Crystal chemistry and thermal behavior of Fe-carpholite from the Pollino Massif, southern Italy

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Abstract

The crystal chemistry and thermal behavior of Fe-carpholite from the Pollino Massif have been investigated by a multi-method approach. A combination of optical microscopy, scanning electron microscopy, μRaman spectroscopy, thermal analysis, room-temperature single-crystal X-ray diffraction, and high-temperature X-ray powder diffraction was employed.

Field and micromorphological observations showed that the studied carpholite occurs in veins embedded in fine-grained metapelites and coexist with quartz, calcite, chlorite, and phengite. In particular, the tiny carpholite crystals are closely associated with quartz, suggesting simultaneous formation.

Structure refinements from single-crystal X-ray diffraction confirm that carpholite crystallizes in the Ccce space group. Anisotropic refinements converged at 2.3 ≤ R (%) ≤ 2.6 and yielded unit-cell parameters a ~13.77 Å, b ~20.16 Å, c ~5.11 Å, and V ~1419 Å³. An XFe [i.e., the molar fraction Fe²⁺/(Mg²⁺Fe²⁺+Mn)] of ~0.6 was derived from the refined occupancy at the M1 site and is correlated to structural expansion mainly along the b and a axes and to geometrical distortions of the M1, M2, and M3 octahedra. μRaman spectrum of unoriented Fe-carpholite crystals exhibits several bands in the 200–1200 cm⁻¹ region, a strong peak at 3630 cm⁻¹ and a weak peak at 3593 cm⁻¹, the latter of which account for the presence of two independent OH groups, as also revealed by the X-ray structure refinement.

The TG curve indicates a total mass loss of 15.6% in the temperature range 30–1000 °C, and the DTA curve shows a broad endothermic band at ~400 °C, extending up to ~650 °C, and weak exothermic peaks at ~700 and 750 °C. The latter may be ascribed to the breakdown of the Fe-carpholite structure and crystallization of new phases. In situ high-temperature X-ray powder diffraction from 30 to 1105 °C revealed no significant changes in XRD patterns from 30 to 355 °C but reflection splittings from 380 °C due to a Fe-oxidation/deprotonation process. The carpholite and deprotonated carpholite phases coexist in the temperature range 380–580 °C, whereas only the deprotonated phase is observed up to 630 °C. Above this temperature, the carpholite structure collapses and the characteristic peaks of spinel and quartz phases are observed. At 1105 °C, spinel, mullite, garnet, cristobalite, and tridymite can be clearly identified. Our results provide insight into the thermal stability of Fe-carpholites and may help understand the thermal evolution of HP/LT metasediments.

Keywords: Fe-carpholite, crystal chemistry, thermal evolution, SEM, single-crystal XRD, high-temperature powder XRD, thermal analysis, μRaman spectroscopy

Introduction

The carpholite group encompasses hydrated inosilicates with general formula \( A_0.1M_1.2M_2.3 [(OH,F)_4 Si_2O_6]_2 \); where \( A = \Box, K, Ba, and Na \); \( M_1 = Mn, Mg, Fe, Al, Li, and Na \); \( M_2 = Al, V^{3+}, Fe^{3+} \); and Ti, and \( M_3 = Al, Mg, V^{3+}, Fe^{3+} \), and Ti (Basso and Carbone 2010). These minerals have a trellis structure based on pyroxene-like I-beam units \([Al,Si,O_6(OH,F)]^{14+}\), which are connected to side-ribbons, defining two different open channels running along the c direction. One of them hosts the \( A \) site, in the dodecahedral coordination, that may be empty or partially occupied by large cations. Similarities of this structure topology with that of the magbasite were recently described by Welch et al. (2014).

Carcpholites have been studied from the point of view of mineral chemistry by several authors since the first half of the 20th century (e.g., Mac Gillivray et al. 1956; Naumova et al. 1974; Goffé 1980; Theye et al. 1992; Oberhansli et al. 2001; Agard et al. 2005; Escuder-Viruete et al. 2011; Vitale et al. 2013 and references therein; Pourteau et al. 2014). From a crystal structure viewpoint, a complete description of carpholite, Mn-Al-Si-O(OH)₅, was provided by Lindemann et al. (1979), and the potassic-carpholite, (K, BOX)(Li,Mn)Al₂Si₂O₆(OH,F), was described by Ghose et al. (1989) and Tait et al. (2004). Basso et al. (2005) published the structure refinement of vanadio-carpholite, Mn(V³⁺,Al)₂Si₂O₆(OH)₅. Although the unit-cell...