

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

ERNESTO MESTO¹, SALVATORE LAURITA², MARIA LACALAMITA¹, ROSA SINISI², GIOVANNA RIZZO², EMANUELA SCHINGARO^{1,*}, AND GIOVANNI MONGELLI²

¹Dipartimento di Scienze della Terra e Geoambientali, Università di Bari Aldo Moro, via Orabona, 4, 70125 Bari, Italy

²Dipartimento di Scienze, Università degli Studi della Basilicata, viale Ateneo Lucano 10, 85100 Potenza, Italy

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, μ Raman 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 $2.3 \leq R (\%) \leq 2.6$ and yielded unit-cell parameters $a \sim 13.77 \text{ \AA}$, $b \sim 20.16 \text{ \AA}$, $c \sim 5.11 \text{ \AA}$, and $V \sim 1419 \text{ \AA}^3$. An X_{Fe} [i.e., the molar fraction $\text{Fe}^{2+}/(\text{Mg}+\text{Fe}^{2+}+\text{Mn})$] 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. μ Raman 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 two 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 – $1000 \text{ }^\circ\text{C}$, and the DTA curve shows a broad endothermic band at $\sim 400 \text{ }^\circ\text{C}$, extending up to $\sim 650 \text{ }^\circ\text{C}$, and weak exothermic peaks at ~ 700 and $750 \text{ }^\circ\text{C}$. The latter may be ascribed to the breakdown of the Fe-carpholite structure and crystallization of new phases. The *in situ* high-temperature X-ray powder diffraction from 30 to $1105 \text{ }^\circ\text{C}$ revealed no significant changes in XRD patterns from 30 to $355 \text{ }^\circ\text{C}$ but reflection splittings from $380 \text{ }^\circ\text{C}$ due to a Fe-oxidation/deprotonation process. The carpholite and deprotonated carpholite phases coexist in the temperature range 380 – $580 \text{ }^\circ\text{C}$, whereas only the deprotonated phase is observed up to $630 \text{ }^\circ\text{C}$. Above this temperature, the carpholite structure collapses and the characteristic peaks of spinel and quartz phases are observed. At $1105 \text{ }^\circ\text{C}$, 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, μ Raman spectroscopy