

Substitution mechanisms and implications for the estimate of water fugacity for Ti-rich phlogopite from Mt. Vulture, Potenza, Italy

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ABSTRACT

The crystal chemistry of Ti-rich phlogopite from deposits of the oldest activity (~740 ka) of Mt. Vulture, Potenza, Italy, was investigated to identify the substitution mechanisms in Ti-rich phlogopite and to determine its potential as a geohygrometer. Substitution mechanisms were determined by electron probe microanalysis (EPMA), single-crystal X-ray diffraction (SCXRD), Mössbauer spectroscopy, and micro-Fourier transform infrared (FTIR) spectroscopy. Magnetite and sanidine from the mica-rich host rocks were also analyzed. Use of the biotite-magnetite-sanidine geohygrometer in these volcanics (essentially trachytic-phonolitic ignimbrites) is exploited.

All investigated phlogopite samples consist of the 1M polytype, with $5.3275(2) \leq a \leq 5.3635(4)$ Å, $9.2211(4) \leq b \leq 9.2958(8)$ Å, $10.1211(5) \leq c \leq 10.281(1)$ Å, and $99.980(3) \leq \beta \leq 100.097(2)^\circ$. Structure refinements in space group *C2/m* converged to $2.42 \leq R_1 \leq 4.00\%$ and $2.04 \leq wR_2 \leq 4.50\%$. $^{57}\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ from Mössbauer analyses ranged from 34(1)–89(1)%. The main bands in the OH-stretching region are 3709, 3682, and 3658 cm^{-1} , and were assigned to 3Mg-OH-K-OH⁻, 3Mg-OH-K-O²⁻, and 2MgFe³⁺-OH-K-O²⁻ local configurations, respectively. The overall crystal chemical features are compatible with the M³⁺-Tschermak substitutions ($^{\text{VI}}\text{M}^{2+} + ^{\text{IV}}\text{Si}^{4+} \leftrightarrow ^{\text{VI}}\text{M}^{3+} + ^{\text{IV}}\text{Al}$, with M³⁺ = Al, Fe³⁺), M³⁺-oxy [$^{\text{VI}}\text{M}^{2+} + (\text{OH})^- \leftrightarrow \text{M}^{3+} + (\text{O})^{2-} + \frac{1}{2}\text{H}_2\uparrow$] and Ti-oxy substitutions [$^{\text{VI}}\text{M}^{2+} + 2(\text{OH})^- \rightarrow ^{\text{VI}}\text{Ti}^{4+} + 2(\text{O})^{2-} + \text{H}_2\uparrow$]. The magnetite composition varies between Mt₈₂Uv₁₈ and Mt₉₃Uv₀₇, whereas the proportion of orthoclase with respect to albite plus anorthite is $0.77 \leq X_{\text{Or}} \leq 0.82$. A partly ionic model was used to estimate annite activity, starting from experimentally determined substitutions in phlogopite. The resulting water fugacity was an order of magnitude lower than that calculated using stoichiometry to determine the phlogopite formula. The results are consistent with the occurrence of a well-developed hydrothermal system that altered the magmatic oxygen fugacity conditions at Mt. Vulture.

Keywords: Ti-phlogopite, crystal chemistry, Mössbauer spectroscopy, FTIR spectroscopy, geohygrometer