CONTRIBUTIONS TO THE 6th INTERNATIONAL SYMPOSIUM ON GRANITIC PEGMATITES

EDITORS

WILLIAM B. SIMMONS

KAREN L. WEBBER

ALEXANDER U. FALSTER

ENCARNACIÓN RODA-ROBLES

SARAH L. HANSON

MARÍA FLORENCIA MÁRQUEZ-ZAVALÍA

MIGUEL ÁNGEL Galliski

GUEST EDITORS

ANDREW P. BOUDREAUX

KIMBERLY T. CLARK

MYLES M. FELCH

KAREN L. MARCHAL

LEAH R. GRASSI

JON GUIDRY

SUSANNA T. KREINIK

C. MARK JOHNSON

A SINGLE-CRYSTAL NEUTRONS DIFFRACTION STUDY OF BRAZILIANITE, NaAl$_3$(PO$_4$)$_2$(OH)$_4$

P. Vignola[1], G. Gatta[1], M. Meven[2,3]

[1] Dipartimento di Scienze della Terra, Universita' di Milano, Via Botticelli 23, I-20133 Milano, Italy
[2] Institut für Kristallographie, RWTH Aachen, Jägerstrasse 17-19, 52056 Aachen, Germany
[3] Jülich Centre for Neutron Science – Outstation at FRM II, Lichtenbergstrasse 1, 85747 Garching, Germany

Brazilianite, ideally NaAl$_3$(PO$_4$)$_2$(OH)$_4$, typically forms equant to elongated monoclinic crystals with yellow to yellowish-green color. In Brazil many gem quality locations for brazilianite are known along the Rio Doce valley mainly in Minas Gerais. Brazilianite occurs as single-crystals or groups up to 20 cm growing in large pockets in the platy albite (cleavelandite) unit of zoned and complex granitic pegmatites. In granitic pegmatites brazilianite is considered a common product of alteration of montebrasite-amblygonite under Na-metasomatic conditions (Simmons *et al.* 2003). Thus far, only a few studies have been devoted to the crystal chemistry of brazilianite (Frondel and Lindberg 1948). Its crystal structure was solved by Gatehouse and Miskin (1974), on the basis of single-crystal X-ray diffraction data, in the space group $P2_1/n$, with a~11.23, b~10.14, c~7.10, and β~97.4° ($Z = 4$). Its structure consists of chains of edge-sharing Al-octahedra linked by P-tetrahedra forming a three-dimensional network, with Na atoms located in cavities parallel to [100]. In the structure model of Gatehouse and Miskin (1974), there are two different configurations of the Al-octahedra: *trans*-AlO$_4$(OH)$_2$ and *trans*-AlO$_3$(OH)$_3$.

The crystal structure of brazilianite has been reinvestigated by means of single-crystal X-ray and neutron diffraction. A prismatic, elongated, single-crystal of pale yellow, gem-quality brazilianite, up to 18 mm in length and 5 mm in diameter, coming from the Telírio pegmatite, Linópolis, Divino das Laranjeiras district (Minas Gerais, Brazil), was used for diffraction experiments and chemical analysis. The brazilianite crystal was taken from a specimen constituted by 4 gem-quality crystals of brazilianite up to 20 mm perched on platy albite (sample of 3x3x2 cm of cleavelandite) and closely associated to zanazziite crystals up to 3 mm. The WDS electron-microprobe analysis shows that our sample of brazilianite from the Telírio claim is homogeneous and approaches an almost ideal composition with the following empirical formula: (Na$_{0.955}$Mg$_{0.003}$Ca$_{0.002}$Sr$_{0.002}$K$_{0.001}$)$_{\sum 0.963}$(Al$_{3.007}$Fe$^{3+}_{0.002}$)$_{\sum 3.009}$(PO$_4$)$_2$(OH)$_4$. The single-crystal X-ray and neutron structure refinement of this study confirm the general structure model of brazilianite described

by Gatehouse and Miskin (1974). The building-block units of the brazilianite structure consist of chains of edge sharing *trans*-AlO$_4$(OH)$_2$ [*i.e.* around Al(2)] and *trans*-AlO$_3$(OH)$_3$ [*i.e.* about Al(1) and Al(3)] octahedra. The two chains are connected, via corner-sharing, by P-tetrahedra to form a three-dimensional framework, with Na atoms located in distorted cavities running along [100]. The Na-polyhedron, here described with a coordination number of 9 (with Na-O$_{max}$ ~ 3.11 Å), is strongly distorted. Gatehouse and Miskin (1974) suggested that the distortion of the Na-polyhedron might be due to the H sites in the [100]-cavity: the effect of mutual repulsion forces the Na site to one side of the cavity, leading to a stronger Na-O interaction with oxygen sites on one side of the cavity than on the other. This can now be confirmed by our neutron structure refinement, as Na – H(4) distance is ~3.06 Å, Na – H(3) is ~3.16 Å and Na – H(2) is ~3.21 Å, and H(4), H(3) and H(2) lie on the same side of the cavity. Both the X-ray and neutron structure refinements show that the Al-octahedra appear to be significantly distorted, with Δ[Al(1)-O]$_{max}$ ~ 0.32 Å, Δ[Al(2)-O]$_{max}$ ~ 0.31 Å, and Δ[Al(3)-O]$_{max}$ ~ 0.17 Å (*i.e.* the difference between the longest and the shortest Al-O distances, based on the X-ray structure refinement). The longest Al-O bond distances are those with the bridging oxygen shared between two Al-octahedra and one P-tetrahedron. The shortest Al-O bond distances are those with oxygen of OH-groups. P-tetrahedra appear to be less distorted, as Δ[P(1)-O]$_{max}$ ~ 0.044 Å and Δ[P(2)-O]$_{max}$ ~ 0.036 Å (*i.e.* the difference between the longest and the shortest P-O distances, based on the X-ray structure refinement). The neutron structure refinement of this study provides an unambiguous location of the H-sites, allowing the description of the H-bonding scheme in brazilianite structure. Five independent H sites have been located, here labelled as H(1), H(2a), H(2b), H(3) and H(4). The configuration of the OH groups (*i.e.* O(1)–H(1), O(2)–H(2a), O(2)–H(2b), O(3)–H(3), O(4)–H(4)), along with the hydrogen bonding scheme, are now well defined (Fig. 1). O(1), O(2), O(3) and O(4) act as *donors*, whereas O(2), O(4), O(9) and O(12) as *acceptors*.

