	0.60	50	18	6	1.01	2.40	4.34	3.34	1.90	15	13	10.2	50	661	29	2	31	2.1	3.8	86
I1	0.19	0.56	49	17	5	0.75	1.33	4.30	3.47	1.32	12	10	8.3	43	572	29	3	36	4.9	3.1	59
F2	0.03	0.53	31	21	12	1.34	1.11	0.55	0.81	3.59	12	38	7.7	43	389	35	6	105	3.8	4.7	204
G2	0.20	0.23	41	21	11	1.54	1.55	1.42	1.96	3.11	13	61	7.4	42	885	24	7	135	0.8	4.5	239
H2	0.24	0.43	49	16	3	0.80	2.42	4.43	4.56	0.71	15	9	6.6	34	820	35	7	149	0.03	8.6	46
T2	0.31	1.57	60	19	4	0.56	1.52	6.00	4.50	0.81	12	2	6.6	28	660	38	4	0.25	0.03	6.1	18
T4	0.27	1.43	60	19	4	0.65	1.45	8.09	5.29	0.87	13	2	9	32	767	40	5	15.8	0.03	5.8	25
RB	1.2	x	43	13	12	7.38	12.1	3.18	1.43	3.94	5	81	3.5	29	237	29	2	254	0.11	1.1	345
RP	2.0	x	61	19	3	0.48	0.94	8.63	5.66	0.83	16	1	10.8	46	948	43	3	10	0.02	4	33

Exch Se = exchangeable Se extracted using 0.11 M acetic acid

RB = Basalt. RP = Phonolite

X = parameter not relevant

4.4 Comparison with other oxyhydroxo anion forming elements

The behaviour of Se is often compared to other oxyhydroxo anion forming (OHA) elements, such as arsenic (As), chromium (Cr), antimony (Sb), molybdenum (Mo), uranium (U) and vanadium (V). All these elements form, depending on their oxidation state, oxohydroxo complexes which are soluble. Molybdenum was present in low concentrations in the Tenerife soils (< LOD of 2 mg/kg for most soils) and therefore not included in this discussion. The other elements (Table 2) lacked correlation with Se contents. The relationship between Se and As concentrations in soils from Tenerife is given in Figure 7. Arsenic should be more similar to Se compared to the other oxyhydroxo anion forming elements, since both have a high chalcophile affinity and their masses are similar. However, even in this case, there was no direct correlation observed between Se and As in the soils.

5 Discussion

Although the objective of this study is to evaluate the effect of weathering on the Se behaviour within volcanic soils, a number of other processes can additionally impact the soils, such as variations in parental rock composition, external inputs (Saharan dust and/or marine aerosols) and sorption processes. These must be constrained in order to isolate the effect of weathering. Here, the different processes potentially affecting the Se behaviour will be evaluated using different analytical tools.

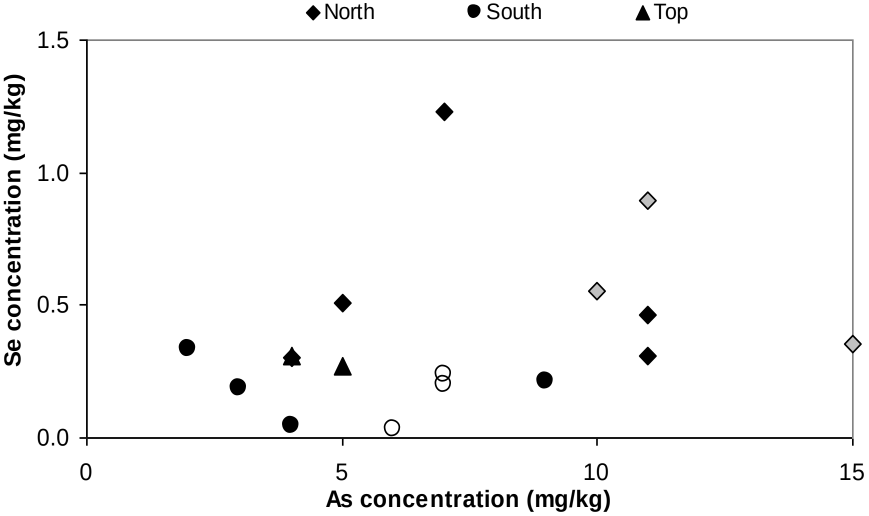


Figure 7: Relation between selenium and arsenic concentration in soils from Tenerife. Black symbols: natural soils. White and grey symbols: agricultural soils.

5.1 Parental material

The exact determination of parental material is important for two reasons. Firstly, the elemental composition of the parental material is often used for normalization purposes. The effect of weathering can only be assessed if the characteristics of the starting material are known. Secondly, parental material has been shown to control Se contents in soils (Fordyce, 2005). In order to estimate the parental material of the soils, the elemental concentrations for phonolite and basalt were compared. Basalts are on average more enriched in Ti, P, V, Sr, Ni, Cu, Sb and Cr and more depleted in

Zr, U, Th, Ta, Hf, Na, K and La than phonolites (this study and Georoc database). Nevertheless, not all of these elements are suitable for the determination of parental rocks. Several elements, such as Cu (vineyards, Flores-Vélez et al., 1996) and P (fertilizers, Nakamaru et al., 2006), are affected by agricultural practices and as a result unsuitable for the determination of the parental material. For example, the vineyard soil from El Sauzal has a Cu concentration one order of magnitude higher than the other soils collected within this study. Other elements, such as Sb, lack sufficient literature values in order to check for the representability of the rock samples collected in this study. Furthermore, Sr, Na, K are mobile elements and will therefore be strongly influenced by weathering processes (Nanzyo et al., 2007; Egli et al., 2008). Figure 8 shows a major element ternary diagram (ALF ternary diagram) on which the relative abundance for soils and rocks are shown. The basalt and phonolite sampled taken in this study fit within the compositional range reported in the literature for basalts (Georoc database). The soils are depleted in the mobile elements (further away from L in Figure 8) compared to the basaltic rocks. These results can be explained by loss of these labile elements during weathering and as a result, Al_2O_3 and FeO_T become relatively enriched.

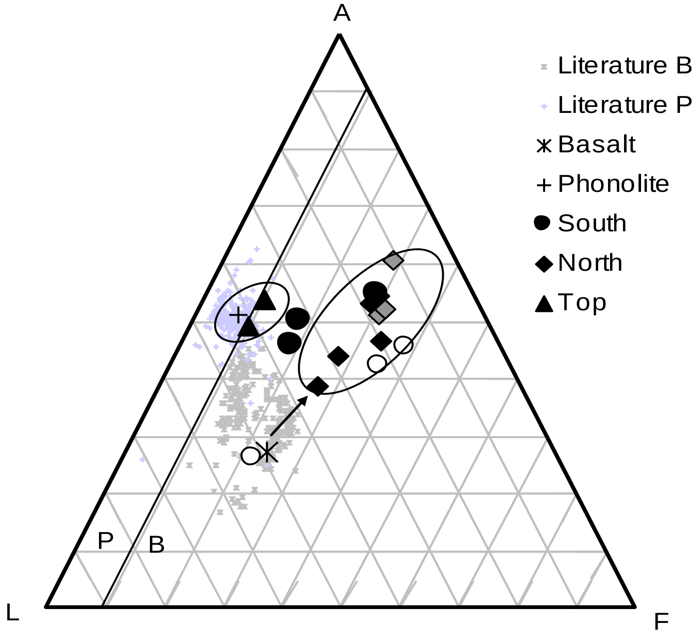


Figure 8: Ternary diagram for soils and rocks from Tenerife. A: Al_2O_3. L: labile (CaO + Na_2O + K_2O+MgO). F: FeO_T. Arrow indicates expected effect of weathering. Literature P=phonolite, B=Basalt, data from Georoc . Black symbols: natural soils. White and grey symbols: agricultural soils.

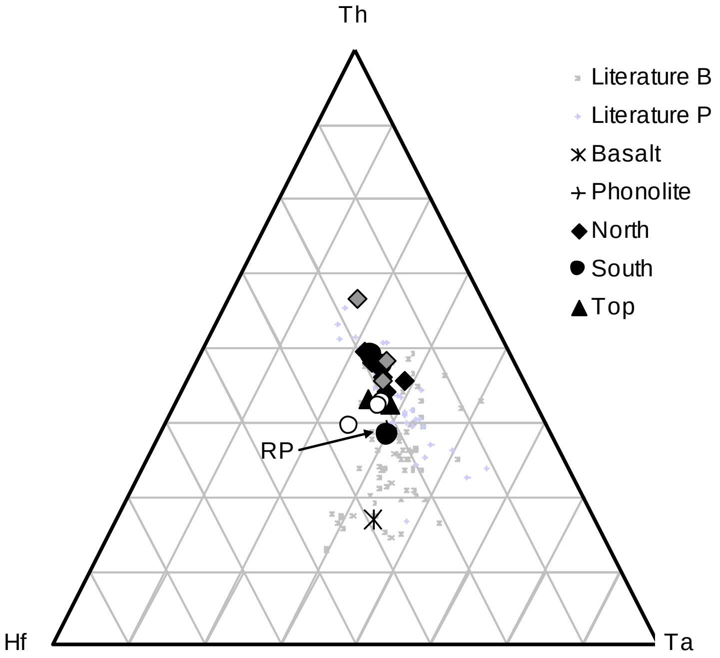
Due to this mobility issues, relatively immobile elements, which are not affected by secondary processes, are widely used in geochemical studies in order to determine the parental material (Kimura and Swindale, 1967; Pearce and Can, 1973; Wood, 1979; Hill et al., 2000). Elements considered as immobile include Al, Sc, Ti, Ga, Y, Zr, Nb, Ce, Hf, Ta, Th, Fe and the rare earth elements. The basic assumption of the immobile behaviour of some elements is point of discussion (Cornu et al., 1999; Price et al., 1999; Hill et al., 2000; Kurtz et al., 2000; Hodson et al., 2002). However, in a geological context components with extremely low aqueous solubility will not be significantly mobilized. Although the total quantity of immobile elements is unaffected, their concentrations change due to secondary processes, such as the loss of mobile elements or the addition of organic matter. Therefore, their relative abundance rather than their concentrations should be considered. For that reason, either elemental ratios or ternary diagrams are commonly used to determine the origin of weathered materials.

