Canadian Mineralogist
Vol. 24, pp. 665-673 (1986)

MOYDITE (Y, *REE*) $[B(OH)_4](CO_3)$, A NEW MINERAL SPECIES FROM THE EVANS–LOU PEGMATITE, QUEBEC

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ABSTRACT

Moydite is a new mineral species from the Evans–Lou granitic pegmatite near Wakefield, Quebec. It occurs as a secondary mineral in cavities within massive quartz and is associated with hellandite, kainosite, lokkaite, xenotime and fergusonite. Its thin, clear yellow plates, 1 × 1 × 0.05 mm, exhibit a vitreous lustre. It is soft and brittle with one good {010} and one poor {101} cleavage. It does not fluoresce in ultraviolet radiation and is not readily soluble in 30% HCl. Optically it is biaxial negative, α 1.588(2), β 1.681(1), γ 1.690(1), $2V$ (meas.) 32(3)°, $2V$(calc.) 34°, $X \| b$, $Y \| a$ with weak dispersion $r > v$. Single-crystal and powder-diffraction X-ray studies show moydite to be orthorhombic, space group *Pbca* (no. 61), with a 9.080(9), b 12.222(9), c 8.911(6) Å and V 988.9(2.5) Å^3. The strongest ten powder-diffraction lines [d in Å(I)(hkl)] are: 6.11(10)(020), 4.50(9)(002,200), 3.179(7)(202), 3.054(3)(040), 2.818(5)(222), 2.749(3)(311,141,113), 2.525(4)(042,240), 2.203(3)(242), 2.091(3)(341,313,152,143) and 1.855(3) (062,260). The average result of the electron-microprobe analyses gives: Y_2O_3 35.0, CaO 0.5, Ce_2O_3 0.8, Nd_2O_3 1.3, Sm_2O_3 1.2, Gd_2O_3 3.4, Dy_2O_3 3.8, Ho_2O_3 1.9, B_2O_3 14.4, CO_2 17.7 and H_2O 20.0 (by difference), which yields the empirical formula $(Y_{0.84}Ca_{0.02}Ce_{0.01}Nd_{0.02}Sm_{0.02}Gd_{0.04}Dy_{0.04}Ho_{0.02})_{\Sigma 0.85}[B_{0.84}O_4H_{4.95}](C_{0.84}O_3)$ based on 7 oxygen atoms or, ideally, (Y,*REE*)$[B(OH)_4](CO_3)$. Corroborative molecular structural information was obtained by Raman microprobe analysis, which furnished a vibrational spectrum consistent with the proposed formula and with other Raman data for borate–carbonates of this type. The measured density, 3.13(3) g/cm^3, agrees reasonably well with the calculated density of 3.01(8) g/cm^3 for $Z = 8$. The name honors Louis Moyd, Curator Emeritus at the National Museum of Natural Sciences.

Keywords: moydite, new mineral species, Evans–Lou pegmatite, carbonate, borate, chemical analysis, electron microprobe, ion microprobe, Raman microprobe, Quebec.

SOMMAIRE

La moydite est une nouvelle espèce minérale découverte dans la pegmatite granitique Evans–Lou, près de Wakefield (Québec). C'est un minéral secondaire dans les cavités du quartz massif, généralement accompagné de hellandite, cénosite, lokkaïte, xénotime et fergusonite. Ses plaquettes jaunes, minces et translucides mesurent 1 × 1 × 0.05 mm et ont un éclat vitreux. Tendre et cassante, la moydite, orthorhombique, possède un bon clivage {010} et un clivage imparfait {101}. Elle n'émet aucune fluorescence dans l'ultraviolet et se dissout malaisément dans une solution de HCl à 30%. Optiquement, elle est biaxe négative, α 1.588(2), β 1.681(1), γ 1.690(1), $2V$(mesuré) 32(3)°, $2V$(calculé) 34°, $X \| b$, $Y \| a$ avec faible dispersion $r > v$. Selon l'examen aux rayons X de cristaux uniques et de poudres, le groupe spatial est *Pbca* (# 61) et la maille, a 9.080(9), b 12.222(9), c 8.911(6) Å, V 988.9(2.5) Å^3. Les dix raies les plus intenses du cliché de poudre [d en Å(I)(hkl)] sont: 6.11(10)(020), 4.50(9)(002,200), 3.179(7)(202), 3.054(3)(040), 2.818(5)(222), 2.749(3)(311,141,113), 2.525(4)(042,240), 2.203(3)(242), 2.091(3)(341,313,152,143) et 1.855(3) (062,260). La moyenne des analyses effectuées à la microsonde donne: Y_2O_3 35.0, CaO 0.5, Ce_2O_3 0.8, Nd_2O_3 1.3, Sm_2O_3 1.2, Gd_2O_3 3.4, Dy_2O_3 3.8, Ho_2O_3 1.9, B_2O_3 14.4, CO_2 17.7 et H_2O 20.0 (par différence), d'où la formule empirique $(Y_{0.84}Ca_{0.02}Ce_{0.01}Nd_{0.02}Sm_{0.02}Gd_{0.04}Dy_{0.04}Ho_{0.02})_{\Sigma 0.85}[B_{0.84}O_4H_{4.95}](C_{0.84}O_3)$ pour 7 atomes d'oxygène ou, idéalement, (Y, terres rares) $[B(OH)_4](CO_3)$. Ces résultats ont été corroborés à la microsonde de Raman, qui a révélé un spectre de vibrations correspondant à la formule proposée et à d'autres données de Raman sur les borates–carbonates de ce type. La densité mesurée, 3.13(3), ne s'écarte pas trop de la densité calculée, 3.01(8) pour $Z = 8$. Le nom du minéral honore Louis Moyd, conservateur émérite du Musée national des sciences naturelles.