Symmetry-related O(2) act both as *donor* and as for "riding motion" (Busing and Levy 1964), range between ~0.992 and ~1.010 Å, the O···O distances between ~2.67 and ~2.93 Å, and the O–H···O angles between ~151 and ~174° (Table 5). The H(2a) and H(2b) are only ~1.37 Å apart. The neutron structure refinement was conducted without any restrain on the site occupancy factor (*s.o.f.*) of H(2a) and H(2b), leading to *s.o.f.* (H2a) = 0.546(6) and *s.o.f.* (H2b) = 0.446(6), respectively. We can thus consider a general *s.o.f.* of 50% of both H(2a) and H(2b), and so the two H-sites are mutually exclusive. Additional test refinements have been

acceptor of H-bond. The O-H distances corrected performed in order to check if this H-site split reflects a lower symmetry than $P2_1/n$, but unsuccessfully. The key to understanding the split in two mutually exclusive H(2a) and H(2b) sites is in the H-bonding scheme of the structure. In fact, if only one "virtual" H(2) site occurs, located between H(2a) and H(2b), it should have an H-bond configuration energetically not favourable with O(2)-H(2)·O(9) ~ 113° and O(2)-H(2)···O(2) ~ 127°, whereas O(2)-H(2a)···O(9) ~ 151° and O(2)-H(2b)···O(2) ~171°.
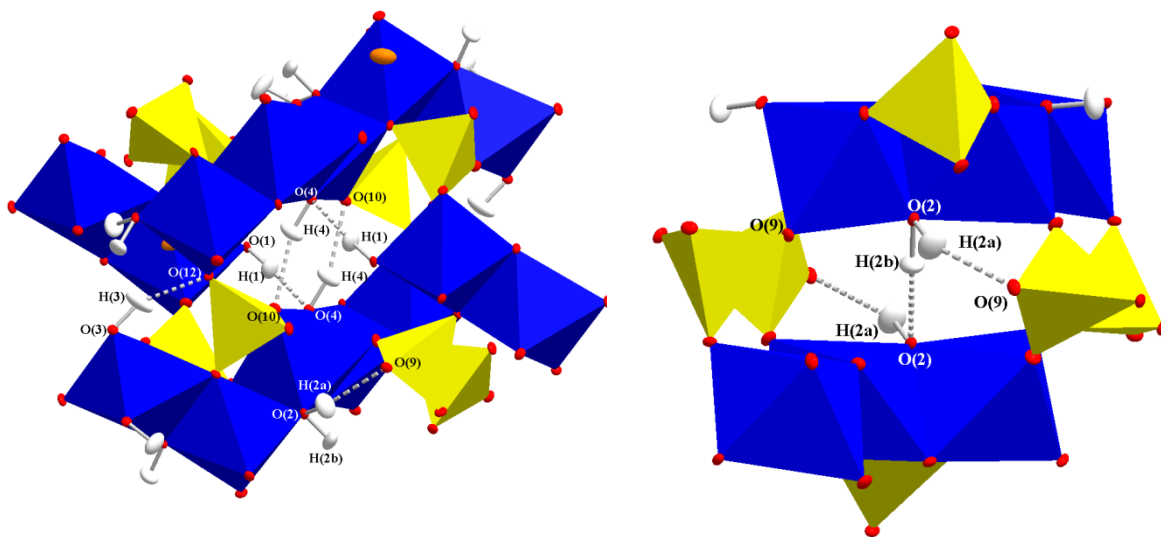

Fig. 1: Hydrogen site locations and, H-bonding scheme in the structure of brazilianite based on the neutron structure refinement of this study. The sites H2a and H2b are mutually exclusive. Thermal ellipsoid probability factor: 60%.

References:

Busing W.R., Levy H.A. (1964): The effect of thermal motion on the estimation of bond lengths from diffraction measurements. Acta Crystallographica, 17, 142-146.

Frondel, C., Lindberg, M.L. (1948) Second occurrence of brazilianite. American Mineralogist, 33, 135–141.

Gatehouse, B.M., Miskin, B.K. (1974): The crystal structure of brazilianite, $NaAl_3(PO_4)_2(OH)_4$. Acta Crystallographica, 30, 1311–1317.

Simmons, W.B., Webber, K.L., Falster, A.U. & Nizamoff J.W. (2003) Pegmatology: pegmatite mineralogy, petrology & petrogenesis. Rubellite Press, New Orleans.