Experimental Report

30/09/2013

Proposal: **5-11-396** **Council:** 4/2012

Title: New insight into the crystal structure of vermiculite : (Mg,Fe3+,Al)3(Si,Al)4O10(OH)2 x 4H2O

This proposal is a new proposal

Research Area:

Main proposer: **GATTA G. Diego**

Experimental Team:

Local Contact: NENERT Gwilherm

Samples: Vermiculite (natural), (Mg,Fe3+,Al)3(Si,Al)4O10(OH)2 x 4H2O

Instrument	Req. Days	All. Days	From	To
D9	10	5	22/05/2013	27/05/2013

Abstract:

Vermiculite is a clay mineral, ideally (Mg,Fe3+,Al)3(Si,Al)4O10(OH)2.24H2O. It is a limited expansion clay with a medium shrink-swell capacity, and has a high cation exchange capacity, leading to a broad spectrum of commercial uses. Previous studies on the crystal structure of vermiculite did not provide: 1) a unique interpretation of the crystal chemistry of the interlayer region, 3) a reliable picture about the Mg-Al-Fe and Si-Al ordering at the octahedral and tetrahedral sites, respectively; 4) the location of the H sites. Hydroxyl orientation has a strong influence on the strength of the ionic intra-layer bonding in layered-materials, and can play an important role in the thermal behaviour of this clay mineral. We selected four large, and rare, single-crystals of natural vermiculite suitable for neutron diffraction. The quality of the crystals was already checked at room conditions by single-crystal X-ray diffraction. We require 10 days beam time on D9 (or D19) for two data collections at 298 and 20 K, respectively, in order to provide two neutron structure refinements of vermiculite with a clear picture of the H-bond configuration and of the octahedral/tetrahedral ordering

New insight into the crystal structure of vermiculite and Li,Be-mica

Experiment n°: 5-11-396

In the framework of a series of studies on the crystal structure of phyllosilicates (Gatta et al., 2011a, 2011b and references therein), the crystal chemistry and crystal structure of a vermiculite from Brinton's Quarry (Pennsylvania, USA) and a Li,Be-bearing mica from the Harding pegmatite (Dixon, Taos Co., New Mexico) have been investigated by constant-wavelength single-crystal neutron diffraction at 20 K inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Single-crystal neutron diffraction data of vermiculite and Li,Be-mica were collected on the high resolution four-circle diffractometer D9 at ILL, with a wavelength of 0.8242(1) Å obtained using the (220) reflection of a new diamond monochromator operating in transmission geometry. The wavelength was calibrated using a germanium single crystal. D9 is equipped with a small two-dimensional area detector, which allows optimal delineation of the peak from the background. The diffraction pattern of the vermiculite crystals show a severe structure disorder, as often observed in this class of materials, hindering a structure refinement. On the contrary, Li,Be-mica crystals had a better quality. A total number of 2626 reflections were collected up to $2\theta_{max} = 79.54°$ from a Li,Be-mica crystal (3.7 x 3.1 x 1.1 mm). For all data, background corrections and Lorentz corrections were applied. Least-squares matching of the observed and calculated centroids of the 896 strongest reflections gave a metrically monoclinic unit cell with: a = 5.0590(4), b = 8.7909(9), c = 19.0176(18) Å and β = 95.459(7) °, with a *C*-centered lattice. The neutron intensity data show that the "average" symmetry of the Li,Be-bearing brittle mica of this study is monoclinic *C*2/*c*. The statistics of distributions of the normalized structure factors suggest that the structure is centrosymmetric (at ~90% likelihood). Two neutron structure refinements were performed in the space group *Cc* (R_1 = 0.0506, 107 ref. parameters and 2239 obs. refl.) and *C*2/*c* (R_1 = 0.070, 113 ref. parameters and 1386 obs. refl.). The Li,Be-mica has a "hybrid" nature of partially di-octahedral and partially tri-octahedral. The neutron structure refinement in the space group *Cc* provides a picture about the (Al,Be,Si)-tetrahedral ordering: the best fit of the refinement was reached with the *T*1 and *T*4 sites occupied by (Be + Al) and *T*2 and *T*3 fully occupied by Si. This leads to a final population of $^{T}(Al_{1.88}Be_{0.12}Si_{2.00})_{\Sigma 4.00}$ *p.f.u.*, in a reasonable agreement with the chemical analysis (see below). The *M*1 site is virtually empty in di-octahedral micas; the neutron refinement provides an unambigous evidence of the occurrence of Li at the *M*1 site. The refined fraction of Li at the *M*1 site ranges between 0.27 - 0.29 *a.p.f.u.*, in excellent agreement with the chemical analysis (see below). The presence of Li, at least at a significant level, at the *M*2 (and *M*3) site can be ruled out, as a full site occupancy with the scattering length of Al was obtained. The location of the H sites and the complex hydrogen-bonding scheme can be now described.

The chemical composition based on ICP-AES analysis leads to the following chemical formula (calculated on the basis of 12 oxygen atoms): ${}^{Ca}(Na_{0.26}K_{0.04}Ca_{0.69})_{\Sigma 0.99}{}^{M}(Li_{0.29}Mg_{0.03}Fe^{3+}_{0.02}Al_{1.78})_{\Sigma 2.12}{}^{T}(Al_{1.73}Be_{0.16}Si_{2.11})_{\Sigma 4.00}O_{12}H_{2.53}$. The virtual excess of H is likely due to the fact that the fraction of H_2O was assumed by difference to 100 wt%, and slightly overestimated.

Further details about the experimental methods and structure refinements are in Gatta et al. (2013).

References

Gatta, G.D., McIntyre, G.J., Sassi, R., Rotiroti, N., and Pavese, A. (2011a) Hydrogen-bond and cation partitioning in 2*M*$_1$-muscovite: A single-crystal neutron-diffraction study at 295 and 20 K. *American Mineral*ogist, **96**, 34-41.

Gatta, G.D., Merlini, M., Rotiroti, N., Curetti, N., and Pavese, A. (2011b) On the crystal chemistry and elastic behavior of a phlogopite 3*T*. *Physics and Chemistry of Minerals*, **38**, 655-664.

Gatta G.D., Nénert G., Guastella G., Lotti P., Guastoni A., Rizzato S. (2013) A single-crystal neutron and X-ray diffraction study of a Li,Be-bearing brittle mica. *Mineralogical Magazine* (under review).