

THE CRYSTAL STRUCTURE OF MOYDITE

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ABSTRACT

The new species moydite, (Y, REE) [B(OH)₄] (CO₃), orthorhombic *Pbca* (No. 61) with $Z = 8$, described in the preceding paper, has had its cell dimensions refined to a 9.089(1), b 12.244(1), c 8.926(1) Å and its novel crystal-structure solved by direct methods, then refined by difference-Fourier synthesis, on 1278 observed (3σ) reflections, to residuals $R = 5.1\%$ and $wR = 3.7\%$. It has a layered structure, with sheets of corner-sharing YO₉ polyhedra, reinforced by trigonal planar carbonate groups. Successive sheets are linked by isolated B(OH)₄ tetrahedra, which attach themselves to them by opposite edges. The results of the crystal-structure analysis were instrumental in confirming the chemical composition of moydite.

Keywords: moydite, novel crystal structure, borate, carbonate, light element.

SOMMAIRE

La moydite (Y, REE) [B(OH)₄] (CO₃) est une nouvelle espèce orthorhombique, de groupe spatial *Pbca* (n° 61) et $Z = 8$, décrite dans l'article précédent. Sa maille a été affinée: a 9.089(1), b 12.244(1), c 8.926(1) Å. Sa structure cristalline, d'un type nouveau, a été résolue par méthodes directes et affinée ensuite, par la méthode de Fourier-différence, sur 1278 réflexions observées (3σ), jusqu'aux résidus $R = 5.1\%$ et R (pondéré) = 3.7%. C'est une structure en couches, dans laquelle des feuillettes de polyèdres YO₉ à sommets communs sont renforcés par des groupements plans CO₃. Les feuillettes successifs sont reliés par des tétraèdres isolés B(OH)₄, qui s'y attachent par deux arêtes opposées. L'analyse de la structure a confirmé la composition chimique.

Mots-clés: moydite, nouvelle structure cristalline, borate, carbonate, élément léger.

INTRODUCTION

Moydite, a new mineral species from the Evans-Lou pegmatite, Papineau Co., Quebec, is described by Grice *et al.* (1986). The authors commenced the crystal-structure determination of moydite knowing the rare-earth-element and yttrium concentrations. The presence of the light elements hydrogen, boron and carbon was known from the initial ion-microprobe results, but relative amounts were uncertain. The success of the structure analysis, supported by subsequent electron-microprobe results, gives credence to this method as a technique to determine chemical composition.

EXPERIMENTAL

A crystal fragment chosen from the type material of moydite (NMNS #50771) and measuring $0.25 \times 0.20 \times 0.05$ mm was used for the data collection. X-ray-diffraction spots on precession photographs are sharp and single for this crystal. Interpretation of these photographs indicates orthorhombic symmetry, with the unique space-group $P2_1/b2_1/c2_1/a$. Intensity data were collected on a fully automated, Nicolet R3m four-circle diffractometer operating at 50 kV and 40 mA with graphite-monochromated MoK α radiation. A set of 25 intense reflections was used to centre the crystal and subsequently refine the cell dimensions: a 9.089(1), b 12.244(1) and c 8.926(1) Å. A unique set of intensity data up to $2\theta = 60^\circ$ was collected by the $\theta:2\theta$ scanning mode with a scan range of $2^\circ 2\theta$ plus the α_1 - α_2 separation, and scan speeds inversely proportional to intensity, varying from 4 to $29.3^\circ/\text{minute}$. Two standard reflections were monitored every 46 measured reflections to check crystal orientation, crystal decrepitation and beam intensity. The crystal remained stable in the X-ray beam, and all fluctuations were within $\pm 2\%$. Of the 1496 intensities collected, 1278 were considered observed ($I > 3\sigma$).

Reduction of the intensity data and refinement of the structure were done by the SHELXTL package of programs. Data reduction included background, scaling, Lorentz and polarization and absorption corrections. For the absorption correction, 12 intense diffraction maxima over the 2θ range of 9 to 56° were chosen for ψ -diffraction-vector scans after the method of North *et al.* (1968). The ψ -scan set of intensity data was used to refine a thin-plate empirical absorption-correction. Absorption correction reduced the merging R of the ψ -scan data set from 14.5 to 1.7% which, when applied to the whole dataset, resulted in relative minimum and maximum transmissions of 0.240 and 0.646.

