Experimental report

31/05/2022

Proposal:	**5-11-447**	**Council:**	4/2021

Title: On the labyrinthine world of natural borates: H-bonding network in probertite, $NaCaB_5O_7(OH)_4 \times 3H_2O$

Research area: Other...

This proposal is a resubmission of 5-11-442

Main proposer: **Giacomo Diego GATTA**

Experimental team: Oscar Ramon FABELO ROSA

Local contacts: Maria Teresa FERNANDEZ DIAZ
Oscar Ramon FABELO ROSA

Samples: $(NH_4)_2Mg(SO_4)_2\ 6H_2O$

Instrument	Requested days	Allocated days	From	To
D9	10	0		
D19	5	5	07/07/2021	12/07/2021

Abstract:

Probertite, $NaCaB_5O_7(OH)_4x3H_2O$, is a complex hydrous borate mineral that is a common constituent of borate deposits. Despite the geochemical and industrial interest on this mineral (as source of B, it contains 50 wt%B_2O_3), only a few studies were devoted to it. Its structure was solved years ago (Rumanova et al. 1966, Menchetti et al. 1982), by single-crystal X-ray diffraction, and no more recent data are available. The aim of the present study is a reinvestigation of the crystal structure/chemistry of probertite by single-crystal neutron diffraction (20 K) and other tecniques, in order to provide:

a) an unambiguous location of all the proton sites and the description of the complex H-bonding network expected in probertite structure, along its low-T induced rearrangement;

b) the anisotropic displacement parameters of all the atomic sites, Hs included;

c) a more robust description of B-coordination environment (e.g., aplanarity of the $BO_2(OH)$-group, tetrahedral distortion of the $BO_3(OH)$- and $BO_2(OH)_2$-groups);

d) a description of the crystal chemistry of this mineral based on modern analytical protocol, with a particular attention to the potential B-, Ca- and Na-substituents.

Experimental Report: “On the labyrinthine world of natural borates: H-bonding network in probertite, $NaCaB_5O_7(OH)_4{\cdot}3H_2O$”

Proposal number 5-11-447
Main proposer Giacomo Diego GATTA
Co-proposer(s) Davide COMBONI ESRF, GRENOBLE FR
Local contact Maria Teresa FERNANDEZ DIAZ, Oscar Ramon FABELO ROSA

Probertite is one of the hydrous borates, with ideal chemical formula $CaNa[B_5O_7(OH)_4]{\cdot}3H_2O$, usually found in sedimentary borate deposits. This mineral is known since the beginning of the nineteenth century. The first studies on this mineral were conducted by Eakle (1929), who provide the first chemical analysis of probertite, and by Barnes (1949) and Clark and Christ (1959), who reported the unit-cell parameters and the potential space group by single-crystal X-ray diffraction. The first (H-free) structural model of probertite was reported by Rumanova et al. (1966), on the basis of X-ray intensity data collected by Weissemberg method, and later reinvestigated and improved by Menchetti et al. (1982), using a single-crystal four-circle X-ray diffractometer, in the space group $P2_1/c$ with $a \cong 6.59$, $b \cong 12.56$, $c \cong 13.43$ Å, and $\beta \cong 99.97°$. Surprisingly, there is almost no data, based on modern standards, about the chemical composition of probertite. The aim of this study is a reinvestigation of the crystal-chemistry of probertite, as one of naturally-occurring borates with the highest B-content (~50 wt% B_2O_3), by a multi-methodological approach based on single-crystal X-ray (at room conditions) and neutron diffraction (at low temperature: 20 K), electron microprobe analysis in wavelength-dispersive mode (EPMA-WDS) along with laser ablation - inductively mass spectrometry (LA-ICP-MS) and LA-multi collectors ICP-MS (LA-MC-ICP-MS), in order to provide: a) the chemical composition of probertite in terms of major, minor and trace components, along with the isotopic signature of B, b) the description of the B-coordination environment (*e.g.*, aplanarity of the triangular $BO_2(OH)$-group, polyhedral distortion of the tetrahedral $BO_2(OH)_2$-groups) and c) the location of all the proton sites, the description of their vibrational regime and the complex H-bonding scheme. As probertite contains B, OH-groups and H_2O molecules (for a total of 25.7 wt% H_2O), it is an excellent candidate for a neutron diffraction investigation.

Neutron diffraction data were collected (at low temperature) using a large single crystal of probertite of 3.1 x 1.5 x 1.5 mm^3, on the four-circle diffractometer D9 at the Institut Laue-Langevin (ILL), Grenoble, France. The crystal was glued at the top of an aluminium pin and placed on a close-circuit displex device operated at 20(1) K (Archer and Lehmann 1986). The experiment was conducted with a wavelength of 0.8359 Å, obtained from a Cu(220) monochromator, and a small two-dimensional area detector. The data collection strategy consisted of a series of ω-scans (for low-

Q reflections) or ω-2θ scans (for high-*Q* reflections), with ω-range varying as a function of the instrument resolution curve. A total number of 2171 unique reflections were collected (with $0 \leq h \leq +9$, $0 \leq k \leq +17$ and $-18 \leq l \leq +18$), ($R_\sigma = 0.0536$), all with $I_o > 2\sigma(I_o)$, with $d_{min} = 0.71$ Å. Integration of the reflections intensity, along with background and Lorentz factor correction, were done with the *Racer* program (written by Clive Wilkinson and Garry McIntyre, ILL integration program suite). Absorption correction was applied, on the basis of shape of the crystal and its composition, using the ILL program *Datap* (the current version of this program is available online). The lattice was found to be metrically monoclinic, with $a = 6.578(3)$, $b = 12.508(3)$, $c = 13.369(5)$ Å, $\beta = 99.93(3)°$ and $V = 1083.4(7)$ Å^3, and the reflection conditions were found to be consistent with the space group $P2_1/c$, in agreement with the previous X-ray experimental findings. Additional details pertaining to the neutron diffraction data are given in the manuscript by Gatta et al. (2022).

The crystal-structure refinement based on the neutron (collected at 20 K) intensity data was conducted in the space group $P2_1/c$ using the SHELXL-97 software (Sheldrick 1997, 2008). Neutron scattering lengths of Na, Ca, B, O and H were taken from Sears (1986). In order to correct the secondary isotropic extinction effect, the formalism of Larson (1967) was used. The starting structural model was that of Menchetti et al. (1982), without any H site. After the first cycles of refinement (with anisotropic displacement parameters), convergence was rapidly achieved, with a series of negative residual peaks in the final difference-Fourier map of the nuclear density. The negative residual peaks observed in the difference-Fourier map of the nuclear density were assigned to the H sites for the next cycles of refinement, as H has a negative neutron scattering length. Ten independent H sites were located, all with realistic H-bonding schemes. With such a complete structure model, convergence was rapidly achieved, the variance-covariance matrix showed no evidence of significant correlation among the refined parameters, and the residuals in the difference-Fourier maps (of nuclear or electron density) were not significant. All the principal mean-square atomic displacement parameters were positive (including those for the H sites for the neutron refinement) and the final $R_1(F)$ was equal to 0.0566 (for 2171obs./281par.) for the neutron refinement. Additional details pertaining to structure refinements are given in Gatta et al. (2022). The structure model based on the neutron refinement is shown in Fig. 1.

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Figure 1. The H-bonding network into the crystal structure of probertite. Displacement ellipsoid probability factor: 70%.