Wood et al (1979) used a triangular diagram of Th-Hf-Ta to distinguish basalts from different volcanic settings. The basalt and phonolite rock samples collected in this study plot separately (Figure 9A). However, literature values for basalts and phonolites show significant variation and overlap in this diagram (Georoc database). Therefore, this approach is not suitable for parental rock determination on Tenerife Island. Nevertheless, the graph shows that the soils fall within the rock field based on literature values and that as a result indeed basaltic and phonolitic rock are the parent materials. This is also confirmed with the observed La/Yb ratios (Table 2) which fall within the range previously determined for volcanic rocks from Tenerife (Georoc database). This indicates that the soils are, as expected, formed from local volcanics and that the deviation from the basaltic field in the ALF ternary diagram (Figure 8) indeed should be caused by weathering.

The Ti-Zr-Y diagram (Pearce and Cann, 1973; Hill et al., 2000) does show different groups for phonolite and basalt. It can be observed that the top samples plot within the phonolite group (Figure 9B). Most soils from the southern flank plot in the zone where both phonolitic and basaltic samples occur, except the one from the banana plantage which falls within the basaltic field. The samples from the northern side of the island plot close to each other, but are depleted in Y and Ti compared to the basaltic rock field. Although Y and Ti are often assumed to be relatively immobile, previous works show that they can be mobilized during weathering (Cornu et al., 1999; Price et al., 1999; Hill et al., 2000; Kurtz et al., 2000; Hodson et al., 2002). If Y and Ti are mobilized during the weathering process while Zr is retained within the soil, the Y/Zr and Ti/Zr should decrease with increasing weathering. In order to investigate this feature in more detail, both ratios were compared to the CIA, which is an indicator for the chemical alteration (Section 4.3 and 5.2). Indeed the Y/Zr and Ti/Zr ratio in general decreases with increasing CIA at the north side of the volcano (Figure 10). The non-basaltic samples do not follow the same trend. This suggests that Y and Ti are not controlled by parental material characteristics only, but are slightly mobilized during weathering. Moreover, it confirms that Zr is retained within the soil and therefore suitable for normalization purposes.

Kimura and Swindale (1967) used Zr and Ni data in order to distinguish the parental rock for volcanic soils from Hawaii, plotting a so-called discrimination function (Zr-1.44Ni) against Zr concentration. Based on this distinction, phonolites and basalts can be discriminated. Also the soils can be divided in two groups using this approach (Figure 11). The soils from the northern flank and the southern samples from close to the coast have a basaltic parental material signature. The soils from the top and the southern flank at altitudes above 1000 m have a phonolitic parental material signature. This corresponds with the geological knowledge that at the southern side where acid materials occur on the surface which cover basaltic formations (Tejedor et al., 2007).

A:



B:

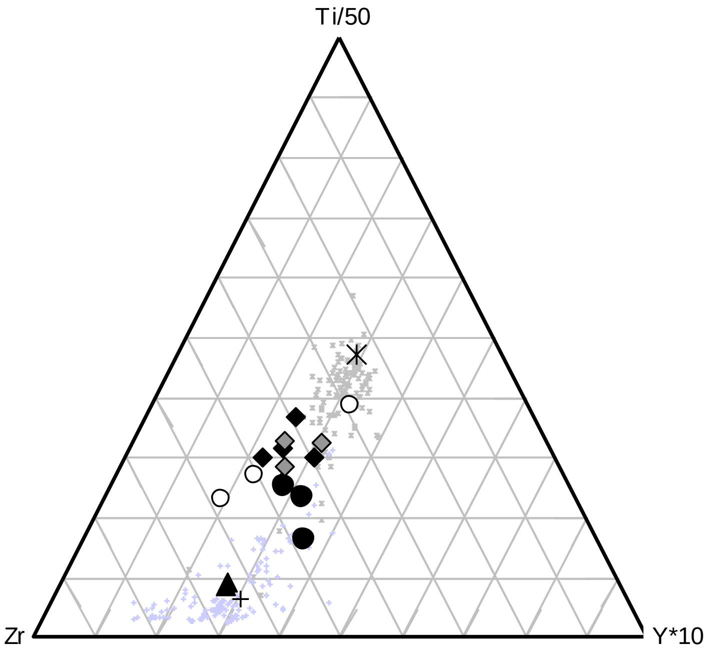


Figure 9: Ternary diagrams often used for parental material determination in weathered material. A: Th-Hf-Ta diagram. B: Ti-Zr-Y ternary diagram. Literature P=phonolite, B=Basalt, data from Georoc. Black symbols: natural soils. White and grey symbols: agricultural soils. RP with arrow indicates phonolite rock.

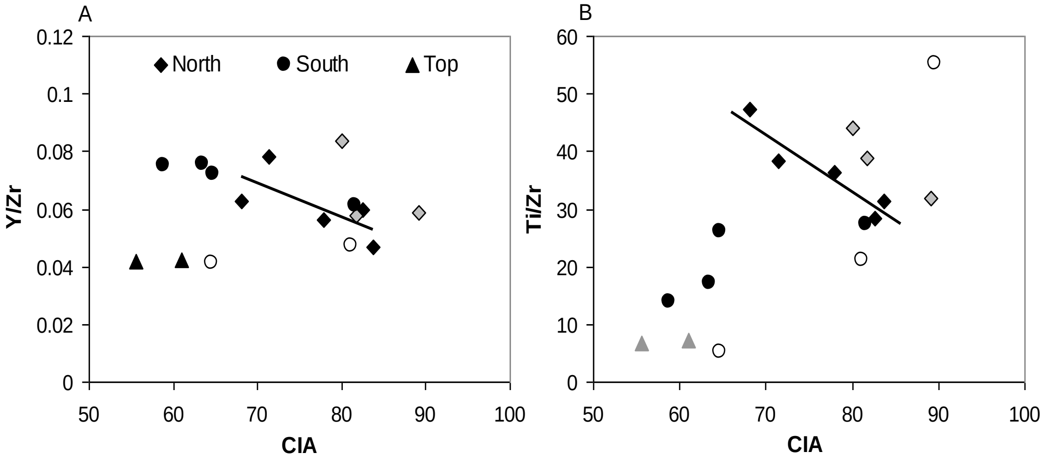


Figure 10: A: Y/Zr and B: Ti/Zr versus CIA for soils from Tenerife. Straight line show tendency for non-agricultural sources from northern flank. Black symbols: natural soils. White and grey symbols: agricultural soils.

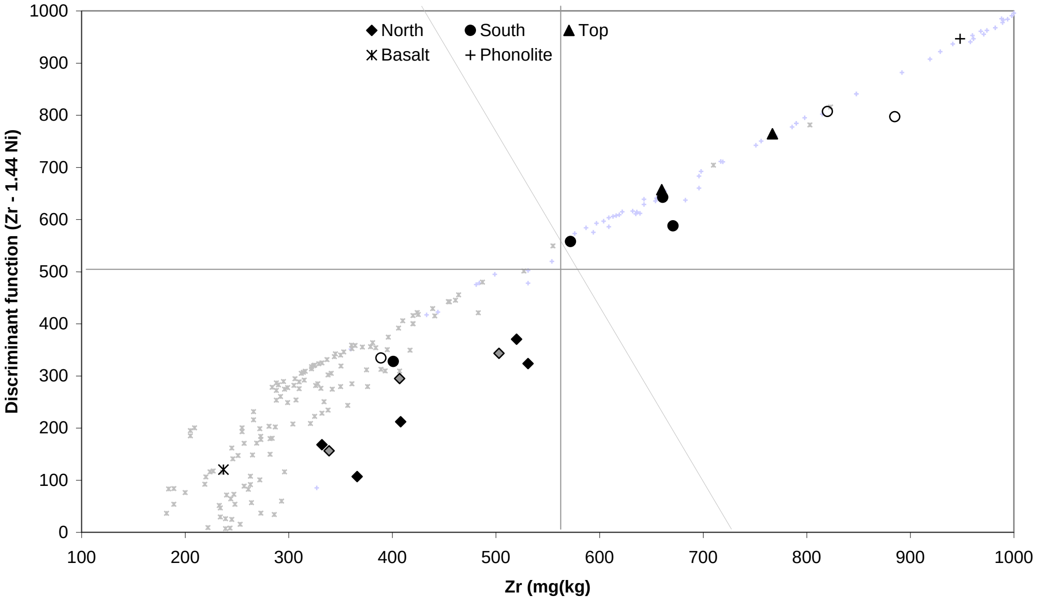


Figure 11: Discriminant function (Zr – 1.44 Ni) against total Zr concentration in soils and unweathered rocks. Black symbols: natural soils. White and grey symbols: agricultural soils.

In general it is assumed that parental materials are homogenous at the scale of a volcanic island like Tenerife. However, in all the graphical representations used in the discussion above, the trace element signatures displayed significant variation even within one rock-type. Some of the extreme values might be caused by weathering. However, also the literature data for rock samples that show little evidence of weathering (those with CIA<50) have significant compositional differences. Moreover, parameters which are expected not to be significantly influenced by weathering (e.g. La/Yb) show high variations within one rock type. These observations mean that parental rock is likely to be highly heterogeneous in trace element composition.

Nevertheless, in summary the soils can be divided in three main groups with different parental rock characteristics:

1) The top samples plot in the phonolite field
2) The samples from the southern flank collected at an altitude above 1000 meter plot in the phonolitic field or between the basaltic and phonolitic field.
3) The samples from the northern side and the southern samples from < 1000 m have basaltic characteristics.

In order to investigate how these parental material variations affect the Se behaviour, the Se content was compared for these three groups. However, as for immobile elements, secondary processes within the soil will change the Se concentration. To correct for this, a common approach is the normalization to the concentration of an ´immobile´ element (Kurtz et al, 2000; Huh et al, 2004). In this study, zirconium (Zr) is used as immobile normalization element. The Ti-Zr-Y ternary diagram (Figure 9B) showed that Zr was retained within the soils. Moreover, similar patterns were observed using hafnium (Hf) or thorium (Th), suggesting that all three can be considered to have an immobile behaviour within the soils from Tenerife.

