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Selenium Retained by Minerals from Volcanic Fumaroles at Fogo Island (Cape Verde)

Selénio Retido por Minerais das Fumarolas Vulcânicas na Ilha do Fogo (Cabo Verde)

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Abstract

Following the last eruption of the Fogo volcano (Cape Verde) that occurred in 2014-15, a study, focused in particular on the selenium retention by minerals, was undertaken on the mineralogy and chemistry of incrustations collected around fumaroles. The incrustations are unique, although indirect sources of information of volcanic degassing and on heavy metal transport by lava. The mineralogical constitution of the fumarole deposits was assessed by X-ray diffraction and the chemical characterization was performed through X-ray fluorescence spectrometry with wavelength dispersive system and by energy dispersive X-ray fluorescence at the European Synchrotron Radiation Facility (ESRF). The most represented compounds/minerals were native sulphur, sodium chloride, calcium sulphates with variable degrees of hydration, anhydrous or hydrated sodium sulphates, hydrated sulphates of potassium and magnesium or sodium and magnesium and a mineral with fluorine. A large span of minor and trace elements were identified (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ba, Ce, Pt, Tl, Pb) carried by minerals, some of them potentially hazardous. Due to this, a speciation study on selenium K-edge was performed at the ESRF. This element can occur in different oxidation states (-2, 0, +4, +6), with the exception of the first, all of which were identified in the present study, and may pass to the hydrological system and be absorbed by plants and thus enhance health problems.

Keywords: selenium, Fogo volcano, fumarole incrustations, speciation.

Resumo

Após a última erupção do vulcão do Fogo, Cabo Verde (2014-15) realizou-se um estudo mineralógico e químico das incrustações fumarólicas, centrado em particular, na retenção do selénio por parte dos minerais. As incrustações são fontes únicas de informação, embora indirectas, sobre a desgaseificação vulcânica e transporte de metais pesados. A constituição mineralógica foi obtida por difração de raios-X e a caracterização química por espectrometria de fluorescência de raios-X com sistema dispersivo em comprimentos de onda e por fluorescência de raios-X com dispersão em energias no European Synchrotron Radiation Facility (ESRF). Os compostos/minerais mais representados foram enxofre, cloreto de sódio, sulfatos de cálcio, com vários graus de hidratação, sulfato de sódio anidro ou hidratado, sulfatos hidratados de potássio e de magnésio ou de sódio e de magnésio e um mineral com flúor. Identificou-se um grande número de elementos (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ba, Ce, Pt, Tl, Pb) presentes em traços nos minerais, alguns deles potencialmente perigosos. Devido a este facto, encetou-se um estudo no ESRF sobre a especiação do selénio através da descontinuidade K. Este elemento pode ocorrer em diversos estados de oxidação (-2, 0, +4, +6), todos eles identificados no presente trabalho à excepção do primeiro, podendo passar para o sistema hidrológico e ser absorvido pelas plantas e assim, potenciar problemas de saúde.

Palavras-chave: selénio, vulcão do Fogo, incrustações fumarólicas, especiação.

Introduction

Fogo Island, in the Cape Verde archipelago, is one of the most active oceanic island volcanoes in the world – was discovered in the 15th century and has mean eruption intervals of approximately 20 years.

The most recent eruption, starting on November 23, 2014 and lasting until February 7, 2015, occurred on a NE-SW trending 700 m-long fissure located on the SE flank of the previous 1995 cinder cone, an adventitious vent developed on the SW flank of younger “Pico do Fogo” volcano (Mata et al., 2017). The latest events (1995 and 2014-15), produced extensive lava flow fields (a’a and pahoehoe) at “Chã das Caldeiras”, that destroyed houses and agriculture (mainly vine and fruit plantations).

The knowledge of the nature and range of heavy elements carried by gases emanating from active fumaroles after a volcanic eruption is vital in the domains of environment and geochemistry. Often, such elements include metals like mercury, lead and thallium, as identified after the 1995 event (Figueiredo et al., 1999). This fact, plays a major health hazard concern as local populations use sulphur and white materials as treatment for some diseases for themselves and for animals (by drinking with water for example). For that reason, a study was undertaken on the mineralogy and chemistry of incrustations collected around fumaroles, focused in particular on the selenium retention by minerals.

Selenium (Se) is an essential nutrient for humans, animals and microorganisms, but it becomes toxic at concentrations slightly above the nutritional levels. This naturally occurring trace element can be released to the environment from many anthropogenic sources such as mining, agricultural, petrochemical and industrial processes and its toxicity is developed along a complex cycle involving adsorption by soil components and later accumulation by plants (Ellis and Salt, 2003). In the environment, Se can occur in several oxidation states ranging from selenide (Se^{2-}) to elemental selenium (Se^0), selenite (Se^{4+}) and selenate (Se^{6+}). It resembles

sulphur in many of its properties and small concentrations of Se commonly replace S in ore minerals and sulphate minerals.