Mots-clés: moydite, nouvelle espèce minérale, pegmatite granitique de Evans–Lou, cabonate, borate, analyse chimique, microsonde électronique, microsonde ionique, microsonde de Raman, Québec.

INTRODUCTION

The application of several analytical techniques is commonly necessary to completely describe a new mineral species. This is especially true for the chemical characterization of minerals bearing light elements (atomic number <11) as major constituents since these are not readily determined by conventional electron-microprobe analysis. The characterization of moydite, a new mineral species from the Evans–Lou pegmatite near Wakefield, Quebec, illustrates an example of combined application of classical X-ray-diffraction techniques and several modern microchemical analysis techniques that lead to a complete and consistent description of both the composition and structure of this new mineral. This paper delineates the analytical approach taken in the characterization of moydite and presents the results that have led to its identification as an yttrium – rare-earth borate–carbonate of ideal empirical formula $(Y,REE)[B(OH)_4](CO_3)$.

The Evans–Lou mine occurs in a granitic pegmatite within the Grenville Province. The mine intermittently produced feldspar and quartz from 1932 to 1952. Of the many pegmatites in the region, several are known to contain minerals that bear rare-earth elements. Mine operators apparently viewed these minerals as troublesome and dumped them as waste at the Evans–Lou deposit as well as other similar mines in the area. It was not until the late 1960s that detailed mineralogical studies were initiated on these interesting and rare components of the pegmatites. To date, 66 mineral species have been identified from the Evans–Lou pegmatite. This includes three new species: wakefieldite (Miles *et al.* 1971), caysichite (Hogarth *et al.* 1974) and moydite (present study). In addition to these, Miles *et al.* (1971) and Hogarth (1972) described several unknowns that have not yet been fully described.

Moydite was found by one of the authors (J.V.V.) in the fall of 1980 on the waste dump. Although it was recognized at the time as a new mineral species, a full description was hampered by difficulties encountered in the determination of the concentrations of the light elements. Overcoming these difficulties required the application of several advanced, synergistic techniques of analysis to help determine the complete elemental composition and to derive internally consistent data on the atomic structure. The name *moydite* honors Mr. Louis Moyd, Curator Emeritus at the National Museum of Natural Sciences, Ottawa and his contributions to mineralogy and the National Mineral Collection of Canada. Both the new mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA. Type material consists of several single crystals (NMNS #50771) in the collections of the National Museum of Natural Sciences, Ottawa, Canada, and the Smithsonian Institution (#162936). A cotype specimen at the NMNS has approximately 15 crystals, each of about 1 mm in size, on a quartz matrix measuring 3×2×2 cm (NMNS #50772).

OCCURRENCE AND PARAGENESIS

Moydite occurs at the Evans–Lou mine, which is located approximately 40 km north of Ottawa in Lot 32, Range VI, Val des Monts Tp., Papineau Co., Quebec. This granitic pegmatite dyke may be traced for some 120 m and has a maximum width of 25 m (Miles *et al.* 1971). The pegmatite has an outer perthite–plagioclase–quartz zone, an intermediate perthite–quartz zone and an inner zone of massive quartz. Hogarth (1972) reported the presence of hellandite crystals up to 0.55 m across approximately one metre from the quartz core. Fergusonite, allanite and yttrian spessartine are found with hellandite in the inner massive quartz–feldspar zones of the pegmatite.

The secondary minerals caysichite, lokkaite, tengerite, kainosite and yttrian synchisite are rare-earth-bearing carbonates formed from the alteration of primary hellandite. Other secondary minerals reported include azurite, malachite, bismutite, uranophane, xenotime, wakefieldite and namibite. These minerals exemplify the diverse chemistry found within this pegmatite.

