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) ≤ a ≤ 5.3635(4) Å, 9.2211(4) ≤ b ≤ 9.2958(8) Å, 10.1211(5) ≤ c ≤ 10.281(1) Å, and 99.980(3) ≤ β ≤ 100.097(2)°. Structure refinements in space group C2/m converged to 2.42 ≤ R ≤ 4.00% and 2.04 ≤ wR ≤ 4.50%. 15Feiv/Feox 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-KOH, 3Mg-OH-K-O²-, and 2MgFe³⁺-OH-K-O²⁻ local configurations, respectively. The overall crystal chemical features are compatible with the MV⁺-Tschermak substitutions [V⁺M²⁺ + IVSi⁴⁺ ↔ V⁺M³⁺ + IVAl, with M⁺ = Al,Fe³⁺], M⁺-oxy [V⁺M²⁺ + (OH) ↔ M⁺²⁺ + (O)²⁻ + ½H₂↑] and Ti-oxy substitutions [V⁺M²⁺ + 2(OH) ↔ V⁺Ti⁴⁺ + 2(O)²⁻ + H₂↑]. The magnetite composition varies between M₉₆UV₁₈ and M₉₆UV₀₇, whereas the proportion of orthoclase with respect to albite plus anorthite is 0.77 ≤ Xₒ ≤ 0.82. A partly ionic model was used to estimate aninite 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

INTRODUCTION

Micas are ubiquitous in the Earth’s crust and can also be found in the upper and lower mantle, in association with other minerals. Micas, regarded as H₂O reservoirs, play a key role in the storage and release of water in the Earth’s mantle through complex reactions (Virgo and Popp 2000). Triocahedral micas are of special interest because they are common phases in metamorphic, sedimentary, and igneous rocks. Therefore, many recent papers are dedicated to determining relationships between crystal chemistry and petrogenesis. For example, the geobarometric and geothermometric potential of triocahedral micas of metamorphic origin has been explored in detail by several authors (Cesare et al. 2003, 2008; Henry et al. 2005 and references therein). In particular, Henry et al. (2005) calibrated a Ti-saturated biotite geothermometer for low- to medium-pressure metapelitic biotite. This geothermometer was used for biotite from the Suwalki massif-type anorthosite (Poland) revealing crystallization temperatures within 729–874 °C (Namur et al. 2009).

Cesare et al. (2003) used a multimethodic approach, including Feiv⁺ and H direct measurements, to study Fe,Cl⁻-free and Ti-rich biotite from anatectic metapelites. The authors indicate that the Ti-oxy mechanism, V⁺M²⁺ + 2(OH) ↔ V⁺Ti⁴⁺ + 2(O)²⁻ + H₂↑ (where M²⁺ = Fe²⁺, Mg), is dominant for Ti-rich biotites equilibrated at high temperature (850 °C). However, halogen, Ti-rich biotites from metapelitic granulites that show reverse Ti-oxy substitutions, i.e., hydroxylation [Ti⁴⁺ + 2(O²⁻) → (Mg, Fe²⁺)₂ + 2(OH)] and fluorination [Ti⁴⁺ + 2(O²⁻) → (Mg, Fe)₂ + 2(F)] were proposed by Cesare et al. (2008). Sassi et al. (2008) found that Ti-oxy substitutions and Feiv⁺-oxy substitutions, V⁺M²⁺ + (OH) ↔ Feiv⁺ + (O)²⁻ + ½H₂↑, predominantly occur in biotites from H₂O-free or H₂O-poor petrologic environments, whereas the Ti-vacancy, 2V⁺M²⁺ ↔ V⁺Ti⁴⁺ + V⁰, is the dominant mechanism in biotite from H₂O-rich petrologic environments.

For micas of igneous origin, it is difficult to establish crystal chemistry/petrogenesis correlations. Some researchers have attempted to link biotite chemical features to the tectonic environment (Feldstein et al. 1996; Shabani et al. 2003). According to Virgo and Popp (2000), a complete biotite chemical analysis, including ferric, ferrous iron, and H₂O contents, is required to

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0003-004X/11/0809–1381S05.00/DOI: 10.2138/am.2011.3772 1381