In the soils with basaltic parental material a wide range of Se contents and mobility is observed (Figure 12). The Se contents within the volcanic rocks are poorly constrained and therefore it is unknown how parental rock variations impact the initial Se concentrations. Nevertheless, there is no correlation between Se content and rock parameters expected to change during magmatic fractionation, but not during weathering (e.g. La/Yb or the discriminant function as used in Figure 8). This suggests that parental rock variations are not the main controlling mechanism for the Se behaviour in soils from Tenerife. The soils with the phonolitic rock as parental material have relatively low Se contents and relatively high Se mobility (Figure 12). The intermediate rocks have both low Se contents and mobility. Therefore, it seems that the Se behaviour is more constant soils derived from phonolitic and intermediate rocks compared to the soils with basaltic parental material. However, they include less soil samples than the basaltic group. Moreover, the soil samples derived from phonolotic rocks have similar weathering regimes, while the basaltic rocks are exposed to contrasting climatic conditions (Table 1, Section 5.2).

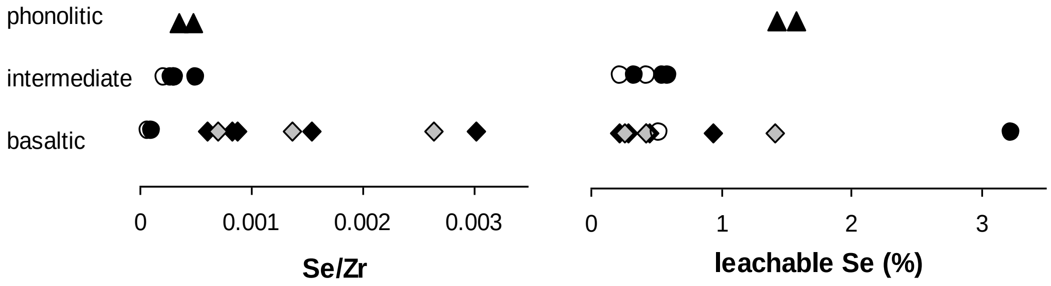


Figure 12: normalized Se content (Se/Zr) and exchangeable Se (%) for the soils divided in three groups based on parental material. Black symbols: natural soils. White and grey symbols: agricultural soils.

5.2 Effect of weathering

Weathering is an extremely important process that controls soil formation, element cycles and nutrients release (Chesworth et al., 2004). The very strong climatic gradient on Tenerife Island causing a large range of weathering regimes was a key point in favour for the selection of this study site to improve the understanding of weathering effects on the chemical fate of Se. As shown in Section 4.2, the CIA varied widely within the collected soils (Figure 6). The observed differences in CIA can be explained by climate differences. The increase in CIA between a distance of 0 and 10 km (expressed as distance from the most north-eastern sample) is caused by more precipitation that enhances the weathering of the soil. Afterwards the CIA decreased with altitude, due to the lower temperature (average annual soil temperature 5.1°C at 3345m compared to 24.4°C at 60m at the northern flank, Rodriguez 2010). At the southwestern coast the climate is desert-like and as a result weathering is low. At 1100 meter at the south flank the weathering is high, but decreases with increasing altitudes. The two phonolitic samples from high altitudes have very similar CIA, due to their proximity. In general, agricultural soils had similar or higher CIAs compared natural soils. Especially the banana plantage soil (south) was highly weathered. One exception is present which can be explained by surface mulching (Hernández-Moreno et al., 2007), causing a lower CIA of the soil-pumice mixture compared to the natural soil due to the low weathering of the pumice pyroclasts. The correspondence between the CIA and expected weathering based on climatic conditions, suggests that the CIA is a suitable proxy to investigate the effect of weathering in this study.

Lithium isotopes can be used to further constrain weathering processes. However, as can be seen in Figure 13, there was no direct relationship between the CIA index and Li isotopes. Moreover, some soils had δ^7Li above the basalt rock, while weathering would decrease the ^{7}Li/^{6}Li ratio due to the preferential uptake of ^{6}Li into secondary minerals (Pistiner and Henderson, 2003; Kisakürek et al., 2004; Pogge von Standmann et al., 2006; Vigier et al., 2009). The phonolite had a lower δ^7Li value (+1.5 ‰) compared to the basalt (+4.9 ‰). It has been demonstrated that there is a lack of per mil-level Li isotope fractionation as a result of crystal–liquid fractionation at temperatures greater than 1050°C (Tomascak et al., 1999). The isotopic differences could be explained by the fact that phonolites have more phenocrysts (Wolff et al., 2000), which can lower the δ^7Li value (Parkinson et al., 2007). Moreover, the rock is slightly weathered, as confirmed by the CIA of 56 (compared to 45 for the basalt), which would also decrease the δ^7Li. However, these processes cannot explain the δ^7Li enrichment measured in the soils compared to these bedrocks. Thus, if the range of δ^7Li values in our soil samples cannot be explained at the first order either by source effect (variation of the parental material) or by weathering effects, it means that external input of lithium has to be considered. This point is discussed in the next section. It implies that CIA rather than δ^7Li is the proper parameter to investigate the role of weathering and climate on the Se behaviour.

In order to investigate the effect of weathering on the Se behaviour, the relationship between the CIA and Se was studied. The normalized Se content (Se/Zr) and exchangeable Se had a low correlation with CIA with a R^2 of respectively 0.18 and 0.21. Nevertheless, some tendencies were observed between total Se concentrations and the CIA. The soils from the top and the southern flank with more phonolitic parental material had relatively low Se contents and low CIA. The Se enriched soils were highly weathered (Figure 14). To eliminate significant variations in parental material, only soils with basaltic parental materials could be considered. Although these soils are exposed to contrasting weathering regimes, also within this group no clear trends were observed. Given the lack of general tendencies, it can be concluded that weathering is not the primary controlling process in Se contents or mobility.

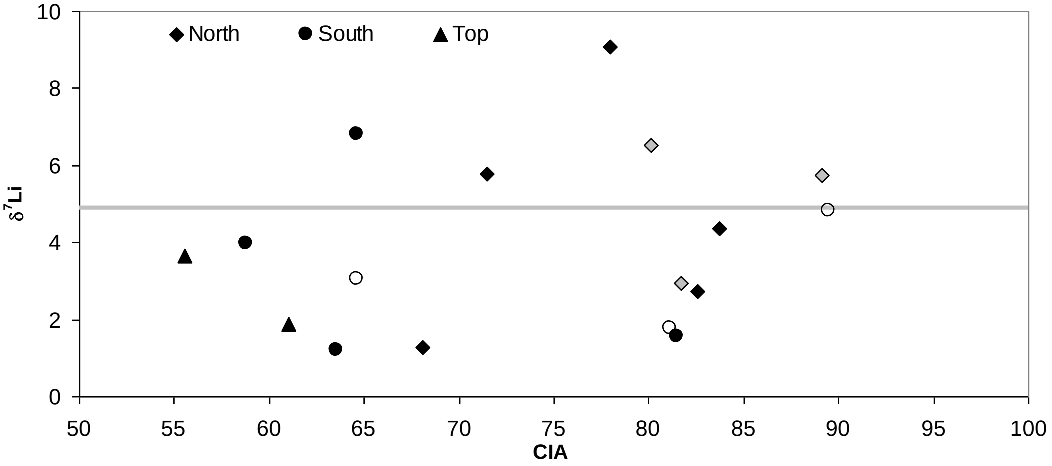


Figure 13: δ^7Li (‰) versus CIA. Black symbols: natural soils. White and grey symbols: agricultural soils.

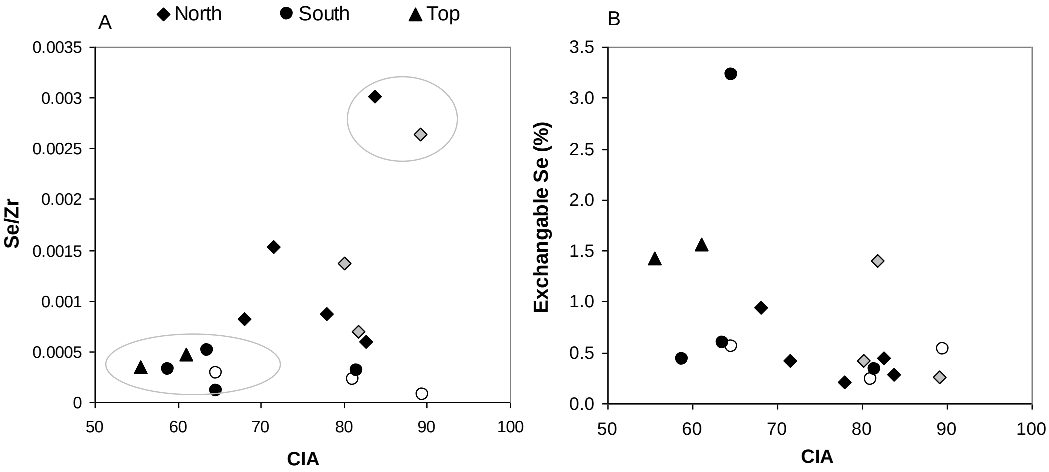


Figure 14: Total (A) and exchangeable (B) Se versus the chemical index of alteration (CIA). Black symbols: natural soils. White and grey symbols: agricultural soils.

5.3 Aerosol input

Lithium isotope signatures (Figure 13) suggested the input of external material. Published work has shown the importance of Saharan dust events in the Canary Archipelago (Mizota and Matsuhisa, 1995; Viana et al., 2002; Alastuey et al., 2005; Kandler et al., 2007). X-Ray Diffraction analyses of the collected soils indicated the presence of quartz in many samples. Since there is an absence of quartz in the parent volcanic materials throughout Tenerife Island, this mineral probably comes via eolian transport from the windward Saharan desert (Mizota and Matsuhisa, 1995). The mineralogical data also support the importance of the input of marine aerosols, since halite has been detected in the most southwestern sample. However, it is currently unknown how this external input could impact the Se within the soils and if this can overprint the signal caused by weathering.