To clarify the speciation state of Se and the nature of Se-carrier phase(s) on incrustations samples, an X-ray absorption spectroscopy study (XANES) using synchrotron radiation was undertaken at Se K-edge, following the previously performed mineralogical characterization and chemical analysis.

Materials and Methods

Two sampling campaigns were performed near the 2014-15 vents (Fig. 1), in November 2016 and in February 2017 and rocks (basaltic lava) plus incrustations were collected.



Fig. 1 – Principal vents of 2014-15 eruption on Fogo Island and incrustations field.

The temperature has been registered near the samples, with a digital thermocouple specially conceived for measuring high temperatures in fractures and fissures. Neighbouring to the principal vent, fumaroles were almost imperceptible, yellow (sulphur) and white materials were deposited on the field as well as orange-red coloured rocks. Along the walls of an unstable fracture with higher temperature, white incrustations were also collected. The highest registered temperature (238°C) was in a hole also with white material inside. Near a smaller vent, with a pit that the eruption has created, called by the local population “vulcãozinho” (little volcano), only white incrustations were found.

The mineralogical constitution of the fumarole deposits was obtained by X-ray diffraction (XRD) after a careful selection using a stereomicroscope. However, the

phase identification was in some cases difficult due to the presence of mixtures. For that reason, a chemical analysis through X-ray Fluorescence Spectrometry with wavelength dispersive system (XRF-WDS) was performed.

The chemical constitution of incrustation samples was also obtained by energy dispersive X-ray Fluorescence (EDXRF) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The high brilliance of synchrotron X-rays, allows for remarkably low limits of detection for most chemical elements, thus enabling the analysis of trace and sub-trace species hosted by a mineral. The experiments were performed with the instrumental set up of beamline BM 25A, using an excitation energy of 20 keV (powdered samples and model compounds were placed between two Kapton foils, a special pure adhesive tape). The energy dispersive spectra (EDXRF) collected during 300 s for each sample were fitted using the PyMca software (Solé et al., 2007). X-ray absorption near-edge spectra (XANES) were collected at the Se *K*-edge (12658 eV for elemental selenium) in fluorescence yield (FY) mode with an energy resolution of $\Delta E/E = 1.5 \times 10^{-4}$ using a 13-element Si(Li) solid-state detector and a Si(111) monochromator. Pure lead metal foil was irradiated in transmission mode for energy calibration purposes.

Results and Discussion

The main phases identified were sulphur (α -S), halite (NaCl), anhydrite (CaSO_4), bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), thenardite and its polymorph-Form III (Na_2SO_4), tamarugite, ($\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), picromerite ($\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), bloedite ($\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$), bianchite ($(\text{Zn}_{0.69}\text{Fe}_{0.21}\text{Mg}_{0.10})\text{SO}_4 \cdot 6\text{H}_2\text{O}$) and ralstonite ($\text{Na}_x\text{Mg}_x\text{Al}_{2-x}(\text{F},\text{OH})_6 \cdot y\text{H}_2\text{O}$). To the best of our knowledge, this is the first time that thenardite and their polymorph was reported as present simultaneously in incrustations, probably due to the weather conditions of Fogo volcano unique to the preservation and study of these minerals.

The highest content obtained for selenium by XRF-WDS (semi-quantitative analysis), was 1000 ppm. The EDXRF spectra (Fig. 2) showed that selenium is mainly carried by sulphur (sample S4), lead and thallium are transported by ralstonite (F27) and arsenic by the mixture of bassanite and anhydrite (F18). Sample F14 is also a mixture of titanite (CaTiSiO_5) and ralstonite. With both techniques, a large span of minor and trace elements were identified (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ba, Ce, Pt, Tl, Pb) carried by incrustations originated through the volcanic gases.

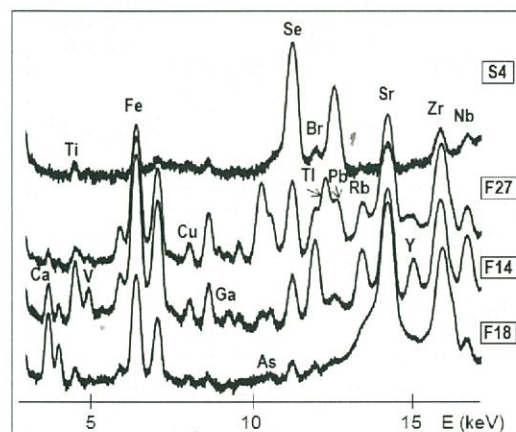


Fig. 2 – Energy dispersive X-ray fluorescence (EDXRF) spectra obtained for incrustations samples irradiated to collect the Se *K*-edge XANES spectra. Only the diagnosis line of each element is assigned.