Moydite was discovered in a large boulder on the rock dump. Its placement within the pegmatite is fairly certain because of the associated minerals. The moydite crystals formed within cavities in massive quartz adjacent to a partly altered hellandite crystal. The breakdown of hellandite undoubtedly provided the source of yttrium, rare-earth elements and boron. Carbonate must have been an essential constituent of the slightly alkaline hydrothermal fluid that percolated through the vuggy quartz. Minerals associated in the same vugs include kainosite, lokkaite, caysichite, xenotime, titanite, yttrian fluorapatite, yttrian spessartine, fergusonite, metatyuyamunite and metatorbernite.

APPEARANCE AND PHYSICAL PROPERTIES

Moydite occurs as platy aggregates of crystals, often with subparallel growth (Fig. 1). Individual crystals are clear yellow, with a vitreous lustre and dimensions up to 1 × 1 × 0.05 mm thick.

The small size of the crystals made it difficult to determine relative hardness. Moydite seems to be quite soft and is definitely brittle with a conchoidal fracture. It has good cleavage on {010} and poor cleavage on {101}. It does not fluoresce in ultraviolet radiation and is not readily soluble in 30% HCl.

FIG. 1. Platy crystals of moydite displaying the dominant forms {010}and {111}; width of field of view is 2 mm (NMNS #50772).

The density determination was carried out on crystals using bromoform diluted with 1:1 butyl alcohol. The resulting average measured density is 3.13(3) g/cm^3.

CRYSTALLOGRAPHY

Morphology

Observed crystals of moydite have a simple morphology: a platy basal pinacoid {010} modified by the rhombic dipyramid {111} and, occasionally, a minor development of pinacoids {100} and {001} (Fig. 1).

Optical data

Moydite is colorless in thin fragments and shows no pleochroism or absorption, but a weak dispersion is evident, with $r > v$. It is biaxial negative, with indices of refraction α 1.588(2), β 1.681(1), γ 1.690(1), $2V$ measured in sodium light (λ 589 nm) 32(3)° and $2V$(calc.) 34°. The optical orientation is $X \| b$, $Y \| a$ and $Z \| c$.

X-ray-diffraction data

X-ray single-crystal precession photographs show moydite to be orthorhombic, with unique space-group $P2_1/b2_1/c2_1/a$. Unit-cell dimensions refined from X-ray powder-diffraction data (Table 1) collected on a 114.6-mm Debye-Scherrer camera using Cu$K\alpha$ radiation yield: a 9.080(9), b 12.222(9), c 8.911(6) Å and V 988.9(2.5) Å^3.

The choice of axes for moydite is such that $c < a < b$, but in the original decision for orientation we recognized that there are similarities to the cell dimensions for ludwigite and lanthanite. Ludwigite $Mg_2Fe(BO_3)O_2$ has cell dimensions a 9.14, b 12.45 and c 3.05 Å (Takéuchi *et al.* 1950); a tripling of the c parameter gives dimensions comparable to moydite. Similarly lanthanite $(La,Ce)_2(CO_3)_3{\cdot}8H_2O$ has cell dimensions a 9.50, b 16.94 and c 8.94 Å (Dal Negro *et al.* 1977). The b parameter is approximately 4/3 that of moydite, and the other two are similar. The crystal-structure relationships of these subcells are discussed in Grice & Ercit (1986).

CHEMICAL COMPOSITION

The high birefringence of moydite suggested that it might be a carbonate species. Owing to paucity of material, direct wet-chemical methods were precluded, and we adopted a variety of microanalytical methods to establish the chemical compo-

TABLE 1. X-RAY POWDER-DIFFRACTION DATA OF MOYDITE

hkl	*d*calc	*d*obs	I	*hkl*	*d*calc	*d*obs	I
020	6.111	6.106	*10	341	2.092	2.091	3
				313	2.090		
111	5.642	5.679	1	152	2.088		
				143	2.085		
200	4.540	4.501	9				
002	4.455			060	2.037	2.035	*2
211	3.841	3.839	1	402	2.022	1.999	1
				323	2.002		
220	3.644	3.625	2	204	1.999		
022	3.600						
				422	1.920	1.855	*3
202	3.180	3.179	*7	134	1.910		
				224	1.900		
040	3.056	3.054	*3				
				260	1.858	1.855	3
222	2.821	2.818	*5	062	1.852		
311	2.790	2.749	3	440	1.822	1.823	1
141	2.754						
113	2.750			044	1.800	1.799	1
240	2.534	2.525	4	115	1.731	1.734	<1
042	2.519						
				170	1.715	1.714	1
241	2.438	2.437	<1				
213	2.435			442	1.686	1.686	*2
142	2.428			502	1.681		
				063	1.679		
331	2.344	2.319	<1	244	1.673		
133	2.320						
				433	1.649	1.648	<1
400	2.270	2.276	<1				
410	2.231			135	1.607	1.607	*1
004	2.227						
				404	1.590	1.590	1
242	2.203	2.203	*3				
				424	1.538	1.538	<1
411	2.165	2.167	1				
420	2.129	2.127	2				
233	2.121						
024	2.093						

Plus weak additional lines at

1.518 1.474 1.469 1.448 1.433 1.414
1.396 1.378 1.356 1.340 1.297 1.284
1.270 1.256 1.240 1.217 1.204 1.180
1.171 1.161 1.152 1.142 1.131 1.123

CuKα Radiation 114.6 mm Debye-Scherrer Camera.

