OVERVIEW of HAZARDOUS ELEMENTS PRESENT in INCRUSTATIONS RESULTING from the 2014-15 ERUPTION of FOGO VOLCANO, CAPE VERDE

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Teresa P. SILVA [1], Daniel de OLIVEIRA [1], João P. VEIGA [2], Paula ÁVILA [3], Carla CANDEIAS [4], Eduardo SALAS-COLERA [5], Rita CALDEIRA [6]

[1] Mineral Resources and Geophysics Research Unit, National Laboratory for Energy and Geology (LNEG), Estrada da Portela, Amadora, Portugal
[2] CENIMAT/I3N, Faculty of Sciences and Technology, Campus de Caparica, New University of Lisbon, Lisbon, Portugal
[3] Mineral Science and Technology Unit, National Laboratory for Energy and Geology (LNEG), S. Mamede de Infesta, Portugal
[4] EpiUnit - Epidemiology Research Unit, Environmental Health Department, Institute of Public Health of the University of Porto, Porto / GeoBioTec - Geobiosciences, Geotechnologies and Geoengineering Research Center, Geosciences Department, University of Aveiro, Portugal
[5] SpLine, Spanish CRG Beamline, European Synchrotron Radiation Facility (ESRF), Grenoble, France
[6] Geology, Hydrogeology and Coastal Geology Unit, National Laboratory for Energy and Geology (LNEG), Amadora, Portugal

Introduction

The **last eruption of the Fogo volcano** (**Cape Verde**) **occurred between November 23, 2014 and February 7, 2015** (Fig. 1), producing extensive lava flow fields (a'a and pahoehoe), that destroyed houses and agriculture (mainly vine and fruit plantations) at Chã das Caldeiras (Fig. 2).

Furthermore, the **hot volcanic gases** (pure or resulting from their interaction with surroundings) emitted through vents and fissures for a long time, transport volatile species that are released to the atmosphere or **deposited by cooling and condensation or sublimation - fumarole incrustations** (Fig. 3).

Minor and trace elements carried by minerals on these materials, **can be hazardous to health**, depending mainly on its nature, concentration and speciation. Therefore, the **chemical characterization of incrustations and altered rocks** were undertaken to **identify possible harmful elements**.

Table 1 – Semi-quantitative normalized chemical analysis (wt%) obtained by **XRF-WDS**.

	F13 Sulphur green	F14 White material	F18 White opaque crystals	F25 White material, hygroscopic	F27 White material
Na		18.1		25.2	6.3
Mg	0.3	8.9	1.0	4.8	10.4
Al	0.6	1.2	4.7	0.3	28.8
Si	6.1	0.7	79.1	0.2	2.2
S	89.9	49.8	5.2	43.0	1.2
Cl	0.9	0.9	1.3	5.0	0.8
K	0.3	17.9	0.6	19.8	2.5
Ca	0.7	0.9	2.6	0.6	38.5
Ti	0.6	0.3	4.0		3.5
Mn		1.0		0.9	0.1
Fe	0.5	0.4	1.4	0.1	4.8
Sr					0.3
Zr					0.1
Ba					0.4

Fig. 1

Fig. 2

Fig. 3

Materials and Methods

The **sampling campaigns** were performed near the 2014-15 vents in November 2016 and in February 2017, and **rocks** (basaltic lava) plus **incrustations** were collected. **Yellow** (sulphur) and **white materials** (Fig. 3) were deposited on the field as well as orange-red coloured rocks.

The **chemical characterization** was achieved through X-ray Fluorescence Spectrometry with wavelength dispersive system (**XRF-WDS**) at the laboratory to obtain a semi-quantitative analysis and through 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** (Fig. 4), using an excitation energy of 20 keV (powdered samples were placed between two Kapton foils, a pure adhesive tape). The EDXRF spectra collected during 300s for each sample were fitted using the PyMca software [1].