Isotopic tracers are useful tools in order to investigate potential input sources. In this light, Sr isotopes are especially helpful since natural mass fractionation effects are negligible. As a result isotope ratios only reflect the relative contributions of Sr from isotopically distinct sources (Mizota and Matsuhisa, 1995; Capo and Chadwick, 1999; Vitousek et al., 1999; Whipkey et al., 2000; Stewart et al., 2001). To evaluate the main controls on the Sr isotopic composition the ^{87}Sr/^{86}Sr is shown in relation to Sr content (expressed as Sr/Zr) for a number of selected soil samples (Figure 15). The variation in Sr/Zr in phonolites (Sr/Zr is 0.46±1.57; 1σ, n=218, Georoc database) and basalts (Sr/Zr is 3.02±1.46; 1σ, n=174, Georoc database) are high. The ^{87}Sr/^{86}Sr ratio has been shown to be around 0.7032 in the volcanic rocks along the Canary Islands (Mizota and Matsuhisa, 1995), which is closed to the values measured in the basalt and phonolite sample collected for this study (0.70325 and 0.70367 respectively; Table 1). Saharan dust has a similar Sr/Zr ratio as the parent rocks (Sr/Zr=0.7±0.52; 1σ, n=9; Moreno et al., 2006), but is significantly more radiogenic (^{87}Sr/^{86}Sr = 0.718±0.003, Mizota and Matsuhisa, 1995). Seawater has a high Sr/Zr and a slightly higher ^{87}Sr/^{86}Sr ratio (0.7092; Dia et al., 1992). During weathering Sr will be mobilized and as a result the Sr/Zr ratio will decrease. However, the Sr isotope ratio will remain similar.

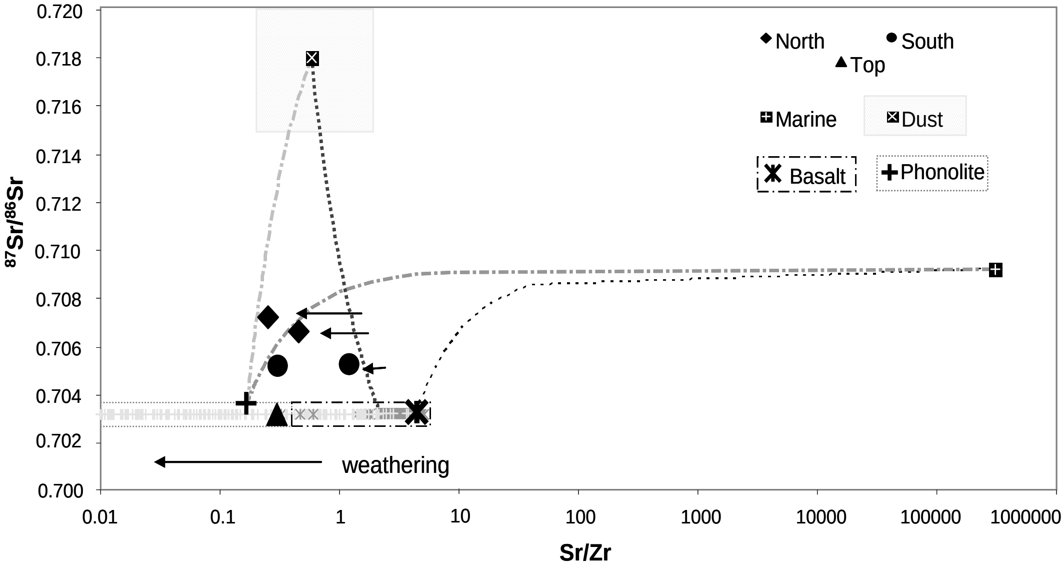


Figure 15: Sr isotopes versus Sr/Zr in the fine-earth fraction (<2mm) for some selected soils. The Sr isotope and Sr/Zr ratio of basalt and phonolite (Georoc; Mizota and Matsuhisa, 1995), marine aerosols (Dia et al., 2002) and Saharan dust (Mizota and Matsuhisa, 1995; Moreno et al., 2006) and their mixing lines are shown. Small grey symbols indicate literature values (Georoc database).

Assuming that the soils with a basaltic parental material were derived from a chemically similar basalt as sampled within this study, the Sr signature could be explained by a combination of Saharan dust input and weathering. This corresponds with the patterns observed in the CIA. The higher the CIA, the more distance from the mixing line between Saharan dust and basalt, indicating more weathering (indicated by arrows in the graph). However, since some basaltic rocks have a lower Sr/Zr ratio (Georoc database) and the Sr/Zr ratio in the parental rock for each location is unknown, it is impossible to distinguish between parental material variations and weathering effects. Previous work showed that both the marine source and the eolian dust input strongly depend on precipitation (Mizota and Matsuhisa, 1995; Vitousek et al., 1999; Stewart et al., 2001; Huh et al., 2004). This corresponds with our observations. The sample collected in the condensation zone with high precipitation (800 mm a year and a similar amount due to condensation) had the highest $^{87}Sr/^{86}Sr$ ratio. The sample collected at the south with low precipitation rate (100 mm) had a lower $^{87}Sr/^{86}Sr$ ratio. For the sample with intermediate composition the controlling processes on Sr are not clear. Variation in the parental rock, marine aerosols and Saharan dust input and weathering could all take place. Although Saharan dust input is needed to explain the Sr characteristics, the marine aerosol input cannot be proven with only Sr isotopes tracing.

Therefore, Li isotopes were used as an additional isotopic tracer. The interpretation of Li isotopes is more complicated, since the δ^7Li values are a function of both sources and weathering processes. Moreover, the isotopic signatures of the endmembers are less well constrained for lithium. For Tenerife rocks only the data from this study were available. Moreover, no data are published for the Li isotopic signature of Saharan dust. Nevertheless, I expect the signature of Saharan dust will be similar to upper continental crust (UCC) which has an average Li concentration of 22 mg/kg (Wedepohl, 1995) and a δ^7Li of 0 ± 2‰ (Teng et al., 2004). Geochemical data from eolian mineral particles from the Sahara-Sahel dust corridor show that indeed on average the Li concentration is close to the UCC. However, significant variations occur depending on the exact source area (Moreno et al., 2006).

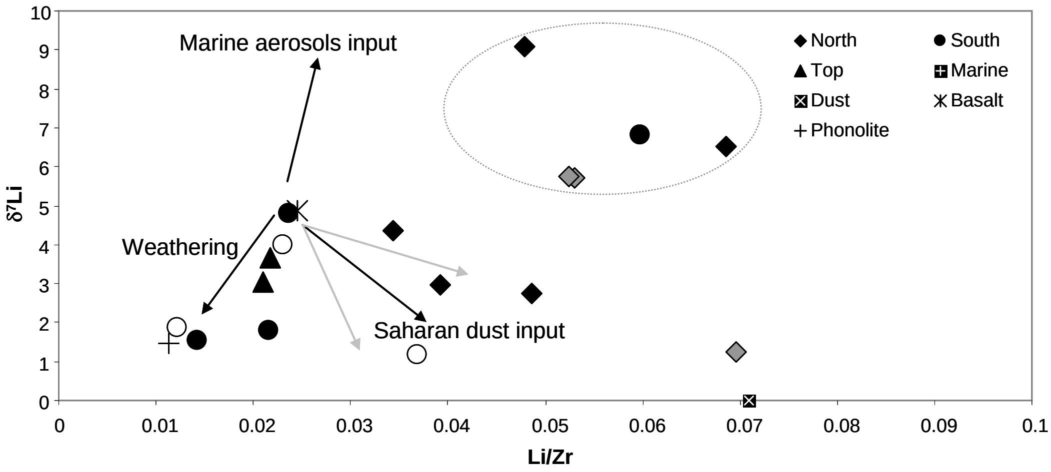


Figure 16: Li isotopes versus Li/Zr for soils and rocks and effect of different processes. Black symbols: natural soils. White and grey symbols: agricultural soils. Circle indicates soil samples for which a marine aerosol is needed to explain the Li characteristics.

All the soils samples from the northern flank and the most southwestern sample had higher δ^{7}Li than expected based on a mixing between basaltic rock and Saharan dust (Figure 16). This would indicate a ^{7}Li-rich source such as marine aerosols (δ^{7}Li = 31‰ for seawater (Millot et al., 2004)). A part of this could be explained by poor constraints on the Li concentration of the different sources, especially for the Saharan dust endmember. Nevertheless, for the four samples closest to the coast at the northern flank and the most southwestern sample (in which halite was also observed) clearly the input of marine aerosols is needed to explain the Li isotopic signatures (circle, Figure 16). For the other samples of the northern flank it seems that Saharan dust input could play a role in the Li characteristics. However, due to the poor constrains on the Saharan dust end member, the input of marine aerosols cannot be excluded. The input of Li derived from marine aerosols and continental dust has already been evidenced on the volcanic islands of Hawaii (Stewart et al., 2001; Huh et al., 2004).

Finally, in Figure 17, Li and Sr isotopic compositions are compared and the different mixing lines between all known sources that can contribute to the Li and Sr budget in the soil samples under consideration are indicated. Unfortunately, even using the combination of these two isotopic tracers, the effect of each process and specifically the contribution of each endmember cannot be precisely estimated. This is mainly due to the fact that the Saharan dust endmember is too poorly constrained for both Sr-Li elemental concentrations and isotopic signatures. The signatures of other endmembers are better known. Nevertheless, as discussed above, the elemental composition of the bedrock might also vary. For example, the average Sr concentrations of basaltic rocks is 821±250 (1σ, n=75, CIA≤50). If variations occur in the definition of the endmembers, consequently, an infinite number of mixing lines can be drawn.