*used in cell refinement

sition and atomic structure of moydite. Available to us were several synergistic techniques of microanalysis both to elucidate the full elemental composition and to derive the atomic-structure relationships consistent with the chemical formula derived by Grice & Ercit (1986) from the crystal-structure determination. These methods encompass quantitative wavelength-dispersion electron-microprobe analysis, ion-microprobe analysis by secondary-ion mass spectrometry (SIMS), and laser-Raman microanalysis (LRM). These instrumental microanalytical techniques are becoming increasingly powerful complementary tools in diverse areas of materials analysis and are beginning to come into use for mineral studies (Roedder 1984, McMillan 1985, Etz *et al.* 1985). Some experimental details and the results of these microanalytical investigations of moydite are discussed in the following sections.

Electron-microprobe analysis

The mineral was analyzed in two laboratories for elemental composition using two types of commercial electron-microprobe analyzers (EMPA) differing in analytical capabilities. Flat-polished grains of the mineral, embedded in an epoxy mount, were are first examined in an ARL-SEMQ electron microprobe not equipped to measure X-ray signals from elements of atomic number less than 11. These measurements employed an operating voltage of 15 kV and a sample current of 0.025 μA, measured on brass. Wavelength-dispersion microprobe scans indicated only Y and several *REE* as major constituents of moydite, and the presence of Ca in minor concentrations. Samples were checked for homogeneity using a small beam-spot, and then analyzed with a large beam-spot (40 μm) to prevent potential decomposition of the sample. The standards used for analysis were the rare-earth-bearing glasses of Drake & Weill (1972) for *REE*, hornblende (Ca), and synthetic $Y_2Si_2O_7$ and $Y_3Al_5O_{12}$ for Y. The data were corrected using a modified version of the MAGIC-4 program. Subsequent SIMS scans indicated the presence of several other rare earths in smaller quan-

TABLE 2. CHEMICAL COMPOSITION OF MOYDITE

	Weight %				No. of Cations[4]		
	NMNH #162936	NMNS #50772	Calc.[3]		NMNH #162936	NMNS #50772	Calc.[3]
Y_2O_3	35.3	34.7	37.4	Y	0.72	0.64	0.80
CaO	0.4	0.6		Ca	0.02	0.02	
Ce_2O_3	0.8	0.8		Ce	0.01	0.01	
Nd_2O_3	1.3	1.2		Nd	0.02	0.02	
Sm_2O_3	1.2	1.2	15.0	Sm	0.02	0.02	0.20
Gd_2O_3	3.3	3.4		Gd	0.04	0.04	
Dy_2O_3	3.7	3.8		Dy	0.04	0.04	
Ho_2O_3	2.7	1.0		Ho	0.03	0.01	
B_2O_3	(15.5)[1]	14.4	14.4	B	1.03	1.10	1.00
CO_2	(19.7)[1]	17.7	18.3	C	1.03	0.84	1.00
H_2O	(16.1)[1]	(21.2)[2]	14.9	H	4.11	4.95	4.00
				O	7	7	7
	100	100	100	D(calc)	3.09	2.92	3.24

[1] calculated from crystal-structure atomic proportions.
[2] by difference.
[3] calculated from ideal formula $(Y_{0.8},Sm_{0.2})[B(OH)_4]CO_3$.
[4] based on 7 oxygen atoms.

tities, in addition to those reported here. The resultant composition is presented in Table 2. Subsequent data obtained from SIMS analysis with the ion microprobe indicated major concentrations of the light elements hydrogen, boron, carbon and oxygen.

At this point in the investigation of moydite, the crystal-structure analysis was attempted using the quantitative and qualitative chemical data available. The unique solution to the structure determination is described by Grice & Ercit (1986), and the chemical formula derived is $(Y_{0.8}, REE_{0.2})[B(OH)_4]CO_3$. The calculated weight percentages of oxides for this formula are given in Table 2.

