EDINGTONITE: THE FIRST TWO CANADIAN OCCURRENCES

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ABSTRACT

Edingtonite from the Ice River alkaline complex, near Field, British Columbia, is found in nepheline syenite. Its formula, $(Ba_{1.92}K_{0.07})_{\Sigma1.99}Al_{4.17}Si_{6.23}O_{20.66} \cdot 7.34H_2O$, is derived from the chemical analysis: SiO_2 36.3, Al_2O_3 20.6, BaO 28.6, K_2O 0.32, H_2O 12.8, total 98.62%. Optically it is biaxial negative with α 1.535(2), β 1.542(2), γ 1.545(2), $2V$ 62(5)°(meas.). Cell refinement yields a 9.583(7), b 9.624(7), c 6.527(6) Å. The density (g/cm³) is 2.73(2) (meas.), 2.75 (calc.). Crystals average 8x2x2 mm with forms {001}, {110}; {111} and {11$\bar{1}$} (point group 222). Twinning is common on (110) (lamellar) and [001]$_{90}$ · (penetration). Edingtonite from the Brunswick No. 12 mine, near Bathurst, New Brunswick, is found as a hydrothermal infilling in a series of metasediments. It has the formula $(Ba_{2.00}K_{0.02})_{\Sigma2.02}Al_{4.23}Si_{6.20}O_{20.78} \cdot 7.22H_2O$, derived from the chemical analysis: SiO_2 35.9, Al_2O_3 20.8, BaO 29.6, K_2O 0.11, H_2O 12.5, total 98.91%. Optically it is biaxial negative with α 1.538(2), β 1.549(2), γ 1.551(2), $2V$ 56(5)°(meas.). Cell refinement yields α 9.551(5), b 9.656(5), c 6.516(6) Å. The density (g/cm³) is 2.78(2) (meas.), 2.76 (calc.). Crystals are as large as 45x10x10 mm with forms {001}, {110}, {101} and {111}, {11$\bar{1}$} and {2$\bar{1}$1}. Twinning was not observed. Saturated edingtonite has eight H_2O molecules. Four H_2O molecules may be removed under vacuum, two by heating from 50 to 150°C and two between 150 and 200°C. The separation of the latter four H_2O molecules in two steps invalidates the structure as presently known. At 30% of relative humidity and 25°C, 1.00 wt.% H_2O is removed from edingtonite.

Keywords: edingtonite, Ice River complex, British Columbia, Brunswick No. 12 mine, New Brunswick, twinning, water molecules, zeolite.

SOMMAIRE

L'édingtonite du complexe alcalin de la rivière Ice, près de Field (Colombie-britannique) se trouve dans une syénite néphélinique. Sa formule, $(Ba_{1.92}K_{0.07})_{\Sigma1.99}Al_{4.17}Si_{6.23}O_{20.66} \cdot 7.34H_2O$, repose sur les données chimiques: SiO_2 36.3, Al_2O_3 20.6, BaO 28.6, K_2O 0.32, H_2O 12.8, total 98.62%. L'édingtonite est optiquement biaxe négative; α 1.535(2), β 1.542(2), γ 1.545(2), $2V$ 62(5)°(meas.). L'affinement de la maille donne a 9.583(7), b 9.624(7), c 6.527(6) Å. Sa densité est de 2.73(2) (mes.) et 2.75 (calc.). Les cristaux mesurent en moyenne 8x2x2 mm et présentent les formes {001}, {110}, {111} et {11$\bar{1}$} (groupe ponctuel 222). Les macles (110) (polysynthétique) et [001]$_{90}$ · (inter-

pénétration) sont communes. L'édingtonite de la mine Brunswick no. 12, près de Bathurst, (Nouveau-Brunswick), se présente sous forme de remplissage hydrothermal dans des roches métasédimentaires. Sa formule, $(Ba_{2.00}K_{0.02})_{\Sigma2.02}Al_{4.23}Si_{6.20}O_{20.78} \cdot 7.22H_2O$, est obtenue par analyse chimique: SiO_2 35.9, Al_2O_3 20.8, BaO 29.6, K_2O 0.11, H_2O 12.5, total 98.91%. Ici aussi l'édingtonite est optiquement biaxe négative; α 1.538(2), β 1.549(2), γ 1.551(2), $2V$ 56(5)°(mes.). L'affinement des paramètres donne a 9.551(5), b 9.656(5), c 6.516(6) Å. Sa densité est de 2.78(2) (mes.), 2.76 (calc.). Les cristaux peuvent mesurer jusqu'à 45x10x10 mm, avec les formes {001}, {110}, {101}, {111}, {11$\bar{1}$} et {2$\bar{1}$1}, sans trace de macle. L'édingtonite saturée possède huit molécules d'eau. Quatre de ces molécules peuvent être libérées sous vide, deux par chauffage progressif de 50° à 150°C et les deux autres entre 150° et 200°C. L'extraction de ces quatre dernières molécules en deux étapes infirme la structure que l'on attribue actuellement à l'édingtonite. À 30% d'humidité relative et 25°C, l'édingtonite perd en eau (H_2O) un pour cent de son poids.