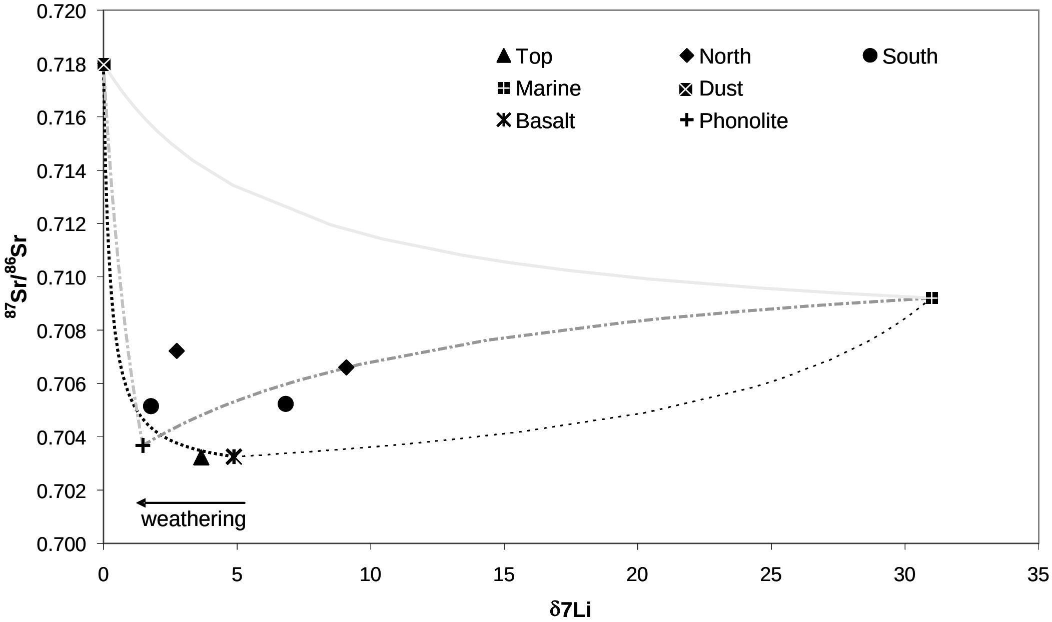


Figure 17: Sr isotopic compositions (^{87}Sr/^{86}Sr) plotted as a function of Li isotopic compositions (δ^7Li, ‰).

From a general point of view, this graph shows that the Sr and Li isotopic compositions result from a combination of local effects such as parental rock composition (some soils samples agree well with the $^{87}Sr/^{86}Sr$ values of the different bed rocks) and weathering processes (some samples display lower δ^7Li compared to the bedrocks), but confirms that the contribution of external inputs is clearly needed in order to explain the whole range of variation for both Sr and Li isotopes. Moreover, it can be observed that the soils plot in between the endmembers, which suggest that all processes affecting the Li and Sr isotopic signatures are characterized by the contribution of these endmembers.

In order to constrain the impact of marine aerosols and Saharan dust input on the Se behaviour, the Li and Sr isotopic signatures against Se/Zr and leachable Se are given in Figure 18. There seems no correlation between δ^7Li and Se contents (18A) or exchangeable Se (18C). This is probably related to the low Se concentration in seawater (0.9 µg/L). Therefore, marine aerosols inputs do not control the Se behaviour within the soils from Tenerife.

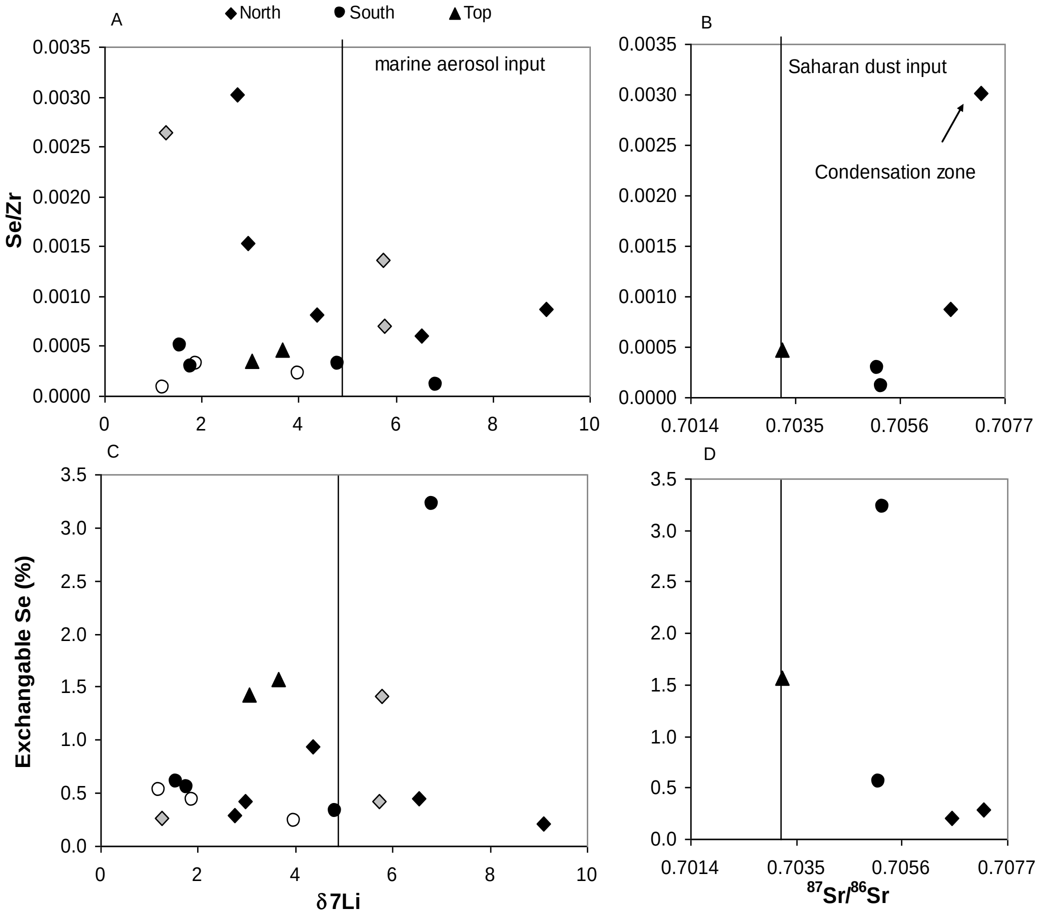


Figure 18: Lithium (A,C) and strontium (B,D) isotopic signatures versus total (A, B) and leachable (C,D) Se concentrations. Black symbols: natural soils. White and grey symbols: agricultural soils.

The highest Se enrichment is observed for the soil with the highest $^{87}Sr/^{86}Sr$ ratio located in the condensation zone. However, with the limited amount of data it is difficult to assess if this is a general tendency. Moreover, as discussed above, the eolian dust input strongly depends on precipitation, as does weathering. Therefore, the link between Se enrichment and Sr isotopic signatures could be explained by the dependence of both on climatic conditions rather than dust input controlling Se behaviour. Additionally, the Se content of Saharan dust is too poorly constrained. In summary, the effect of Saharan dust input on the Se distribution on Tenerife Island should be investigated in more detail. There is no relationship observed between the Sr isotopic signature and the exchangeable Se.

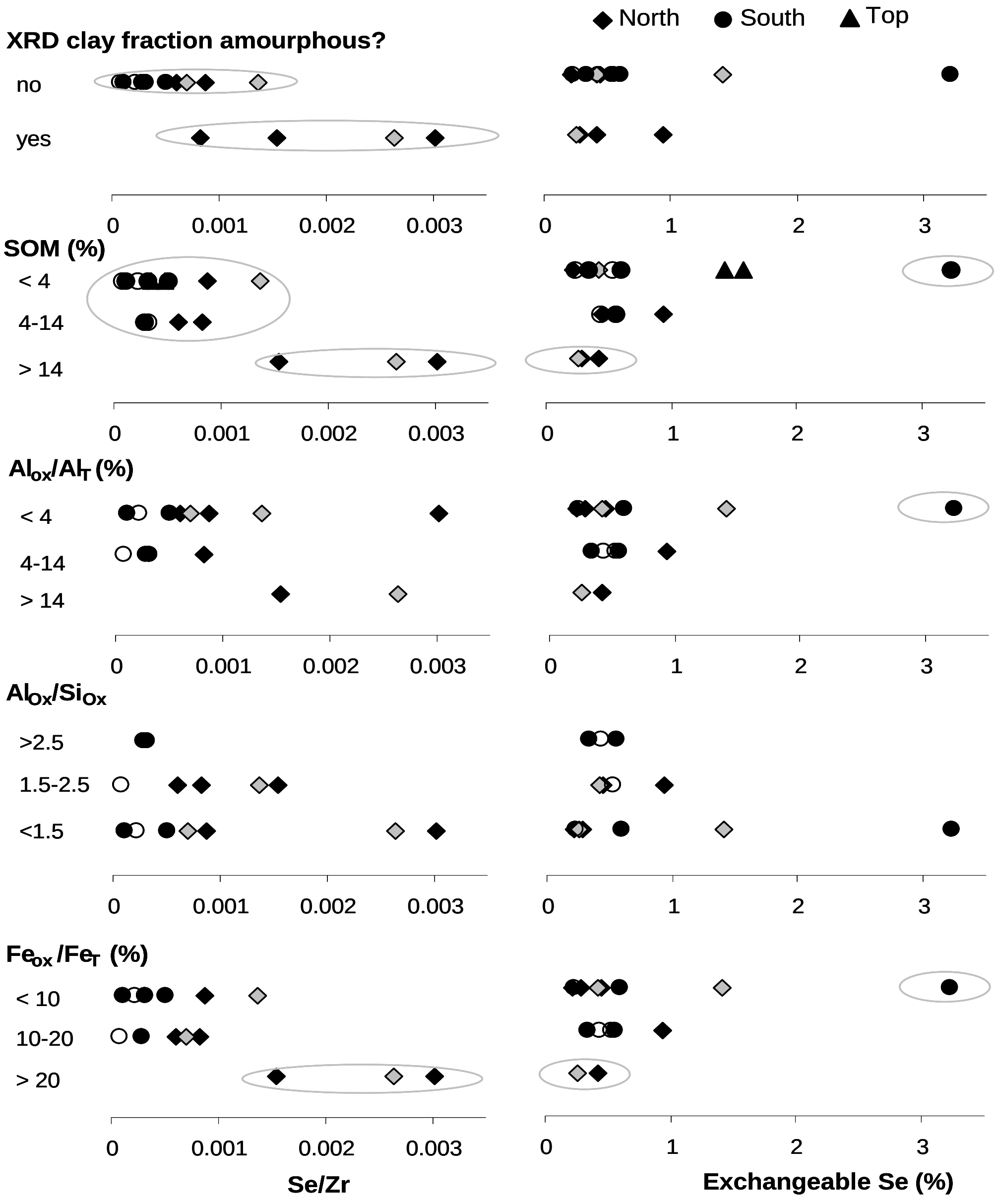


Figure 19: Potential adsorption phases versus Se/Zr and exchangeable Se. Black symbols: natural soils. White and grey symbols: agricultural soils.

