

XRD, micro-XANES, EMPA, and SIMS investigation on phlogopite single crystals from Mt. Vulture (Italy)

F. SCORDARI,^{1,*} M.D. DYAR,² E. SCHINGARO,¹ M. LACALAMITA,¹ AND L. OTTOLINI³

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

²Department of Astronomy, Mount Holyoke College, South Hadley, Massachusetts 01075, U.S.A.

³CNR-Istituto di Geoscienze e Georisorse (IGG), Sezione di Pavia, Via A. Ferrata, 1, I-27100 Pavia, Italy

ABSTRACT

Selected phlogopite flakes from Mt. Vulture in southern Italy were studied using a combination of single-crystal techniques: electron microprobe analysis (EMPA), secondary ion mass spectrometry (SIMS), single-crystal X-ray diffraction (SCXRD), and micro-X-ray absorption near-edge spectroscopy (XANES). The latter technique was employed to analyze the structure of the Fe-*K* absorption edge over the region from 7080–8100 eV and to determine Fe³⁺/ΣFe at a micrometer scale, albeit with large error bars due to known effects of orientation on pre-edge energy.

The annite component, Fe/(Mg+Fe), of the samples studied ranged from 0.16 to 0.31, the Ti content from 0.11 to 0.27 atoms per formula unit (apfu) and the Ba content from 0.03 to 0.09 apfu. SIMS analysis showed H₂O (wt%) = 1.81–3.30, F (wt%) = 0.44–1.29, and Li₂O (wt%) = 0.001–0.027. The intra single-crystal chemical variability for major/minor elements (Mg, Fe, Al, Ba, Ti, and K) was found particularly significant for samples VUT191_11 and PG5_1, less significant for the other samples of the set. SIMS data relative to crystals VUT187_24, VUT191_10, VUT191_11, and VUT187_28 showed a noteworthy variation in the concentrations of some light elements (H, Li, and F) with coefficient of variation CV (as 1σ%) up to ~18% for H₂O.

The analyzed micas belong to the 1M polytype. Structure refinements using anisotropic displacement parameters were performed in space group *C2/m* and converged at $3.08 \leq R \leq 3.63$, $3.32 \leq R_w \leq 3.98\%$. Micro-XANES results yielded Fe³⁺/ΣFe from 51–93%. Previous Mössbauer data from powdered samples suggested Fe³⁺/ΣFe values ranging from 49–87%. However, the Fe³⁺ content determined by both techniques is sometimes remarkably different, in part because of the large errors (±10–15%) presently associated with the micro-XANES technique and in part because the Fe³⁺ content of a single crystal may significantly depart from the average value obtained from routine Mössbauer analysis.

The combination of EMPA, SIMS, and micro-XANES resulted in the characterization of the samples at a comparable spatial scale. By means of in-situ data and the results of crystallographic investigations, the occurrence of different relative amounts of M³⁺-oxy [^{VI}M²⁺ + (OH)⁻ ↔ ^{VI}M³⁺ + O²⁻ + ½H₂↑], Ti-oxy substitutions [^{VI}M²⁺ + 2(OH)⁻ ↔ ^{VI}Ti⁴⁺ + 2O²⁻ + H₂↑], and Ti-vacancy (□) substitution (2^{VI}M²⁺ ↔ ^{VI}Ti⁴⁺ + ^{VI}□) was ascertained for the studied samples.

Keywords: Volcanic phlogopite, micro-XANES, SIMS, crystal chemistry, substitution mechanisms