Cation ordering in Pb\(^{2+}\)-bearing, Mn\(^{3+}\)-rich pargasite from Långban, Sweden

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ABSTRACT

A multi-analytical approach using electron microprobe analysis, X-ray structural refinement, and polarized single-crystal Fourier transform infrared spectroscopy was used to characterize short-range and long-range structures of a Pb\(^{2+}\)-bearing, Mn\(^{3+}\)-rich pargasite. Site populations, derived from the results of site-scattering refinement and stereochemoanalytical analysis, demonstrate that Pb\(^{2+}\) is strongly ordered at the A-site in the monoclinic \(2C/m\) amphibole structure. This finding is in agreement with the observed ordering of Pb\(^{2+}\) in the rare Pb\(^{2+}\)-bearing \(P2_1/a\) amphibole joesmithite, but is in contrast to a Pb\(^{2+}\) preference for the M4 site suggested by some studies on element partitioning between \(2C/m\) amphiboles and melts. Mn\(^{3+}\) is strongly ordered at the M2 site in structure of the present amphibole. Contrasting results obtained for mean M2-O bond lengths and reported local Mn\(^{3+}\)-O bond lengths as well as between bond-length distortion of the mean M2 polyhedron and the local Mn\(^{3+}\)-centered M2O\(_6\) octahedron in pargasite indicates that the structural relaxation of this polyhedron is complete or nearly so.

Keywords: Amphibole, pargasite, lead, manganese, structure refinement, IR spectroscopy

INTRODUCTION

The \(2C/m\) symmetry is by far the most common structure-type in which amphibole supergroup minerals crystallize. The wide range of chemical compositions encountered in these amphiboles suggests that this is the most flexible of the six known amphibole structure-types.

In a recent report on an unusual Mn\(^{3+}\)- and Pb-bearing pargasite from the famous Långban deposit (Jonsson and Hälenius 2010), it was suggested, on the basis of results obtained by optical absorption spectroscopy, that Mn\(^{3+}\) was ordered at the M2 site of the amphibole structure. This suggestion agrees with the observed strong ordering of trivalent transition metal cations at the M2 sites in the majority of clino-amphiboles (e.g., Ghose et al. 1986; Oberti et al. 1993). So far, the oxy-amphiboles ungarrettite, obertiite, and dellaventuraite with trivalent transition elements as, e.g., fluorine. The matrix corrections were performed according to the Armstrong-CITZAF method (Armstrong 1995). The amphibole formula was calculated assuming 46 negative charges per formula unit (Table 1).

Experimental methods

One selected gem quality, ca. \(150 \times 200 \times 100 \mu m\), pargasite single crystal from the original specimen (NRM 20100001) described by Jonsson and Hälenius (2010) was used in the present investigation. The same crystal was studied by means of X-ray single-crystal diffraction, subsequently Fourier transform infrared spectroscopy in the OH stretching frequency range and finally chemical analysis by electron microprobe techniques.

Electron microprobe analysis

The chemical composition of the studied crystal was determined by means of electron microprobe techniques (EMP), using a Jeol JXA-8530F Hyperprobe equipped with four wavelength dispersive spectrometers and a field emission gun operated at 15 kV accelerating potential and 10 nA beam current at a beam diameter of 1 \(\mu m\). Element standards used were albite (Na), orthoclase (K), Al\(_2\)O\(_3\) (Al), CaSi\(_2\)O\(_6\) (Ca and Si), MgO (Mg), MnTiO\(_3\) (Mn and Ti), Fe\(_2\)O\(_3\) (Fe), and vanadinite (Pb). Wavelength dispersive scans revealed no detectable amounts of any additional elements as, e.g., fluorine. The matrix corrections were performed according to the Armstrong-CITZAF method (Armstrong 1995). The amphibole formula was calculated assuming 46 negative charges per formula unit (Table 1).

X-ray structure refinement

X-ray diffraction measurements were performed at the Earth Sciences Department, Sapienza University of Rome, with a Bruker KAPPA APEX-II single-crystal diffractometer, equipped with CCD area detector (6.2 \(\times\) 6.2 cm\(^2\) active detection area, 512 \(\times\) 512 pixels) and a graphite crystal monochromator, using MoK\(_\alpha\) radiation.