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

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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 Fe/VFe at a micrometer scale, albeit with large error bars due to known effects of orientation on pre-edge energy.

The anhite 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 ΔM polytype. Structure refinements using anisotropic displacement parameters were performed in space group C2/m and converged at 3.08 ≤ R ≤ 3.63, 3.32 ≤ R ≤ 3.98%. Micro-XANES results yielded Fe/MFe values ranging from 49–87%. Previous Mössbauer data from powdered samples suggested Fe/VFe values ranging from 49–87%. However, the Fe/VFe 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 Fe/VFe 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 [M3+–oxy(OH) ↔ M4+ + O2− + ½H2O], Ti–oxy substitutions [V4+ + 2(OH) ↔ 0.5Ti4+ + 2O2− + H+], and Ti-vacancy (□) substitution (2V4+ + 2□ ↔ 2V4+ + □) was ascertained for the studied samples.

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

INTRODUCTION

Historically, accurate knowledge of cation and anion populations in natural mica solid solutions has been hampered by the lack of complete chemical analyses. More recently, the determination of Fe3+/ΣFe by Mössbauer spectroscopy on bulk samples has become routine, though chemical characterization of the anion site (i.e., quantitative evaluations of OH−, O2−, Cl−, and F−) is much less common. Such complete chemical characterization combined with structural analysis is needed to evaluate the extensive chemical disorder that affects cation sites of micas, because homo- and heterovalent substitutions occur at interlayer (K, Ba, Ca, Na, NH4, H2O, H2O, □, where □ stands for vacancy), octahedral (Mg, Mn, Fe2+, Fe3+, Ti3+/4+, Al, Cr, Li, □), and tetrahedral (Si, Al, Fe, Ti) sites. This complicates assessment of the substitution mechanisms in micas, particularly in cases when multiple valence states and multiple substitutions may occur. As an example, Ti can be incorporated into the mica structure via: (1) cation substitution at the octahedral site with formation of vacancies, 2V4+ ↔ 0.5Ti4+ + □, where M stands for Mg, Fe2+, and Mn3+. This is also known as the Ti-vacancy mechanism (Forbes and Flower 1974); (2) cation substitution at the octahedral site accompanied by the loss of protons at the anion site, V4+ + 2(OH) ↔ 0.5Ti4+ + 2O2− + H+. The Ti–oxy mechanism (Bohlen et al. 1980) and/or (3) a coupled octahedral–tetrahedral cation substitution, V4+ + 2Si4+ ↔ 0.5Ti4+ + 2Al3+, the Ti-Tschermak substitution (Robert 1976). A combination of the above mechanisms may also occur, as well as other, rarer substitutions (Waters and Charnley 2002). Very recently, substantial Ti–oxy and Ti-vacancy substitutions have been found by Sassi et al. (2008) in biotite from high-grade metapelitic xenoliths, whereas Cesare et al. (2008) found that Ti may also be involved in a “fluorination” mechanism, Ti4+ + 2O2− ↔ (Fe, Mg)3+ + 2F−. Different authors have ascertained that Fe3+–oxy substitutions

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