CRYSTAL-STRUCTURE ANALYSIS

The phasing of a set of normalized structure-factors gave a unique E-map with the co-ordinates of the single heavy atom (Y, REE). The positional and thermal parameters of this general site alone were refined to give a residual index $R = 26\%$. From this initial model a series of refinements, with difference-Fourier maps, showed additional atomic

sites that were arbitrarily assigned the scattering factors for oxygen. At $R = 16\%$ with a Y and nine "O" sites, it became important to differentiate between the light atoms B, C and O; this was facilitated by studying bond lengths associated with the various sites.

Average cation-oxygen bond lengths from other mineral structures with their corresponding co-ordinations [] are: C[III] = 1.25 Å, B[III] = 1.35 Å, B[IV] = 1.50 Å, and Y[IX] = 2.50 Å. These differences in bond lengths made it relatively easy to identify the cation sites, and it became apparent there was one Y, one B, one C and seven O sites, each in a general position with a multiplicity of eight. This model refined to $R = 6.0\%$, and gave the first solid evidence as to the cell contents: (Y,REE) $H_4BO_4(CO_3)_3$, with $Z = 8$. The presence of H was known from the ion-microprobe scans, but the required number of H atoms, four, came from charge-balance considerations.

The final steps of the least-squares refinement involved a model of anisotropic thermal vibration, which slightly reduced R to 5.2%. At this stage in the crystal-structure refinement, the ΔF synthesis map was relatively smooth, with only minor differences in electron density ($\sim 1 e^-/\text{\AA}^3$) associated with the Y site. There was no positive indication of the H sites.

The absorption edge of Y, $\lambda = 0.7276 \text{ \AA}$, is slightly above the wavelength of MoK α radiation, $\lambda = 0.7107 \text{ \AA}$; this gives rise to severe absorption-correction problems. Knowing this fact the authors employed an isotropic extinction parameter in the Fourier calculations. The effect was not dramatic, lowering the

TABLE 3. MOYDITE: BOND-VALENCE SUMS (v.u.)

Site	Calc	Site	Calc	Site	Sum	Ideal
Y-01a	0.274	B-04	0.784	Y	3.07	3
01b	0.395	05	0.708	B	2.92	3
02a	0.423	06	0.689	C	4.08	4
02b	0.297	07	0.741	01	1.96	2
03	0.524			02	2.02	2
04	0.303	C-01	1.294	03	2.01	2
05	0.263	02	1.303	04	1.09	1
06	0.270	03	1.486	05	0.97	1
07	0.325			06	0.96	1
				07	1.07	1

final least-squares refinement with 87 parameters to R -indices of $R = 5.1$ and $wR = 3.7\%$. It should also be noted that at least part of the effect might be due to secondary extinction, because moydite crystals diffract with intense, sharp peaks, indicative of a high degree of crystal perfection. The final positional parameters and equivalent isotropic temperature-factors (none of the atoms display marked thermal anisotropy) are given in Table 1, and the bond lengths and angles in Table 2. Observed and calculated structure-factors and anisotropic temperature-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Although the location of the four H sites could not be determined from the Fourier synthesis, their distribution could be readily deduced from bond-valence calculations. Individual bond-valences and their sums to the various sites are given in Table 3, based on the constants of Brown (1981) and the bond lengths of Table 2. Ideal compositions and occupancies of the sites were adopted for the purposes of the calculations. The accuracy of the results allows for the confident assignment of protons to oxygen sites O4, O5, O6 and O7. This precludes any possibility of H_2O molecules.

The bond-valence calculations show sites O4, O5, O6 and O7 to be occupied by hydroxyl groups; this is the expected result, as these anions are tetrahedrally bonded to boron. In minerals, boron has never been found to bond to H_2O , nor in carbonates does carbon ever bond to OH or H_2O . The reason for this follows simply from consideration of the Pauling bond strengths for regular polyhedra. The residual bond-strengths of oxygen for each possible carbon and boron co-ordination complex are: trigonal planar C^{4+} has $O^{-0.67}$, trigonal planar B^{3+} has $O^{-1.00}$ and tetrahedral B^{3+} has $O^{-1.25}$. None of these oxygen atoms would attract two H^+ atoms, but either boron co-ordination complex (tetrahedral or trigonal planar) could attract one H^+ . In keeping with this argument Christ & Clark (1977) pointed out that hydrogen would have a preference for tetra-

