Chemical Geology 289 (2011) 235–244

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Selenium mobilization in soils due to volcanic derived acid rain: An example from Mt Etna volcano, Sicily

G.H. Floor [a,b,*], S. Calabrese [c,d], G. Román-Ross [a,e], W. D´Alessandro [d], A. Aiuppa [c,d]

[a] University of Girona, Dep. Chemistry, Campus de Montilivi s/n, 17071, Girona, Spain
[b] BRGM; Sec. Metrology, Monitoring, Analysis, BP 45060 Orleans, France
[c] University of Palermo, Dept. DiSTeM, via Archirafi 36, 90123 Palermo, Italy
[d] Istituto Nazionale di Geofisica e Vulcanologia, sezione di Palermo, via Ugo La Malfa 153, 90146 Palermo, Italy
[e] Amphos 21 Consulting S. L. Passeig de Garcia i Faria 49, 08019 Barcelona, Spain

ARTICLE INFO

Article history:
Received 10 September 2010
Received in revised form 30 July 2011
Accepted 8 August 2011
Available online 19 August 2011

Editor: J. Fein

Keywords:
Selenium
Volcanic soils
Geogenic
Volcanoes
Contamination
Groundwater

ABSTRACT

The significant amounts of selenium (Se) emitted by volcanoes may have important impact on human health due to the narrow range between nutrition requirement and toxic effects for living organisms upon Se exposure. Although soils play a key role in determining the level in food and water and thereby human health, little is known about the behaviour of Se in volcanic soils. In this work we evaluated the Se release during rainwater–soil interaction under controlled conditions using soils collected on the flanks of Etna volcano and synthetic rain. Selenium concentrations in soil leachate solutions displayed a spatial distribution, which cannot be explained by plume deposition, total Se soil concentrations or the presence of Fe oxides. Instead, Al compounds and to a minor extent SOM were identified as the active phases controlling the selenate mobilization during interaction with sulphate-containing rainwater. This shows the importance of soils as reactive interfaces. Selenium is mobilized when volcanic-derived acid rain interacts with poorly developed soils close to the crater. This geogenic process might influence the chemical composition of groundwater and as a result, human health.

1. Introduction

Volcanoes are an important natural source of selenium (Se). Selenium is an essential element, but can be toxic too, depending on its concentration with a relatively narrow safe intake range from 40 ro 400 μg/day (Rayman, 2000). Selenium is volatilized in the magmatic plumbing system and as a result tens of kilograms Se per day might be released by a single volcano (Faivre-Pierret and Le Guern, 1983; Hinkley et al., 1999; Allen et al., 2000; Aiuppa et al., 2003a). Nevertheless, the chemical fate of Se around volcanoes is poorly constrained as Se emissions have been only studied for a few volcanoes (Mather et al., 2003). Selenium speciation measurements in volcanic plumes are not available, but high temperature thermodynamic models and the comparison with coal combustion suggest the presence of H_2Se, elemental Se and SeO_2 (Suzuoki, 1964; Symonds and Reeds, 1993; Monahan-Pendergast et al., 2008). Oxidation and cooling processes in the atmosphere 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; Calabrese et al., submitted; Table 1). Additionally, this interaction between volcanic gases and atmospheric water causes huge variations in rainwater pH (from 2 to 7), both in space (km scale) and time (weeks–months; Aiuppa et al., 2006). 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 environmental conditions, including direct plume fumigation, acid rain (Delmelle et al., 2001, 2003; Bellomo et al., 2007) and fresh ash input (Agnelli et al., 2007; Egli et al., 2007), which cause strong physico-chemical 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 Naumann, 2001). They can have high Se concentrations (e.g. 6–15 mg/kg in Hawaii compared to 0.4 mg/kg as worldwide average), but in contrast show low Se mobility (Byers et al., 1938; John et al., 1975; Nakamaru et al., 2005). This low mobility is believed to originate from adsorption on Fe and Al minerals (John et al., 1975; Nakamaru et al., 2005), which have been widely reported as potential adsorption phases for Se (Balistrieri and Chao,

---

[*] Corresponding author currently at: EC-Joint Research Centre- Institute for Reference Materials and Measurements, Retieseweg 111, 2440 Geel, Belgium. Tel.: +34 619935580.
E-mail addresses: Geerke.FLOOR@ec.europa.eu, geerke.floor@aquatrain.eu (G.H. Floor).