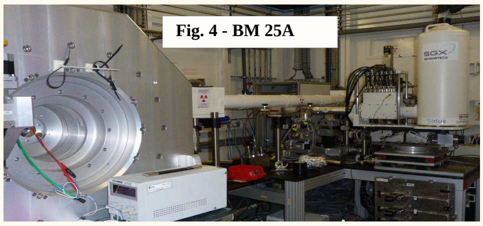

Fig. 4 - BM 25A

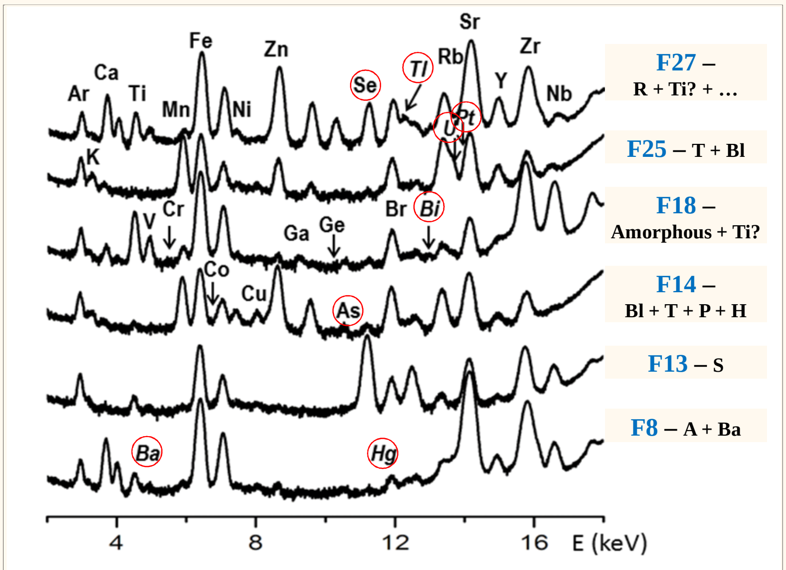

Fig. 5 – **EDXRF spectra** obtained for incrustations samples.
Only the diagnosis line (**K or L**) of each element is assigned.
The **mineralogical constitution** of samples is also presented:

A – **Anhydrite** ($CaSO_4$),
Ba – **Bassanite** ($CaSO_4.1/2H_2O$),
Bl – **Bloedite** [$Na_2Mg(SO_4)_2.4H_2O$],
H – **Halite** (NaCl),
P – **Picromerite** [$K_2Mg(SO_4)_2.6H_2O$],
R – **Ralstonite** [$Na_xMg_xAl_{2-x}(F,OH)_6.yH_2O$],
S – **Sulphur** (α-S),
T – **Thenardite** (Na_2SO_4),
Ti – **Titanite** ($CaTiSiO_5$).

Results and Discussion

The **chemical characterization** obtained **for incrustations and altered rocks** is exemplified in data presented on Table 1 and Fig. 5. **A large span of minor and trace elements, some of them potentially toxic, 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, Hg, Tl, Pb, Bi, U.

The **crystal structure of the carrier mineral phase strongly constrains the range and content of elements that may be hosted** in the various structural sites available, however the **presence of some heavy metals**, e.g. **Hg, Tl, Bi, U, plays a major environmental concern** as local populations use sulphur (the main mineral in incrustations) and white materials as treatment for some diseases.

The crystal structure of **common sulphur** is built up by the packing of S_8 molecules restraining the diadochic replacements to **Se and As** in solid solution. Indeed, the **highest content obtained for Se** by **XRF-WDS** was **1000 ppm (1mg/g)**, being **0.3mg/day** the tolerable upper intake level [2].

The **white materials are mainly sulphates** (anhydrite, bassanite, gypsum, thenardite) **incorporating As, Ba, Pt, Hg, Pb, Bi and U**, while the **toxic metal Tl** (highest content, 2000 ppm) is carried by ralstonite, an hydrated aluminum fluoride (Fig. 5).

The presence of these geohazardous elements was also noticed following the 1995 eruption of the same volcano [3] endangering the local population. The type and diversity of minerals recognized, suggests that the **volcanic gases of the last eruption were poorer in water content and K, but richer in Ca and Na**. From the halogens group **the presence of F, Cl and Br were noticed in the two events**.

A **speciation study on Se** was already performed and **different situations were observed**: **Se^{6+}** in a mixture of bassanite and anhydrite, **Se^{4+}** in ralstonite and **Se^0** in a sulphur sample.

A more complete chemical study by EDXRF and the ascertaining of the speciation state(s) of arsenic, thallium and lead (potentially toxic elements) are foreseen.

References

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