## Crystal chemistry of phlogopite from Vulture-S. Michele Subsynthem volcanic rocks (Mt. Vulture, Italy) and volcanological implications

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## ABSTRACT

Volcanic activity at Mt. Vulture lasted about 750 ka and produced SiO<sub>2</sub>-undersaturated volcanic rocks that can be classified as old (~700 ka), intermediate (~600–550 ka), and young (~130 ka). The intermediate deposits consist of pyroclastic falls and flows and lavas with compositions ranging from phonolite to foidite. A recent revision of the stratigraphic setting allowed these deposits to be classified into one synthem (the Barile Synthem) and further subdivided into four subsynthems (Toppo S. Paolo, Rionero, Vulture-S. Michele, and Ventaruolo). In the present investigation, trioctahedral micas from sample VUT191 in the Vulture-S. Michele Subsynthem are considered. The host rock has modal diopside (20.2%), analcime (22.8%), plagioclase (27.8%), haüyne (5%), phlogopite (8.9%), and magnetite (6.3%). The micas were studied using chemical (EPMA, C-H-N, SIMS), structural (SCXRD), and spectroscopic (Mössbauer) methods.

EPMA of 36 crystals from thin sections and 6 discrete crystals selected for the structural analysis showed remarkable compositional variability, as follows (in wt%):  $SiO_2 = 33.14-38.01$ ,  $Al_2O_3 =$ 15.56-20.45, MgO = 13.02-20.81, FeO<sub>tot</sub> = 6.34-14.08, TiO<sub>2</sub> = 2.34-6.02, K<sub>2</sub>O = 6.03-9.48, Na<sub>2</sub>O = 0.50-0.78, and BaO = 0.89-4.06; all crystals proved to be phlogopite. Elemental C-H-N analyses yielded  $H_2O = 2.86 \pm 0.36$  wt%. The water content was also determined by SIMS on two single crystals, labeled VUT191 2 and VUT191 19, which yielded values of  $3.81 \pm 0.12$  and  $1.72 \pm 0.08$  wt% H<sub>2</sub>O, respectively. Mössbauer investigation showed that all the iron in VUT191 mica is octahedral with  $Fe^{2+} = 25.5\%$  and  $Fe^{3+} = 74.5\%$ , confirming that Vulture micas are particularly  $Fe^{3+}$ -rich, as also found from previous investigations. Structure refinements using anisotropic displacement parameters were performed in space group C2/m and converged at  $1.89 \le R \le 3.17$ ,  $2.09 \le R_w \le 3.43\%$ . All of the analyzed micas belong to the 1M polytype but exhibit remarkable variations in the c parameter from 10.1569(4) to 10.2458(4) Å. The chemical and structural parameters indicate that the studied micas can be divided into two groups: the first encompassing strongly dehydrogenated micas affected mainly by Ti-oxy  $[^{VI}M^{2+} + 2(OH)^- \leftrightarrow ^{VI}Ti^{4+} + 2O^{2-} + H_2]$  and  $M^{3+}-oxy [^{VI}M^{2+} + (OH)^- \leftrightarrow ^{VI}M^{3+} + O^{2-} + \frac{1}{2}H_2]$ . with  $M^{3+} = Fe^{3+}$ ,  $Al^{3+}$ ] substitutions. The second group consist of samples in which vacancy-bearing mechanisms. 2  $^{VI}M^{2+} \leftrightarrow ^{VI}Ti^{4+} + ^{VI}$  and 3  $^{VI}M^{2+} \leftrightarrow 2^{VI}M^{3+} + ^{VI}$  occur.

**Keywords:** Volcanic phlogopite, Mössbauer spectroscopy, structure refinement, CHN, SIMS, crystal chemistry, substitution mechanisms