0009-2541/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2011.08.004

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

1990; Dynes and Huang, 1997; Parida et al., 1997; Wijnja and Schulthess, 2000; Duc et al., 2003; Peak et al., 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.

Mount Etna is the largest active volcano in Europe and has been persistently active over the past few thousand years. It is among the most intensely monitored volcanoes of the world (Bonaccorso et al., 2004) and is one of the few volcanoes for which Se flux has been estimated (Aiuppa et al., 2003a). Selenium contents have also been studied in rainwater (Calabrese, 2009; Calabrese et al., submitted) and in groundwater (Giammanco et al., 1996; Brusca et al., 2001; Aiuppa et al., 2003b). 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 in soils and specifically during soil–rainwater interaction.

The Etnean aquifers, the only water resource for about one million inhabitants around Mount Etna, are enriched in Se. Concentrations up to 66 μg/L have been reported, which is above the WHO guideline of 10 μg/L. Aiuppa et al. (2000) estimated that the aquifers discharge around 2 t/a Se. Several studies (Giammanco et al., 1996, 1998; Aiuppa et al., 2000, 2003b; Brusca et al., 2001) identify three main sources for trace elements: (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; (b) mixing processes with saline brines rising from the sedimentary basement below Etna; and (c) contamination from agricultural and urban wastewaters. However, rainwater could also cause a significant contribution for 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 Se discharge from the aquifer (Table 2). Nevertheless, as rainwater interacts with the soils during infiltration, adsorption and desorption processes can occur (Bellomo et al., 2003, 2007). Therefore, soil–rainwater interaction will determine the magnitude of this flux. For this reason, in this study we evaluated this soil–rain interaction in lab controlled experiments with samples collected from the flank of Etna volcano and synthetic acid rainwater. The effect of 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.

Table 2
Estimated Se fluxes around Mount Etna. Comparison shows similar order of magnitude for Se released by the aquifer and potential rainwater flux towards the aquifer (data in bold).

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

2. Etna volcano

Mount Etna is a large stratovolcano, covering an area of 1200 km^2 and reaching an elevation of 3300 m high (Tanguy et al., 1997). Recent eruptions from the summits and flank vents, which occasionally interrupt passive degassing, have typically emitted lavas and tephras with hawaiitic composition (~48% SiO_2,Tanguy et al., 1997). Etna volcano is considered to be one of the major volcanic gas emitters in the world, accounting for approximately 10% of worldwide volcanic emissions of CO_2 and SO_2 (Allard et al., 1997; D'Alessandro et al., 1997). Its estimated contribution to the annual atmospheric budget for alkali and heavy metals is 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 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 cause 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, whereas 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 hydrographical network and 75% of the rain water directly infiltrates into the aquifer (Aiuppa et al., 2003b).

Soil development in the Mount Etna area is controlled by the parental material, age, the morphology (e.g. slope) and climate (Dazzi, 2007). Moreover, depending on volcanic activity, winds can carry and deposit abundant pyroclastic material (Egli et al., 2007). The limited amount of published soil studies in the area focusses on the relationship between vegetation and soil nature and shows that the soils have vitric properties (Certini et al., 2001; Egli et al., 2007). Soil organic matter, imogolite-type materials (proto-imogolite allophane and well-developed imogolite), oxyhydroxide contents and weathering decrease with increasing altitude (Egli et al., 2007). Agricultural cultivation over the last centuries or even millennia has modified 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, 2007). The vegetation limit varies between 1800 and 2200 m, depending on the exposure to volcanic material and climatic conditions. In this study, most of the samples are non agricultural soils.

The only previous work conducted 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 et al., 2007). The contribution of pyroclastic material has a strong influence on the soil properties (Agnelli et al., 2007; Egli et al., 2007). In recent times, the largest deposition of new pyroclastic material resulted from the eruptions in 2001 and 2002–03. In 2001 pyroclastic products were dispersed almost exclusively in the SE and SSE directions 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 the deposition of pyroclastic