

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

SILVIA MATARRESE,¹ EMANUELA SCHINGARO,¹ FERNANDO SCORDARI,^{1,*} FRANCESCO STOPPA,² GIANLUIGI ROSATELLI,² GIUSEPPE PEDRAZZI,³ AND LUISA OTTOLINI⁴

¹Dipartimento Geomineralogico, Università degli Studi di Bari, via E. Orabona 4, I-70125 Bari, Italy

²Dipartimento di Scienze della Terra, Università G.d'Annunzio, via dei Vestini, 3, I-66100 Chieti, Italy

³Dipartimento di Sanita' Pubblica, Sezione di Fisica, Plesso Biotecnologico Integrato, via Volturmo 39, I-43100, Parma, Italy

⁴CNR-Istituto di Geoscienze e Georisorse (IGG), Sezione di Pavia, via Ferrata, 1, I-27100 Pavia, Italy

ABSTRACT

Volcanic activity at Mt. Vulture lasted about 750 ka and produced SiO₂-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 subsynths (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%): SiO₂ = 33.14–38.01, Al₂O₃ = 15.56–20.45, MgO = 13.02–20.81, FeO_{tot} = 6.34–14.08, TiO₂ = 2.34–6.02, K₂O = 6.03–9.48, Na₂O = 0.50–0.78, and BaO = 0.89–4.06; all crystals proved to be phlogopite. Elemental C-H-N analyses yielded H₂O = 2.86 ± 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 ± 0.12 and 1.72 ± 0.08 wt% H₂O, respectively. Mössbauer investigation showed that all the iron in VUT191 mica is octahedral with Fe²⁺ = 25.5% and Fe³⁺ = 74.5%, confirming that Vulture micas are particularly Fe³⁺-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 ≤ *R* ≤ 3.17, 2.09 ≤ *R_w* ≤ 3.43%. All of the analyzed micas belong to the 1*M* 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}M²⁺ + 2(OH)⁻ ↔ ^{VI}Ti⁴⁺ + 2O²⁻ + H₂] and M³⁺-oxy [^{VI}M²⁺ + (OH)⁻ ↔ ^{VI}M³⁺ + O²⁻ + ½H₂, with M³⁺ = Fe³⁺, Al³⁺] substitutions. The second group consist of samples in which vacancy-bearing mechanisms, 2 ^{VI}M²⁺ ↔ ^{VI}Ti⁴⁺ + ^{VI}□ and 3 ^{VI}M²⁺ ↔ 2 ^{VI}M³⁺ + ^{VI}□ occur.

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