5.4 Sorption processes

X-Ray Diffraction analyses revealed that the soils relatively enriched in Se had only amorphous compounds in the clay fraction. Previous works recognized amorphous Fe and Al minerals as important carriers for Se, which significantly affect the Se contents and mobility (Ballistrie and Chao, 1990; Duc et al., 2003; Fernández-Martínez and Charlet, 2009). Moreover, SOM has been reported to influence the behaviour of Se and the formation of Al phases (Gustafsson and Johnsson, 1992; Wang and Mulligan, 2006). In order to investigate the role of sorption processes on the behaviour of Se, the Se content and mobility was compared for groups with differences in SOM and Al and Fe phases (based on oxalate extractable and total concentrations). In Figure 19 it can be observed that the soils relatively enriched in Se reflected in high Se/Zr ratios have high percentages of SOM (>14%) and amorphous Fe phases (Fe_{ox}/Fe_T > 20 %). These soils have relatively low exchangeable Se. The soils with higher Se mobility (>1%) all have low percentages of SOM and amorphous Fe. This corresponds with sorption processes on SOM and/or amorphous Fe compounds in which Se is retained in the soil. As a result, Se contents are high and the mobility is low. In contrast, there seems to be no correlation between the Se content and amorphous Al phases. Firstly, a soil with high Se content has a low percentage of amorphous Al (Al_{ox}/Al_T < 4 %). Secondly, there is no link between the Al_{ox}/Si_{ox} ratio and the Se content and exchangeable Se. For example, soil samples with a Al_{ox}/Si_{ox} ratio below 1.5 show a wide range of both Se enrichment and Se mobility (Tables 1 and 2).

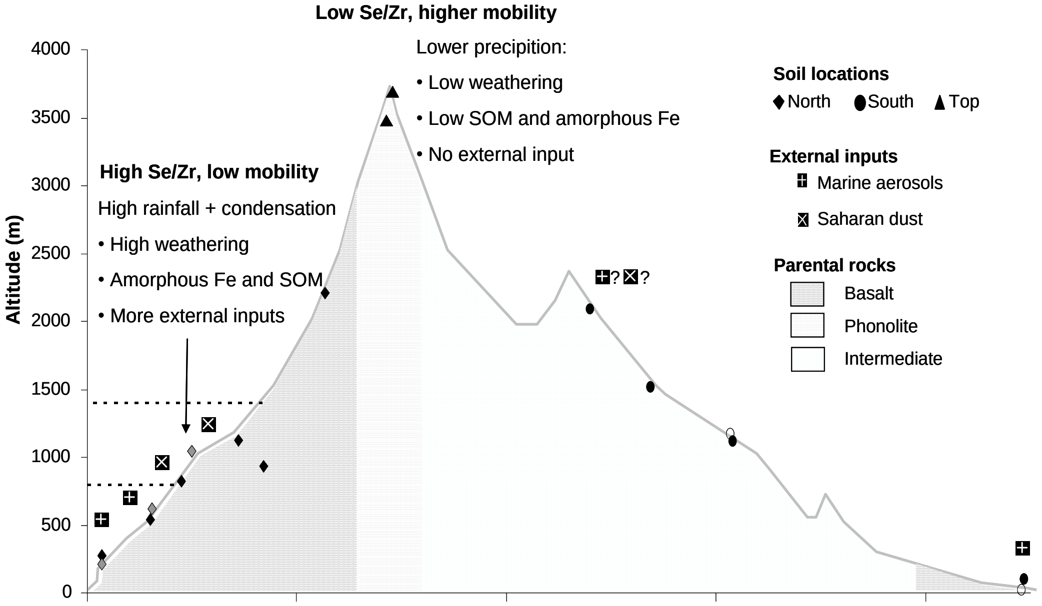


Figure 20: Summary of the main results. Black symbols: natural soils. White and grey symbols: agricultural soils.

In Section 4.1 it was observed that the soil enriched in Se are at the north side of the Island and especially those in the condensation zone (800-1400 m) with high precipitation. The preferential formation of non-crystalline materials strongly depends on the weathering and the climate. Rapid weathering releases elements faster than crystalline minerals can form and as a result metastable amorphous compounds with rapid precipitation kinetics will be favourable. Therefore, the mineralogical composition of the colloidal fraction of soils strongly depends on the post-depositional weathering environment such as soil temperature, rainfall and leaching and organic matter accumulation (Parfitt et al., 1983; Shoji et al., 1993). Since sorption processes on these materials seem to be the key control in the Se behaviour within the soils, weathering and climate indirectly play a role. The controlling mechanisms are summarized in Figure 20.

5.5 Comparison with As

In Section 4.3 it was observed that Se behaves differently from other OHA elements. The As enrichments versus the CIA is given in Figure 21. The samples from the top and the southern flank, having a more phonolitic composition, show lower As enrichments compared to the basaltic samples from the northern flank. However, there is some correlation between the CIA and As enrichment on the island (R^2= 0.57). At the northern side of the island, where parental material is relatively uniform (Section 5.1) and the climatic gradient high, the correlation is better (R^2=0.66).

These results suggest that a combination of bedrock differences and weathering processes can explain the general spatial distribution of As soil content in Tenerife. In the case of Se, no direct correlation between Se contents and weathering is observed. However, there was a link between the formation of secondary amorphous phases and Se enrichment. In contrast for As no enrichment is observed for the sample were no crystalline minerals were detected in the clay fraction (* in Figure 21). This clearly demonstrates the contrasting controlling processes for As and Se behaviour in the soils from Tenerife.

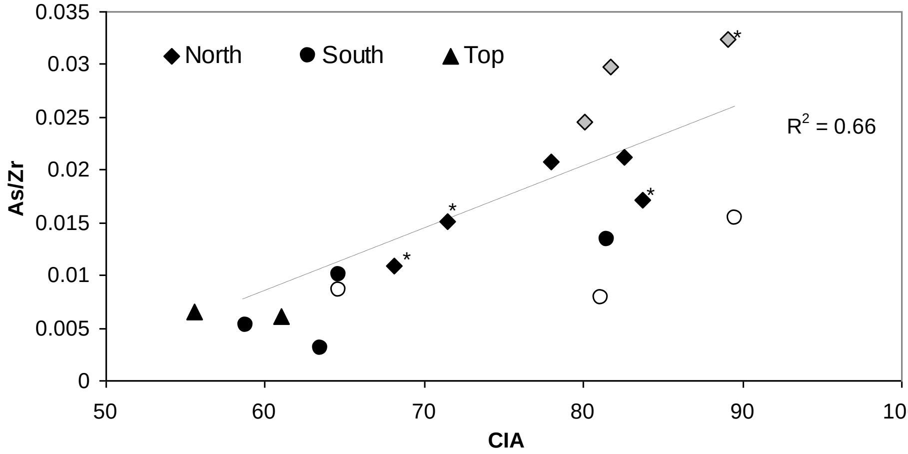


Figure 21: *As enrichment (As/Zr) versus the chemical index of weathering (CIA). The general trend for soil samples from the northern side of the island is given. * are samples with amorphous clay fraction (XRD analyses). Black symbols: natural soils. White and grey symbols: agricultural soils.*

6 Conclusions

I investigated the Se content and mobility within volcanic soils from Tenerife. Selenium contents vary between 0.03 and 1.23 mg/kg and are comparable to the worldwide soil average. Between 0.2 and 3.2% of this Se is exchangeable.

The collected soils have a wide range of weathering stages with CIAs between 55 and 90. However, there is no correlation between Se and CIA, suggesting that weathering is not the main controlling processes for the Se distribution. This is remarkable, since Tenerife was selected because of its strong climatic gradient. Nevertheless, even in this system with a wide range of climatic conditions, the effect of weathering could not be assessed using topsoils from along the island. Therefore, a number of other processes were constrained that might control Se behaviour.

Although in soil studies on Tenerife the parental material is often assumed to be uniform, a detailed investigation of published data indicates that there is a range of trace element characteristics in the volcanic rocks from Tenerife. Based on several immobile elements, the parental materials of the soils can be divided in three groups: basalts, phonolites and intermediate rocks. Nevertheless, differences in parental material do not play an important role in the chemical fate of Se, since the Se contents and mobility vary within the soils formed from basaltic materials alone.

Strontium isotopic signatures and the presence of quartz minerals clearly indicate the input of Saharan dust to the soils. Lithium isotopes also show an important contribution of marine aerosols for the samples close to the ocean. The presence of halite is one of the soil samples also support this result. However, there is no evidence that these contributions affect the Se distribution within the island.

It was found that sorption processes play a key role in the Se behaviour. Soils rich in amorphous Fe compounds and SOM have a higher Se enrichment, but in contrast low exchangeable Se. Since the formation of these compounds strongly depends on climatic conditions and weathering regime, the weathering has an indirect impact on Se behaviour.

The behaviour of Se is often compared to As and other oxy-anion forming elements. However, different distributions were observed for the two elements. The As enrichments could be to a large extent explained by the combination of weathering (based on the CIA) and parental rock differences (soils with basaltic parental material more enriched than those with phonolitic parental material). The assumption that these elements behave geochemically similar appears to be invalid within soils from the volcanic island of Tenerife.

In summary, two extreme Se behaviours could be recognized. At the top of Mount Teide low precipitation occurs and samples are characterized by low soil organic matter (SOM) and amorphous Fe compounds, low weathering and there is no evidence for external inputs. These soils have low Se contents with high mobility. In contrast, soils collected around 1000 m at the northern flank within the condensation zone have high levels of SOM, amorphous Fe compounds, significant input of external inputs and high weathering. These soils are characterized by high Se contents, but low geochemical mobility. This clearly demonstrates the importance of soil mineralogy and sorption processes in the Se behaviour within these soils.