Selenium *K*-edge X-ray absorption spectra (Fig. 3) were collected for the selected incrustations samples, as well as for Se-O model compounds (commercial products, previously checked by XRD in the laboratory), chosen to configure various formal valences and geometrical coordinations of Se cations: selenite (Se^{4+} , pyramidal coordination) and selenate (Se^{6+} , tetrahedral coordination). The energy of the strong absorption maximum (the so-called white line) was highlighted to allow for an easy comparison of spectra. In the ground state, Se has an electronic configuration $[\text{Ar}] 3d^{10} 4s^2 4p^4$.

The white line is due to the dipole-allowed $1s \rightarrow 4p$ electron transition and its intensity rises with the increase of 4p electron vacancies.

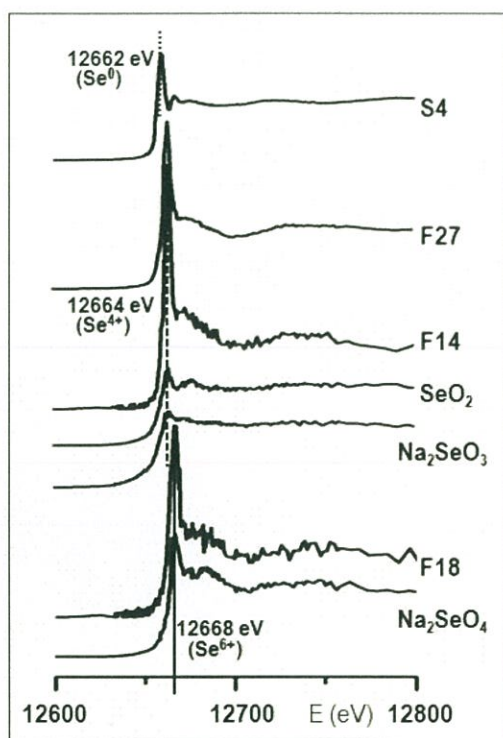


Fig. 3 – Se K-edge XANES spectra collected from incrustations compared to the spectra obtained for selenite and selenate model compounds

As the outer valence electrons are removed and the redox state of selenium increases, the absorption edge energy is therefore expected to shift towards higher values as a result of the decrease in shielding of the core 1s electrons (Figueiredo et al., 2014). Different situations for Se speciation were observed: Se^{6+} tetrahedral (sample F18, bassanite and anhydrite), Se^{4+} pyramidal coordination (F14 and F27, ralstonite) and Se^0 in sample S4 due to diadochic replacement of S by Se.

Conclusions

The fumarole incrustations resulting from the gaseous exhalation were mainly constituted by native sulphur and sulphates plus chlorides and fluorides. A large span of minor and trace elements were identified carried by incrustations, some of them potentially health hazardous. Se resembles sulphur in many of its properties and frequently replaces S. High levels of Se allied to different speciation states found in incrustations samples, configures a health worry to local populations. A more complete chemical study by EDXRF and the

ascertaining of the speciation state of arsenic, thallium and lead are foreseen.

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References

- Ellis, D.R., Salt, D.E., 2003. Plants, selenium and human health. *Curr. Opin. Plant Biol.*, 6, 273-279.
- Figueiredo, M.O., Silva, T.P., Basto, M.J., Ramos, M.T., Chevallier, P., 1999. Indirect monitoring of heavy metals in volcanic gases by synchrotron X-ray microprobe (μ -SRXRF) qualitative analysis of sublimates. *J. Anal. At. Spectrom.* 14, 505-507.
- Figueiredo, M.O., Silva, T.P., Veiga, J.P., Batista, M.J., Salas-Colera, E., De Oliveira, D.P., 2014. Selenium Speciation in Waste Materials From an Exhausted Iberian Pyrite Belt Mine. *J. Mater. Sci. Res.* 3, 22-30.
- Mata, J., Martins, S., Mattielli, N., Madeira, J., Faria, B., Ramalho, R.S., Silva, P., Moreira, M., Caldeira, R., Moreira, M., Rodrigues, J., Martins, L., 2017. The 2014-15 eruption and the short-term geochemical evolution of the Fogo volcano (Cape Verde): Evidence for small-scale mantle heterogeneity. *Lithos* 288-289, 91-107.
- Solé, V.A., Papillon, E., Cotte, M., Walter, Ph., Susini, J., 2007. A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra. *Spectrochim. Acta* 62, 63-68.