

Ions, vapors and/or nanoparticles penetrating volcanic edifices?

J.H. OBENHOLZNER (1), J. L. PARKS (2),
M. EDWARDS(2) AND P. FULIGNATI(3)

¹NHM/Volcanology, Postfach 417, A-1014 Vienna,
Austria/Europe; (obenholtzner@a1.net)

²Virginia Polytechnic Institute And State University, 418
Durham Hall, Blacksburg, VA 24061-0246, USA;
(jparks@vt.edu; edwardsm@vt.edu;)

³Dipt. di Science della Terra, University of Pisa, Via S. Maria,
53, 56126 Pisa, Italy;(fulignati@dst.unipi.it.

A top-sealed plastic tube with a diameter of ca. 15 cm had been buried ca. 70 cm deep vertically at the base of La Fossa volcano, Vulcano island, Italy, next to the front of the obsidian flow. The tube had been filled with layered rock and quartz wool to condense vapors emanating from the soil. At ca. 75 cm below the surface the sample had been exposed to vapors from Sept. 2005 to April 2006. The leached sample had not been in touch with the ground. 2 other glass wool cushions (ca. 10 cm thick, uncompacted) had been underneath to minimize capillary effects. A rock wool layer not touching ground revealed nucleated sylvite (KCl ~10 μm in size) and barite (BaSO_4 ~5-10 μm in size) crystals by SEM/EDS in its basal portion. Other very small (< 2 μm) particles were observed on the rock wool fibers but we could not identify them because they were suddenly volatilized by the electron beam. The bright appearance in backscattered images suggests that these particles may be metal compounds. The nucleation of sylvite and barite documents the presence of ions. Leaching of the quartz wool at room temperature with deionized H_2O and ICP-MS analysis documented 4 groups of elements: 1. positive signal: Mg, K, Ca, Cr, Mn, Ni, (Ba); low to moderate volatility at magmatic conditions. 2. unclear signal: Al, Si, P, Fe; low volatility at magmatic conditions. 3. no signal: V, As, Se, Mo, Co. As, Se, Mo, V are considered to be highly volatile, Co got a low volatility. 4. positive signal: Cu, Zn, Cd, Sn, Pb, W; high volatility at magmatic conditions. Leaching with nitric acid documented also V and Fe, and produced higher values for all elements, except K and Sn. This experiment documents for the first time an unknown element transport by vapors/gases through a volcanic edifice interacting with hydrothermal and magmatic gases. More information can be found at <http://www.iugg2007perugia.it/webbook/>

Volatiles in arrojadite: combining single-crystal XRD and FTIR microspectroscopy

R. OBERTI ^{1*}, G. DELLA VENTURA², F. BELLATRECCIA²
AND F. RADICA²

¹ CNR-IGG, UOS Pavia, Italy,(oberti@crystal.unipv.it)

² University of Roma Tre, Rome, Italy

Arrojadites are complex phosphates typically found in granitic pegmatites or hydrothermal veins, although their occurrence in metamorphic rocks suggests wider conditions of formation. Re-examination by EMP, LA-ICP-MS and single-crystal XRD analysis of a set of samples from various occurrences lead to revise the structure, the formula and the nomenclature of the group [1,2]. The correct structural model for arrojadite implies three OH-groups: two of these (W1 and W2) have similar local environment (they bridge three octahedra), crystallographic orientation and hydrogen-bond system. W3 is connected with the apical oxygen of a newly defined tetrahedron in the structure, and is involved in a bifurcated hydrogen bridge with surrounding oxygen atoms. Raman spectra reported in [1] show two higher-frequency, intense and convoluted bands which were assigned to specific local environments of W1 and W2; an additional low-frequency, broad and weak feature in the spectra could not be assigned with certainty. We report in this work on a FTIR study of various samples studied in [1,2]. Chemical zoning of the volatile components was checked by FTIR imaging using an FPA detector fitted on a Bruker Hyperion 3000 microscope. In contrast with the Raman spectra, the FTIR patterns show a very intense and broad absorption extending from 3500 to 2900 cm^{-1} . Single-crystal XRD has shown that F is ordered at the W1 site, and this generates a significant modification of the FTIR pattern, as observed on holotype fluoro-arrojadite-(BaFe) from Sidi Bou Kricha (Morocco).

The FTIR spectrum of holotype arrojadite-(KNa) from Rapid Creek shows also an intense doublet at 3190-3087 cm^{-1} which can be assigned to NH_4^+ groups, as later confirmed by EMPA. The orientation of the absorber (i.e. the O-H bond) with respect to the crystallographic axis can be determined from polarized-light measurements along the principal optical direction [4]. In all the samples, no evidence of molecular water is present in the NIR 4000-6000 cm^{-1} region.

[1] Cámara *et al.* (2006) *Am. Mineral.* **91**, 1249-1259.

[2] Chopin *et al.* (2006) *Am. Mineral.* **91**, 1260-1270. [3]

Libowitzky & Rossman (1996) *Phys. Chem. Miner.* **23**, 319-327.