The availability of a second electron microprobe, the JEOL Superprobe 733, equipped for the detection of low-atomic-number elements, made it attractive to examine the mineral specifically for elements B and C, as it was expected that these elements, though easily detected, might not be accurately quantifiable by ion-microprobe analysis. The JEOL Superprobe 733, operating at a voltage of 15 kV and a probe current of 0.025 μA, measured on a Faraday cup, was used for all elements except B, which was determined separately with an operating voltage of 5 kV and a sample current of 0.050 μA. The following standards were used for analysis: the rare-earth-bearing glasses of Drake & Weill (1972) for Nd, Sm, Gd, Dy and Ho, synthetic CeF_3 for Ce, synthetic $Y_3Al_5O_{12}$ for Y, calcite for Ca and C, and synthetic BN for B. The data were corrected using the $\Phi(\rho Z)$ program (Bastin *et al.* 1984), and the results are given in Table 2. Two other crystals from an adjacent vug were analyzed. They are similar to each other and show a slight increase in Y_2O_3 to 38.3 wt.% and a corresponding decrease in the total of rare-earth elements.

The two sets of electron-microprobe data compare very well for Y and all rare-earth elements except Ho, where different spectral lines were used by the two analysts. Of special interest are the data for B and C from the JEOL microprobe. The counting statistics for both of these light elements were sufficiently favorable to expect reasonably precise quantitative results. The B peak was counted for 40 seconds with an average peak:background ratio of 5.2 and an average standard deviation of 3.8%. The duration of each carbon analysis was 20 seconds, with an average *P*:*B* ratio of 3.0 and a standard deviation of 2.6%. The problems encountered were specimen deterioration under the beam and the choice of suitable standards for reliable quantitative results. Calcite proved a good standard for C, but the three available standards for B gave variable results, with BN giving results close to the ideal composition. Use of a boron metal standard gave consistently low results, whereas the B_2O_3 standard gave consistently high results when compared to the ideal composition. Although the latter seemed a logical choice as a standard, the porous nature of the material undoubtedly accounts for the high estimate of the amount of boron present.

Table 2 includes the electron-microprobe data measured by the ARL–SEMQ (NMNH #162936) and by the JEOL Superprobe 733 (NMNS #50772), as well as the ideal formula derived by Grice & Ercit (1986) in their structure determination. It should be noted that in the structure analysis, the *REE* + Ca site was refined using the scattering curves of yttrium (the most abundant element in this site) and samarium (the average scatterer of the remaining elements). Although the 0.2 atoms of Sm give a good approximation to the scattering power of Ca + *REE* (other than Y), its calculated weight percent is high in comparison to the measured values. The marked effect of varying amounts of *REE* on the calculated density is evident in Table 2, and the average D_{calc} [3.01(8)g/cm^3] for the two microprobe analyses agrees reasonably well with the D_{meas} [3.13(3)g/cm^3].

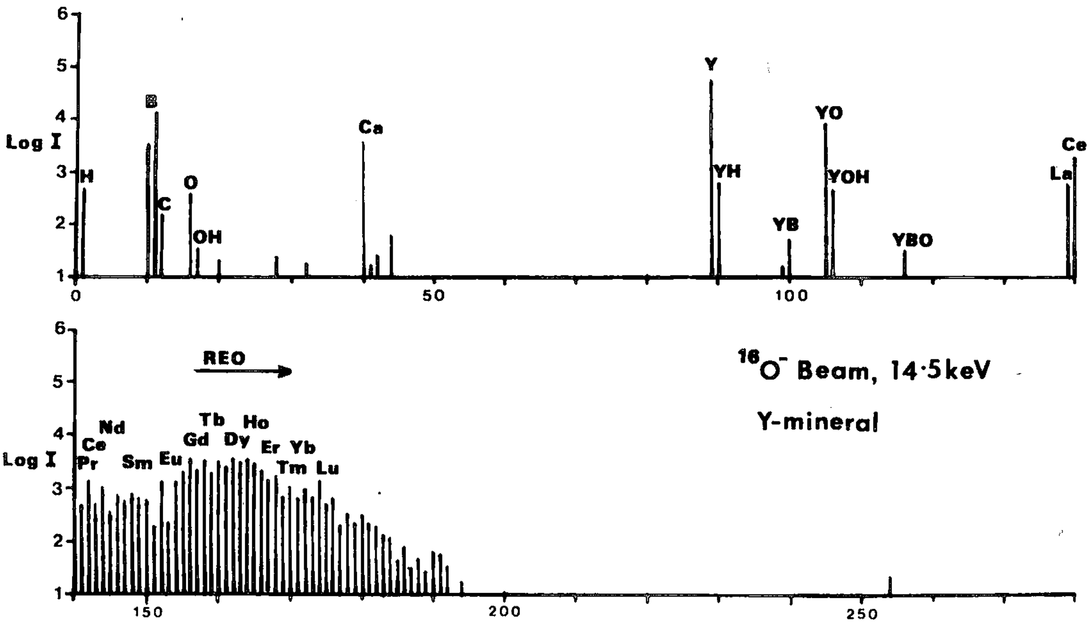

FIG. 2. SIMS spectrum of moydite (Etz *et al.* 1985).