Mots-clés: édingtonite, complexe de la rivière Ice, Colombie-britannique, mine Brunswick no. 12, Nouveau-Brunswick, macle, molécules d'eau, zéolite.

INTRODUCTION

The rare barium zeolite *edingtonite*, $Ba_2Al_4Si_6O_{20} \cdot 8H_2O$, has been found in Canada at two occurrences: 1) Zinc Mountain ridge, east side of the Ice River valley, 25 km south of Field, Yoho National Park, Kootenay District, British Columbia, and 2) Brunswick No. 12 mine, 2350 level, East Stope, near Bathurst, Bathurst parish, Gloucester County, New Brunswick. The mineral was first described by Haidinger (1825) from the area of Old Kilpatrick, Dumbartonshire, Scotland; since then, it has been reported from the Böhlet mine, Westergotland, Sweden (Nordenskjöld 1895), near Staré Ransko, East Bohemia, Czechoslovakia (Novák 1970), the Podol'skoye deposit, southern Urals, U.S.S.R. (Ismagilov 1977), Jacupiranga, Saõ Paulo State, Brazil (National Museum of Natural Sciences collection), and the Ice River alkaline complex, British Columbia (Grice & Gault 1981).

GEOLOGICAL SETTING

The Ice River alkaline intrusive complex consists

of a suite of ijolites, syenites, carbonatites and late-stage pegmatites (Currie 1975) in the Yoho and Kootenay National Parks region of southeastern British Columbia. The complex, approximately 18x6 km in dimension, was emplaced about 245 million years ago into sedimentary rocks of Cambrian and lower Ordovician age. During the mid-Mesozoic, the sedimentary rocks were intensely folded and faulted but the igneous rocks remained relatively unaltered. Edingtonite occurs in isolated zeolite- and carbonate-rich pockets in nepheline syenite. It is a late-stage mineral in these pockets, which were, in themselves, one of the last phases of the complex to form. The mineralogy of the pockets is simple; the major constituents are calcite, natrolite and edingtonite. Occurring rarely are the species ancylite, catapleiite, acmite, pyrite and galena.

The Brunswick No. 12 deposit, about 26 km southwest of Bathurst, New Brunswick, is a massive-sulfide body occurring in sedimentary and volcanic rocks of the Tetagouche Group of Early to Middle Ordovician age (Luff 1977). The area was intensely deformed during the Ordovician and again in Devonian time, resulting in the separation of the sulfide orebody into four zones. Edingtonite occurs in open fractures in veins at the 2350 level of the East Ore Zone. The area in which the edingtonite is found was sheared and fractured as the footwall metasediments were folded around the hanging-wall iron formation. The mineral assemblage of the veins include edingtonite, chalcopyrite, galena, pyrite, sphalerite, barytocalcite, calcite, dolomite, quartz, greenalite and lizardite, and is apparently derived from ascend-ing hydrothermal fluids reacting with massive sulfides, argillites and siliceous tuffs.

CRYSTALLOGRAPHY

Edingtonite is orthorhombic, pseudotetragonal. The crystal structure has been refined recently by Galli (1976) in space group $P2_12_12$. This refinement has shown Si and Al to have an ordered distribution in the chains, similar to that found in natrolite. This ordering lowers the symmetry of the structure from that determined earlier by Taylor & Jackson (1933), in tetragonal space-group $P\bar{4}2_1m$.