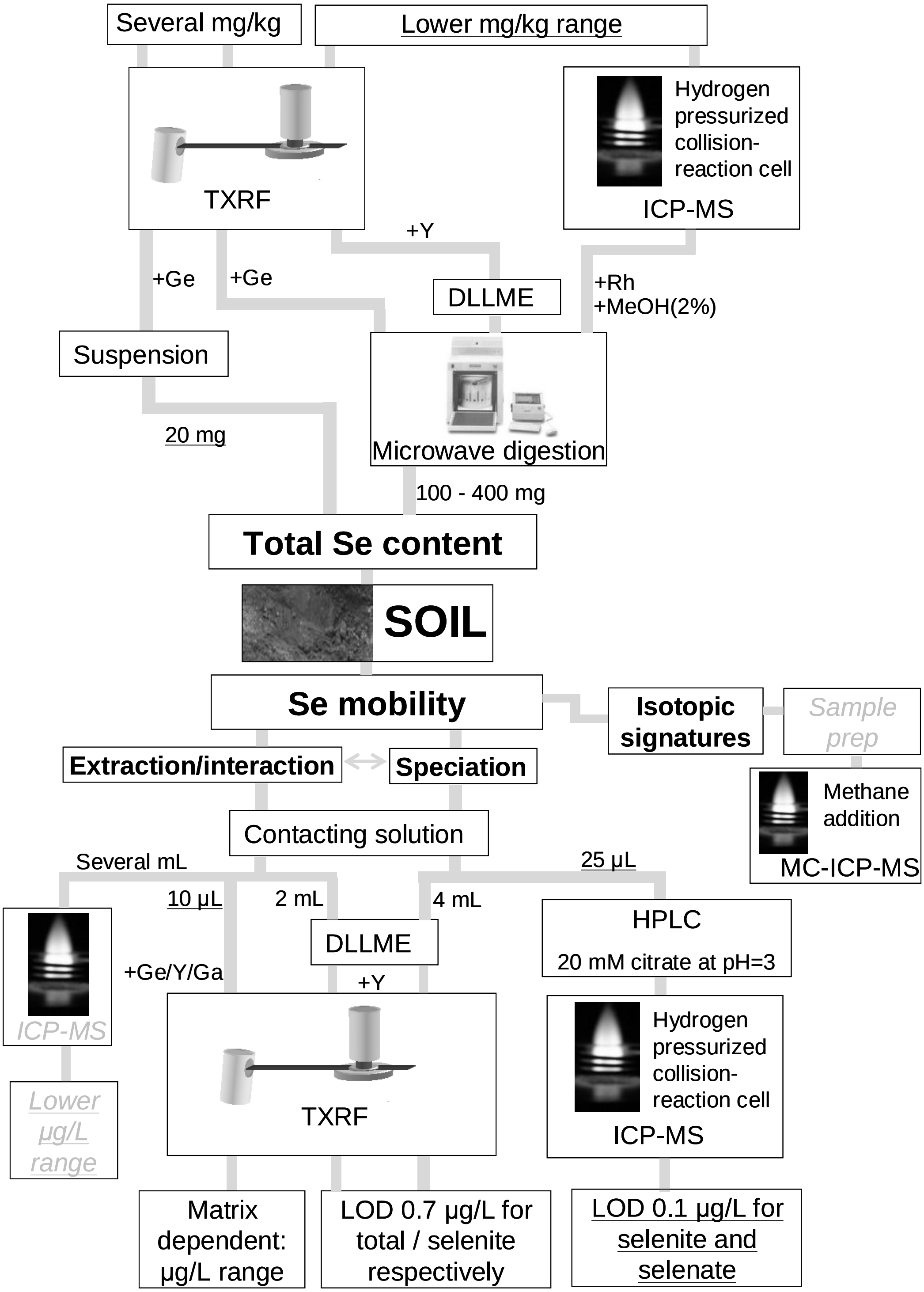
General discussion

1 Analytical considerations

Selenium (Se) determinations in geological samples are extremely challenging. In this thesis, different analytical tools were developed to precisely and accurately measure Se in complex geochemical matrices. Different methods are complementary and the best approach for a specific study strongly depends on both sample characteristics (concentration, matrix, sample volume available) and resources (equipment available in laboratory, analyses costs). Knowledge on analytical techniques is therefore central for the study of Se within Earth´s system. In order to determine the most appropriate analytical approach for specific samples, the limit of detection (LOD) and required sample volume need to be considered, as illustrated in Figure 1.

For the quantification of total Se in soils both Total Reflection X-ray Fluorescence (TXRF) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were used (Chapter 3). Direct analyses of soil suspensions by TXRF are rapid, cheap, provide multi-elemental information and require only 20 mg of soil. However, the LOD was in the mg/kg range, making this method only favorable for Se-enriched soils. Therefore, two other methodologies were presented with LODs relevant for environmental levels. Soil digest analyses by ICP-MS using a hydrogen-pressurized collision-reaction cell, methanol addition and $^{78}Se^{+}$ as monitoring isotope showed procedural blank values <0.03 mg/kg and accurate results. In this case a minimum of around 100 mg of solid powder is required. Nevertheless, for samples where the sample mass is not a critical issue, as the case for soils, 400 mg was used. A dispersive liquid-liquid micro-extraction (DLLME) of a soil digest prior to TXRF analyses which isolate the Se from the soil matrix revealed a LOD of 0.05 mg/kg, one order of magnitude below the average worldwide Se soil content. Since a standard addition approach is needed for quantification, in this case 400 mg soil powder is required. Compared to direct TXRF analyses, these methodologies are more time-consuming, since a digestion procedure is required.

To understand the Se mobility, two types of experiments can be performed: studies on the Se behavior during water-solid interaction and/or specific extractions to indentify the Se carrier. In these contact solutions, both total Se and Se speciation can be determined (Chapter 4). For total Se quantification of mass limited samples direct TXRF analyses are useful, since only 10 µL is needed and determinations are multi-elemental. However, the LOD strongly depends on the sample matrix and will be too high in more complex matrix for many environmental applications. Nevertheless, this approach is very suitable for lab controlled experiments of mass limited samples. Again the use of a DLLME procedure prior to TXRF measurements or ICP-MS determinations gave lower LODs, but several mLs of solution were necessary. For Se speciation analyses High Performance Liquid Chromatography (HPLC) coupled to ICP–MS revealed best sensitivity and required lowest sample volume. However, since HPLC-ICP-MS is an expensive methodology due to the high argon consumption during the chromatographic separation, a DLLME procedure combined with TXRF analyses



Underlined text: lowest limit of detection (LOD) or required sample volume

Cursive text: method not developed within this PhD thesis, but has been applied.

Figure 1: Overview of the analytical methodologies used within this dissertation.

provides an easy and cheap alternative to obtain inorganic Se speciation. Both methodologies are suitable for acidic samples rich in Fe and Al, since they are employed at low pH conditions, preventing Fe and Al precipitation.

Natural variations in Se isotopes are another tool to better understand Se mobility. Selenium isotopes participate to a slightly different extent in chemical reactions. In this dissertation improvements for the mass spectrometric analyses were investigated. It was showed that pseudo-high resolution cannot resolve argon polyatomic ions (Chapter 5). Potentially higher mass resolution will be available in the future, making this approach applicable to Se isotopic measurements. However, improvements for sensitivity will also be a major issue in this development, since high mass resolution is accompanied by a reduction in transmission efficiency and natural Se concentrations are low. Methane addition slightly increased Se sensitivity and decreased the intensities of interferences. As a result, the analyte-interference ratio is higher and the precision is improved three times. Precision is a key issue in Se isotope ratio measurements, taking into account that natural variations are low (few ‰). Therefore, the use of a methane-mixed plasma seems to be very useful in Se isotopic analysis which should be applied to standards and samples in the future. Additionally, other approaches to remove the Ar dimers should be explored. The use of a collision-reaction cell has been proven to be very successful in reducing the Ar dimers. However, only one manufacture develops multi collector ICP-MS machines equipped with this device. It is often assumed that a collision-reaction cell is not needed if the apparatus has the possibility of high resolution. Nevertheless, for Se isotopes it seems to be advantageous if multi collector-ICP-MS apparatus were also equipped with a collision-reaction cell. Although high mass resolution is straightforward and applicable to a wide range of elements, chemical resolution is a different and complementary approach.

Another reason that knowledge on analytical techniques is indispensible in Se geochemical studies is that analytical problems strongly affect the accuracy of the obtained data. The presence of a spectral interference or the use of an inappropriate internal standard will lead to inaccurate concentrations, which can lead to misleading geochemical interpretations. The results presented in this thesis show that extreme care should be taken for the measurements of Se in complex samples due to the occurrence of numerous matrix effects. It was showed that using $^{82}Se^+$ in soil digestions in ICP-MS measurements without a ocotupole reaction system (ORS) will significantly overestimate the Se content, due to the formation with $^{1}H^{81}Br^+$ and $^{66}Zn^{16}O^+$ (Chapter 3). In TXRF analyses spectral overlap occurs between Br-K_α and Se-K_α peaks, lowering the LOD. Moreover, spectral interferences occurred between matrix elements (Zn) and internal standards (Ge, Ga), which hampered the fitting. Other matrix effects (non-spectral interferences) influence the sensitivity. For Se determinations by TXRF is was showed that the LOD decreased in more complex samples, because the general spectral background increased and high concentrations of some specific elements (Fe, Zn) could reduce the excitation current of the X-ray tube.

Chemical pretreatments can be used to remove matrix elements or to isolate Se from the matrix. In this dissertation a liquid-liquid micro-extraction (LLME) has been combined with TXRF analysis for the first time, which significantly improved the LOD.

The performance of other sample preparation techniques combined with TXRF analyses should also be evaluated. In this light, especially other types of LLME are promising sample treatments, taking into account the micro-analytical capability of TXRF spectrometry and the simplicity of these methods. Although previous works exist on other LLME for Se determinations (Figureroa et al., 2005; 2006; Xia et al., 2006; Bidari et al., 2008; Saleh et al., 2009), they have so far not been applied to complex geological matrices and/or combined with TXRF. In Se isotope studies new sample preparation techniques will be even more critical. Especially for volcanic environments where Se might be present in different redox states, simple approaches to convert all Se to selenite and remove matrix elements, will be essential. However, matrix effects are also expected in sample preparation. In this PhD thesis it was shown that the extraction efficiency of the used DDLME strongly depends on the sample matrix (Chapter 3 and 4). For soil leachates external calibration of Se standards could be used for Se quantification. However, for soil digestions the extraction efficiency was lower and therefore a standard-addition approach had to be used. This showed that the performance of chemical pretreatment should be evaluated separately for each matrix type.