Secondary-ion mass spectrometry

Following the initial EMPA analyses, the specimens were examined by ion microscopy, a spatially resolved form of secondary-ion mass spectrometry (SIMS), to determine whether light elements ($Z < 11$) are present. Because of the insulating character of the specimen, a primary ion-beam of $^{16}O^-$ ions at an energy of 5.5 keV was used for the analysis. Secondary-ion signals were collected from apertured areas of 60 μm and 20 μm diameter. Energy filtering was used to reduce the contribution of molecular ions. An example of a mass spectrum obtained from the new mineral is shown in Figure 2. In addition to the Y, *REE* and Ca detected by EMPA, the SIMS spectrum reveals major signals for H, B, C and O. Because of the implantation of O from the primary ion-beam, the detection of O is meaningless.

Quantitative SIMS analysis was attempted by the method of relative sensitivity-factors determined from standards. Unfortunately, no standards similar to the new mineral, either natural minerals or synthetic compounds, were available. The materials available that were utilized as standards included synthetic yttrium carbonate $Y_2(CO_3)_3{\cdot}3H_2O$ for the C:Y ratio, and gaudefroyite $Ca_4Mn_3(BO_3)_3(CO_3)(O,OH)_3$ and canavesite $Mg_2CO_3(HBO_3){\cdot}5H_2O$ for the B:C ratio. Unfortunately, the strong matrix-effects that are encountered in SIMS analysis resulted in inconsistent results. For example, the B:C atom ratio was determined as 12:1 with gaudefroyite and 3:1 with canavesite. The C:Y atom ratio was determined to be 2.5:1 with synthetic yttrium carbonate. The SIMS results are thus internally inconsistent and not in good agreement with the EMPA or results of the crystal-structural analysis.

The principal contribution of the SIMS analysis was thus the recognition of the presence of major light-element components in the new mineral. This stimulated subsequent quantitative analysis of the light-element component by EMPA.

Raman microprobe analysis

Vibrational spectroscopy, especially infrared absorption, has been extensively used for the structural and molecular characterization of minerals (McMillan 1985, Ross 1972a). Infrared absorption and Raman data on borate minerals are quite sparse despite the excellent correlation that has been obtained in numerous studies between the vibrational spectrum and the structure of the mineral. In general, the Raman spectra of minerals are discussed in terms of their structural order, and the most general tool in the analysis of crystal spectra is known as factor-group analysis (McMillan 1985, Griffith 1975). For minerals with several molecular groupings, the assumption from first principles is that the spectra are composed of a set of internal modes of each of the molecular units (*e.g.*, CO_3^{2-}, BO_3^{3-}, SO_4^{2-}, H_2O) in the crystal, plus a set of lattice or external modes characteristic of specific crystal-structures. The spec-