TABLE 1. MOYDITE: POSITIONAL AND THERMAL PARAMETERS

Site	x	y	z	$U(eq) \times 10^4$
Y	0.0146(1)	0.4991(1)	0.2272(1)	83(1)
B	0.0032(24)	0.2490(16)	0.2415(30)	149(24)
C	0.2622(10)	0.5454(7)	0.0268(8)	113(22)
O1	-0.2792(5)	0.4688(5)	-0.1692(6)	132(16)
O2	-0.1267(7)	0.4550(6)	0.0164(6)	166(18)
O3	0.3680(7)	0.5565(6)	-0.0617(7)	202(20)
O4	0.1019(7)	0.3172(6)	0.1534(6)	155(21)
O5	-0.0944(7)	0.3256(6)	0.3258(6)	159(21)
O6	0.0879(7)	0.1795(7)	0.3505(7)	176(23)
O7	-0.0844(7)	0.1700(6)	0.1538(7)	165(21)

O4, O5, O6 and O7 are OH-sites.

TABLE 2. MOYDITE: BOND LENGTHS (Å) AND ANGLES ($^\circ$)

Y-01a	2.491(5)	B-04	1.456(24)	O4-B-07	115(2)
01b	2.364(5)	05	1.494(23)	O5-B-07	111(1)
02a	2.341(6)	06	1.504(24)	O6-B-07	104(1)
02b	2.465(6)	07	1.477(23)	O4-B-05	106(1)
O3	2.270(6)	Mean	1.483		109
O4	2.455(8)				
O5	2.505(7)	C-01	1.292(9)	O1-C-02	114(1)
O6	2.496(8)	02	1.290(10)	O1-C-03	123(1)
O7	2.431(8)	03	1.252(10)	O2-C-03	123(1)
Mean	2.424	Mean	1.278		120

O4, O5, O6 and O7 are OH-sites

hedrally co-ordinated boron over trigonal planar co-ordinated boron in a crystal structure with both types of polyhedra.

The ideal formula for moydite based on results of the electron microprobe (Grice *et al.* 1986) and the crystal-structure analysis is $(Y, REE)[B(OH)_4]CO_3$. Based on the chemical analysis the composition of the Y site was initially set at $(Y_{0.80}, Sm_{0.20})$, where the Sm scattering curve was chosen as an average for the REE. When refined, the composition of the Y site converged at $Y_{0.90}Sm_{0.10}$, which indicates a reduced number of electrons at this site. This could be a result of anomalous-absorption effects, as

already discussed, or it could be interpreted as partial occupancy of the site. The latter is supported by the empirical formula $(Y_{0.68}Ca_{0.02}Ce_{0.01}Nd_{0.02}Sm_{0.02}Gd_{0.04}Dy_{0.04}Ho_{0.02})\Sigma_{0.85}$.

Moydite has a layer structure with sheets, perpendicular to Y, of corner-sharing YO_9 polyhedra reinforced by trigonal planar carbonate groups (Fig. 1). These sheets are linked *via* edge-sharing along the Y axis by isolated $B(OH)_4$ tetrahedra, accounting for the $\{010\}$ cleavage. Hydrogen atoms likely occupy the channels parallel to the Z axis.

Moydite belongs to a very rare class of minerals, borate-carbonates; five others are known to date:

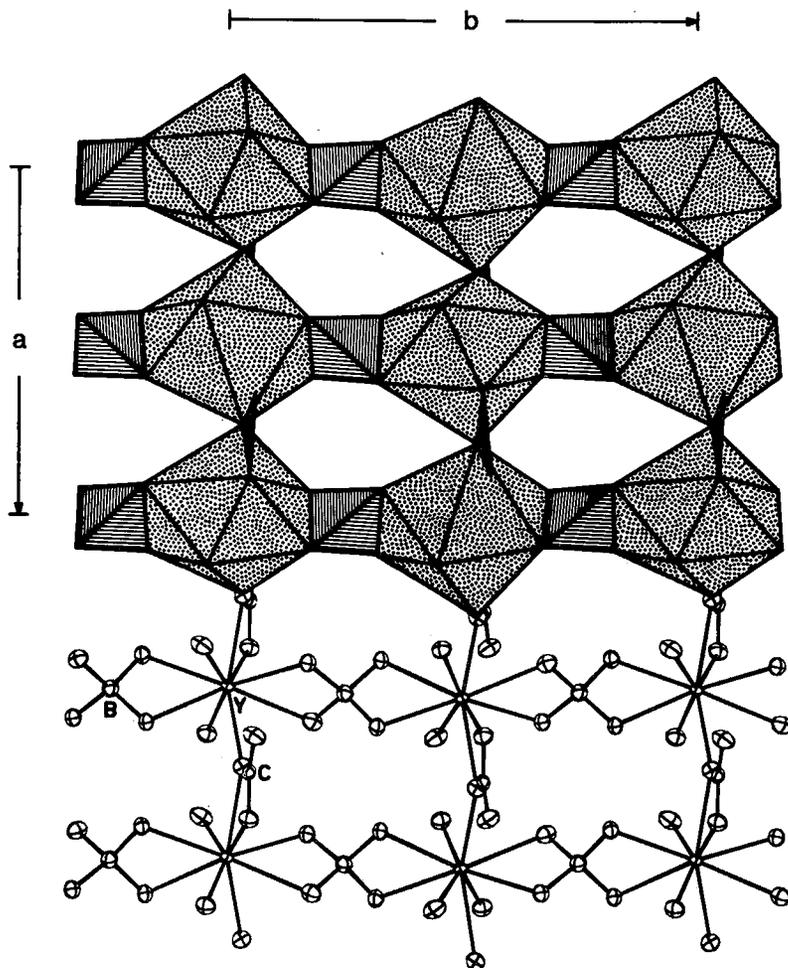


FIG. 1. A Z-axis projection of the moydite structure. The top half of the diagram is a polyhedral representation; YO_9 polyhedra are stippled, $B(OH)_4$ tetrahedra are hatched and CO_3 triangles are solid black. The bottom half of the diagram is the equivalent ball-and-spoke representation of the structure. The YO_9 and CO_3 polyhedra form sheets perpendicular to Y that are linked by the $B(OH)_4$ tetrahedra.

canavesite $Mg_2(CO_3)(HBO_3) \cdot 5H_2O$, borcarite $Ca_4Mg[B_4O_6(OH)_6](CO_3)_2$, carboborite $Ca_2Mg(CO_3)_2[B(OH)_4]_2 \cdot 4H_2O$, gaudefroyite $Ca_4Mn^{3+}_{3-x}(BO_3)_3(CO_3)(O,OH)_8$, and sakhaite $Ca_3Mg(BO_3)_2(CO_3) \cdot nH_2O$ with $n < 1$.

None of the known crystal structures of the borate-carbonate minerals (all but that of canavesite have been completed) resemble that of moydite. Even carboborite (Ma *et al.* 1981), which has independent $B(OH)_4$ tetrahedra and CO_3 groups, bears no resemblance. Yet early in the investigation of this new mineral, Grice *et al.* (1986) recognized that moydite has a cell similar to that of lanthanite $(La,Ce)_2(CO_3)_3 \cdot 8H_2O$, and of ludwigite $Mg_2Fe(BO_3)_2$.

The cell dimensions of lanthanite, a 9.50, b 16.94 and c 8.94 Å, resemble those of moydite, a 9.08, b 12.22 and c 8.91 Å, in the a - c plane because four large La - or Y -polyhedra having a cluster diameter of 4.5 Å define the dimensions of this plane in the two respective structures. In the structure of lanthanite (Dal Negro *et al.* 1977), the b dimension is controlled by two La -polyhedra, two carbonate groups and two water molecules, whereas in moydite the b dimension is only 3/4 that of lanthanite because only two Y -polyhedra and two borate tetrahedra need be accommodated.

Ludwigite has cell dimensions a 9.14, b 12.46 and c 3.05 Å (Takéuchi *et al.* 1950); tripling its c parameter makes a cell comparable to moydite. Moore & Araki (1974) discussed ludwigite as one of many compounds having a "3-Å wallpaper structure". This 3-Å repeat is the length of an octahedral edge. Although the crystal structures of moydite and ludwigite do not resemble each other, there are strong similarities in the cell parameters for these and many other compounds. After all, 3 Å is a typical O-O distance, and perhaps the authors have only realized the earth is not flat. For this conclusion, we apologize to our former teacher, Professor Robert Ferguson, to whom we dedicate this paper.

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