Although a range of analytical tools for Se determinations in complex geological samples were developed, the advances of methods for Se determination in complex samples remains a major issue in order to improve the understanding of Se cycling in volcanic environments.

2 Geochemical studies

After development of the required analytical tools, two geochemical case studies were chosen. Etna volcano, located at Sicily (Italy), is the largest active volcano in Europe and has been persistently active over the past few thousand years, causing regular events of acid rain (Chapter 6). On Tenerife, one of the Canary Islands (Spain), strong gradients in climate and weathering processes have been reported (Chapter 7).

For the Mount Etna field site it was shown that acid rain – soil interaction can mobilize Se from the soils close to the crater towards the groundwater with potential consequences for the health of the population around the volcano (Chapter 6). Trace element deposition from the plume was excluded as the main process controlling the Se concentrations in soils or leachates. Since previous work demonstrated the influence of the volcanic emissions on rainwater and plant leaves, this shows the importance of soils as reactive interfaces. However, it should be investigated if plume deposition can also be excluded during increased volcanic activity and around other volcanoes. Previous work at Masaya volcano shows an influence of the volcanic activity on the soil pH (Parnell, 1986; Delmelle et al., 2003), which has not been detected in this study with Etnean soils. This could be explained by differences in parental material homogeneity and/or the plume dispersion characteristics. However, it indicates that local dynamics play a key role in the soil processes. Therefore, the mechanisms controlling Se mobility in soils should be evaluated around several volcanoes. Moreover, the Se flux from the acid rain – soil interaction towards the aquifer is currently unknown. Other Se sources for the groundwater are the input of geothermal water and leaching from the host basalt. Future work should better constrain how the different potential sources can explain the Se distribution within the aquifer. Selenium isotopes could be a potential tool to assess the individual contributions. To use Se isotopes as a source tracer, the different sources should have diverse Se isotope signatures. With the current knowledge on Se isotope ratio systematics, it is impossible to predict if different isotope signatures are present in the materials (e.g. host rocks, soils, volcanic gases, rain, ground and hydrothermal waters). Another complication is that Se is also affected by redox transformations. The oxidation of volcanic gases in the atmosphere is not expected to induce any fractionation. However, reduction processes along a flow path within the aquifer will increase the $\delta^{82/76}$Se. So even if Se isotopes could be a useful constrain, the interpretation of Se isotope ratios could be challenging. Reactive transport modelling (RTM) could also be used to better assess the contribution of leaching from the soils. One critical step in RTM is the model formulation to show which processes control the chemical fate to include the corresponding reactions in the RTM. The processes indentified in this work could form the base for RTM in this setting.

The study with topsoils across different climate zones on Tenerife Island showed that Se contents and mobility were not directly related with weathering, assessed using the chemical index of alteration (Chapter 7). This might be linked to a number of other processes which additionally impact the soils, such as trace element variations within parental materials along the island and the input of external sources (Saharan dust, marine aerosols). The isolation of the effect of weathering could be simplified by the use of a climo-sequence along one singular lava flow with low external inputs. However, the selection of such study site will be extremely difficult. Even in soils at Hawaii there is evidence for the input of continental dust (Stewart et al., 2001; Huh et al., 2004), while this island is located more than 3000 km from the nearest continent. Moreover, active volcanoes could cause input of fresh ash, which will also complicate the interpretation. Alternatives in order to study the effect of weathering on Se could be the study of a soil profile or an experimental approach (e.g. column experiment). On one hand, the advantage of a soil profile study is that with the proper selection of field sites, variations in parental material and external inputs can be easier constrained. However, the weathering regime will be similar too. On the other hand, the advantage of the experimental approach is that chemical and physical conditions can be tightly constrained and individual parameters can be systematically varied. Conversely, the rates over which natural chemical weathering occurs cannot be reproduced by experimental studies (White and Brantley, 2003).

Often arsenic (As) and Se are studied simultaneously, since it is assumed that their chemical fates are similar taking into account that they both form soluble oxyhydroxo complexes. However, the results from both field studies indicate that As and Se do not have the same behaviour within volcanic soils. At Tenerife Island the As distribution could to a large extent be explained by differences in parental rock and weathering regimes, while for Se a strong influence of the presence of soil organic matter (SOM) and amorphous compounds was detected. In soils from Mount Etna it was shown that sulphate competition could release selenate anions, while this mechanism did not release As. Consequently, As and Se leachable contents do not correlate for soil samples at high altitudes with frequent fresh volcanic ash input. These results also indicate the importance of mineralogy and sorption processes for controlling Se mobility in volcanic areas. Nevertheless, the responsible compounds seem to be different in each setting. At Etna volcano the non-crystalline Al phases control the Se release. Since selective extractions indicate that a wide range of amorphous compounds are present, it remained unclear which Al compounds play a key role. In contrast, at Mount Teide volcanic soils rich in amorphous Fe compounds and SOM have a higher Se content and a low Se mobility. Future work should focus on the molecular-scale within these soils. Although mechanistic studies exist for individual minerals, Se sorption has not been characterized for all compounds present in volcanic soils. For example, Se sorption on volcanic glass has not been assessed yet. Moreover, adsorption studies at a mechanistic level on soils, which are a mixture of different compounds, are scarce. The understanding of these processes at molecular scale will be highly beneficial for the knowledge on Se in volcanic soils. However, the LOD of in-situ spectroscopy techniques is currently one order of magnitude above the worldwide average Se concentrations in soils. Therefore, the development of the new synchrotron generation with higher brightness and consequently better sensitivity is needed prior to the application to samples with Se levels as observed in these field sites.

Based on the performed studies it can be concluded that there is a strong relationship between the development of the soil and the Se behaviour. At Mount Etna most Se is released during acid rain–soil interaction in poorly developed soils frequently influenced by the input of volcanic ashes. Although volcanic ashes have been identified as important Se sources, there is a lack of Se studies in fresh volcanic ashes. Taking the importance of volcanic ash as parental material for agricultural soils, future studies on Se in volcanic ashes are clearly needed. Also the results from Tenerife Island point out that unweathered materials have a higher potential for Se leaching. In contrast, the formation of secondary minerals will retain the Se within the soils, causing Se enriched soils with low Se mobility. Thus, the field studies demonstrate that sorption processes and soil mineralogy control the Se behaviour in volcanic soils.

Conclusions

As described in the introduction, two main objectives were defined for this PhD thesis:

1. To develop analytical protocols for Se determinations in complex matrices
2. To improve the understanding of the processes affecting the mobility of Se in volcanic soils

In this section, major conclusions for both objectives are summarized.

Objective 1: To develop analytical protocols for Se determinations in complex matrices

- Total Se determinations by inductively coupled plasma – mass spectrometry (ICP-MS) using $^{82}Se^+$ will significantly overestimate the Se content due to spectral interferences. Therefore, Se determinations should be performed using ^{78}Se with a hydrogen pressurized collision cell and 2% methanol addition. Some sample aliquots without methanol should be analysed as a control to check that all interferences are properly resolved.
- Direct TXRF analyses of complex solutions suffer from matrix interferences, due to the increased background and the high content of matrix elements (e.g. Fe and Zn) which reduces the excitation current of the X-ray tube. For Se determinations at environmental levels (limit of detection (LOD) 0.7 µg/L and 0.05 mg/kg) a DDLME procedure using APDC as complexing agent should be performed prior to TXRF analyses to isolate Se from the sample matrix. However, direct Se determinations by TXRF without sample pretreatment are easy and fast and therefore suitable for lab controlled experiments (LOD ~ 10 µg/L or 1 mg/kg).
- Selenium speciation at trace levels for acidic samples should be performed with a low pH mobile phase to prevent Al and Fe mineral precipitation which can alter the speciation. The optimum mobile phase is 20 mM ammonium citrate adapted to pH 3 with nitric acid and the addition of 2% methanol, in which selenite and selenate can be separated within 10 minutes with a LOD of 0.1 µg/L using $^{78}Se^+$ for detection.
- The separation of Se isotopes and Ar polyatomic ions requires a mass resolution beyond the capabilities of present-day multi-collector ICP-MS instrumentation. The precision of selenium isotopic measurements can be improved three times by the addition of a small amount of methane to the plasma.

Objective 2: To improve the understanding of the processes affecting the mobility of Se in volcanic soils

- The Se release during acid rain – soil interactions at Mount Etna depends on three different factors: the sulphate content in the rainwater, the amorphous Al phases present in the soils and the occurrence of selenate within the soils. Adsorbed selenate is released in soils close to the craters from the non crystalline materials due to the competition of sulphate for adsorption sites. Since re-adsorption is unlikely for selenate, this has implications for the Se contents within the aquifer, the only water source for the 1 million people in the surroundings of this volcano.

- The Se behaviour in soils from the volcanic islands of Tenerife cannot be directly linked with the weathering intensity of the soil. A range of other processes affect the chemical properties of the soils, such as variations in parental material and external inputs of Saharan dust and/or marine aerosols. However, these mechanisms seem not to play a key role in the chemical fate of Se in this environment. Samples rich in amorphous Fe compounds and SOM are enriched in Se and have a low Se mobility, indicating the importance of sorption processes within the soils. Since the formation of amorphous compounds strongly depends on the climate, weathering has indirectly an influence on the Se behaviour.
- The assumption that As and Se behave geochemically similar seems not to be valid in both field setting investigated within this PhD thesis.
- Soils act as active reactive interfaces and thereby form an important factor in the Se cycling in volcanic environments. There is a strong link between the behaviour of Se and the soil development. In young volcanic ash soils Se can be easily released. However, in more developed soils Se is strongly retained by secondary minerals, and as a result Se mobility is low. This shows that Se mobility is controlled by sorption processes and as a result the mineralogy in volcanic soils plays a major role in the Se behaviour.

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