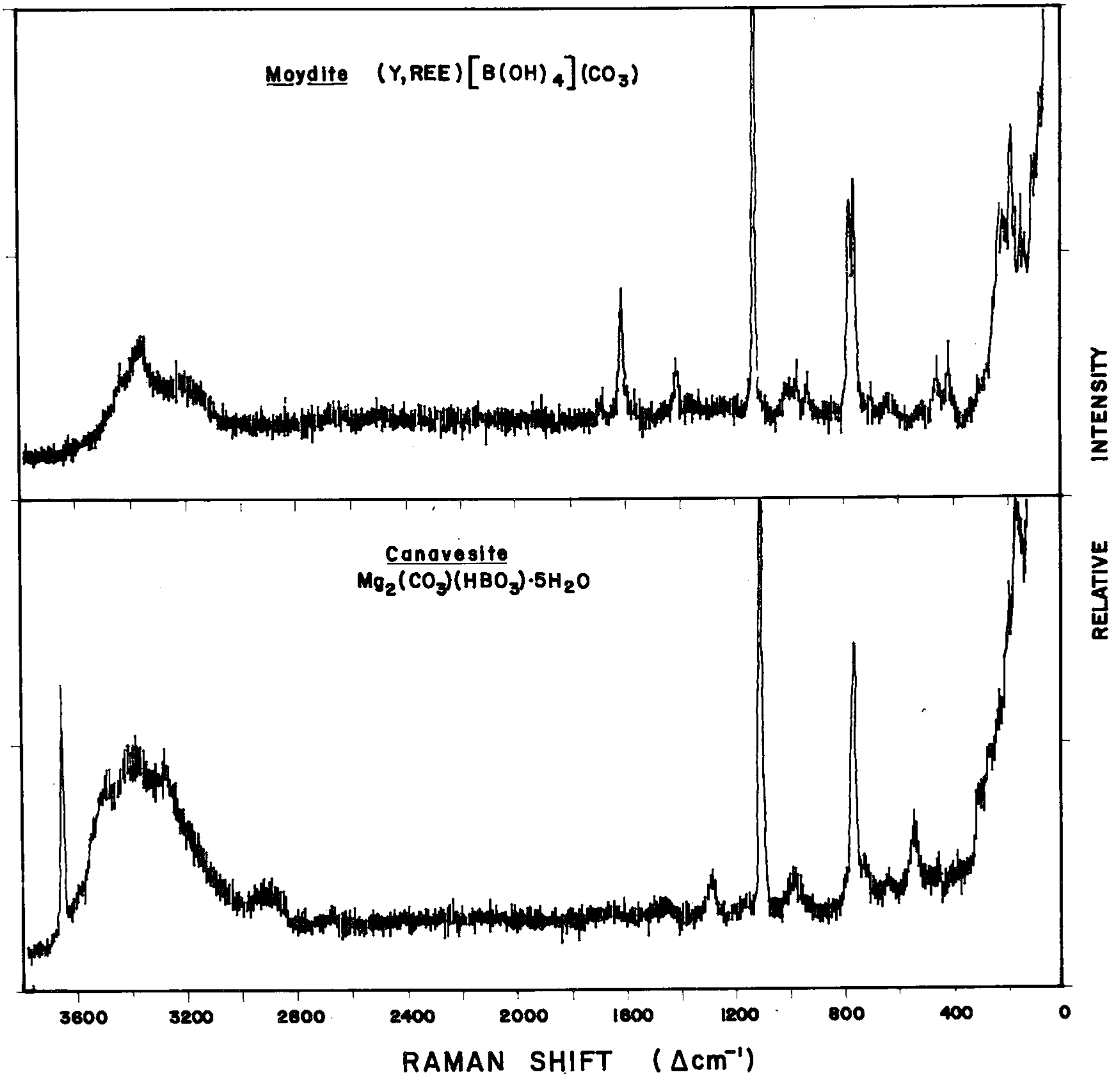

FIG. 3. Raman spectra of single microscopic grains of moydite and canavesite, analyzed on LiF substrate (514.5 nm excitation).

tra of borates show great variety and complexity due to the many possible anions that these minerals may contain (Farmer 1974). Among the many possible groups of atoms or species that indicate this structural diversity are BO_3^{3-}, $(B_3O_6)^{3-}$, BO_4^{5-}, and $B(OH)_4^-$, and one would expect that each vibrating unit should have its distinct vibrational spectrum.

The results presented here have sought to substantiate these implicit structural relationships embodied in the chemical formula derived for moydite. Thus we used laser-Raman microanalysis (LRM) to investigate the new mineral as well as several other natural and synthetic borates and carboborates to relate their spectra to their known compositions and structures (Etz *et al.* 1985). With the development of Raman microprobe spectroscopy over the past decade, it has become feasible to routinely probe microscopic domains and acquire the Raman spectra of single particles or microscopic volumes with dimensions of a few cubic micrometres (Rosasco 1980). Earlier work with the Raman microprobe on other natural and synthetic minerals has shown that such measurements can be performed nonintrusively, yielding direct molecular information not obtainable by any other microprobe technique (Rosasco & Blaha 1980, Grynpas *et al.* 1982). The Raman spectra of moydite and the related reference minerals and various borate and carbonate standards were obtained with the Raman microprobe developed at the National Bureau of Standards (Rosasco 1980, Etz 1979). The instrument employs a scanning double monochromator with detection by coded photomultiplier tube and signal processing by photon counting. The acquisition of data is done by computer; the digital spectra stored on hard disk form a library of micro-Raman spectra for qualitative intercomparison. The spectra were excited with the 514.5 nm line of an argon–krypton laser. No spectral interferences due to sample fluorescence were encountered. Irradiance levels, directed at the sample in a beam spot approximately 10 μm in diameter, range from 20 to 50 kW/cm^2. The spectra were recorded with 5 cm^{-1} resolution, from single microscopic (approximately 10–30 μm) grains supported by a lithium fluoride substrate.

Additional results of these investigations are given by Etz *et al.* (1985). Shown in Figure 3 are the spectra of moydite and of a second borate–carbonate, the mineral canavesite. It is beyond the scope of this paper to provide a rigorous interpretation of the spectra of these minerals based on factor-group analysis (McMillan 1985). For the purposes of this study it will suffice to identify the prominent bands in the spectra and relate these to the expected Raman-active vibrational modes characteristic of the constituent molecular species. From this perspective, the spectra of moydite and canavesite appear remarkably similar, having several features in common in spectral regions diagnostic of borate and carbonate vibrational units. Most readily recognized are the fundamental vibrational bands of the carbonate grouping. In the spectrum of moydite, the dominant feature is the strong, sharp band with a peak at 1124 cm^{-1} (ν_1, CO_3^{2-} symmetric stretching); other modes attributed to carbonate, though much weaker, appear with Raman shifts at approximately 1410 and 700 cm^{-1}. Other features in the spectrum must be considered to arise from scattering by the $B(OH)_4^-$ species. In reported (Etz *et al.* 1985, Ross 1972b) infrared-absorption and Raman studies of the mineral cahnite $Ca_2[B(OH)_4][AsO_4]$, assignments have been made of the vibrational frequencies for the tetrahydroxoborate group. From these published data, the fundamental vibrations of the tetrahedral $B(OH)_4^-$ grouping would be expected at approximately 760 cm^{-1} (ν_1 mode), with other groupings of bands at approximately 415, 455 and 520 cm^{-1}, as well as in the region of 900 - 1010 cm^{-1}. Bands at these frequency positions are observed in the spectrum of moydite which, by analogy with the asssignments made for $B(OH)_4^-$ in cahnite, would suggest the existence of discrete tetrahydroxoborate species in the structure of the mineral. Since moydite is nonhydrated, the complex broad band in the region 3100 - 3600 cm^{-1} must be attributed to O–H stretching vibrations in the $B(OH)_4^-$ ions. The pronounced, sharp band of medium intensity at 1610 cm^{-1} cannot, at this time, be assigned to any vibrational entity in the crystal structure. Observed on the spectrum of moydite are also several prominent lattice-modes. Canavesite is a recently discovered mineral and has not yet been characterized by vibrational spectroscopy. The spectrum (Fig. 3) is that of a typical microscopic fiber. A band due to carbonate vibrations is the carbonate (ν_1) band at 1106 cm^{-1}. Other carbonate bands are much weaker, as is the case for moydite.

The similarity in the spectra of the two minerals moydite and canavesite requires that one examine them in detail for any features that would allow a distinction to be made between the spectral contributions of the tetrahedrally $B(OH)_4^-$ group *versus* those of the trigonal HBO_3^{2-} species. The borate fundamentals in various minerals containing discrete BO_3^{3-} units fall into the range 870 - 1020 cm^{-1}(ν_1), 680 - 810 cm^{-1}, 1100 - 1300 cm^{-1}, and 550 - 670 cm^{-1}. This observation leads to the realization that it is difficult to make specific, unequivocal assignment of bands for these types of borate species on these minerals. Thus the pronounced band centred at 765 cm^{-} is clearly a borate vibration and can most likely be attributed to the ν_1 stretching frequency of the BOH vibrating unit of either the $B(OH)_4^-$ or the $HOBO_2^{2-}$ group. Other aspects of these spectra are equally unclear and need additional insight from further studies. For example, the assignment of the observed bands in the spectrum of canavesite needs to take into account both free and bonded O–H modes. Again, the complex, broad band in the region 3100 - 3600 cm^{-1} is attributed to O–H stretching modes from vibrations of the $HOBO_2^{2-}$ ion and from those of the H_2O molecules of the hydrated crystal. A prominent feature in the spectrum of canavesite is the sharp band with a peak at 3656 cm^{-1}. It seems unlikely that this band can be assigned to an O–H vibration of either the water molecule or the $HOBO_2^{2-}$ ion.

The interpretation of the borate spectra examined in this work supports all other structural evidence that the new mineral contains borate groups bonded to hydrogen. Our present understanding of the subtleties of these spectra and their relation to structural variances does not allow us to draw definite conclusions regarding the presence of either trigonal or tetrahedral borate groups in the structure of the new mineral.

SUMMARY

The analyses of light elements for micro amounts of material has always been problematical. For moydite, three different techniques for determining boron and carbon contents met with uneven success. The ion microprobe has excellent detection-limits for these elements, but present experience shows the need for standards close in chemical composition and crystal structure in order to minimize matrix corrections, which are not well understood to date. Advances in technology and data handling for the electron microprobe can now give at least good semiquantitative results, but users are cautioned in the choice of standards. Wherever possible, it seems that the crystal-structure analysis remains the strongest technique for a chemical determination. With a good set of X-ray-diffraction data, the electron densities with bond lengths and bond valences yield a unique chemical determination. Ungaretti *et al.* (1981) have used these techniques with good results on a number of amphiboles.

ACKNOWLEDGEMENTS

The authors thank Drs. D. Smith, University of Alberta and R. Packwood, CANMET, for their early investigation and suggestions on the chemistry of this new mineral. The manuscript was improved by the helpful and encouraging remarks of two anonymous referees.

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Received March 25, 1986, revised manuscript accepted June 21, 1986.