Edingtonite crystals from the Ice River are generally well-formed, white, cloudy, pseudotetragonal prisms with good single, or on some specimens, double terminations. Size of the crystals averages 8x2x2 mm; they often form drusy coatings on calcite crystals. The simple morphology includes the forms: prism $m\{110\}$, two disphenoids $o\{111\}$ and $p\{11\bar{1}\}$, and the basal pinacoid $c\{001\}$ (Fig. 1a). On most crystals, the disphenoids are almost equally developed, giving the morphology a tetragonal ap-

FIG. 2. Edingtonite from Ice River showing penetration twin [001]. Forms present on each individual are o, p and m. The width of the twinned crystal is 1 mm.
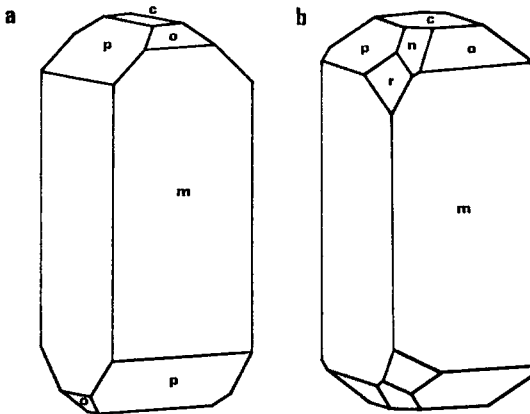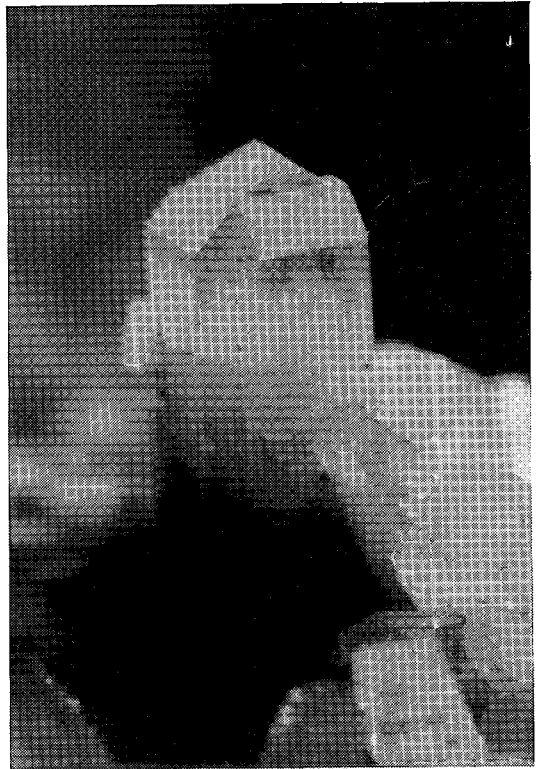

FIG. 1. Idealized drawings of edingtonite. Crystals from a) the Ice River complex, with the following forms: prism $m\{110\}$, disphenoids $o\{111\}$ and $p\{11\bar{1}\}$, and basal pinacoid $c\{001\}$, and b) the Brunswick No. 12 mine, with the following forms: prisms $m\{110\}$ and $n\{101\}$, disphenoids $o\{111\}$, $p\{1\bar{1}1\}$ and $r\{2\bar{1}1\}$, and basal pinacoid $c\{001\}$.
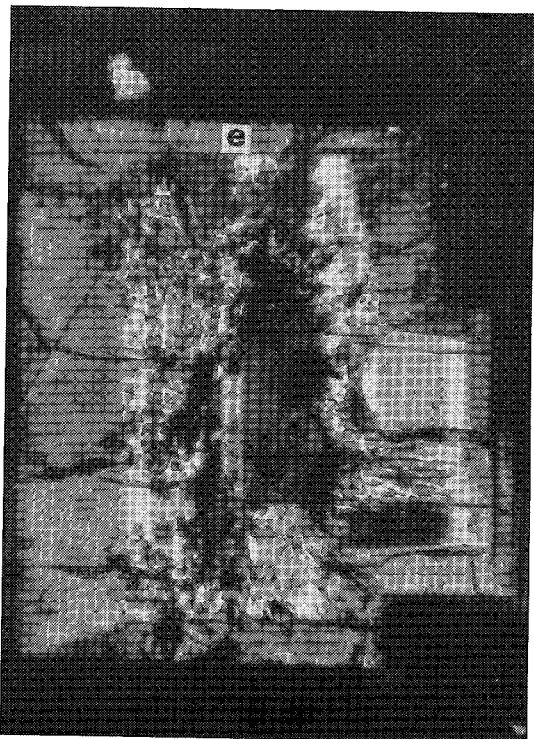
FIG. 3. Edingtonite from Ice River, transmitted light with crossed polars, (001) section; crystal width is 1 mm. Section shows [001] twin, multiple intergrowths and epitactic overgrowth (e).

TABLE 1. CRYSTALLOGRAPHIC DATA FOR EDINGTONITE

		Ice River, B.C.		Brunswick No. 12 Mine, N.B.
Unit Cell:*	a	9.583(7)Å	a	9.551(5)Å
	b	9.624(7)Å	b	9.656(5)Å
	a	6.527(6)Å	a	6.516(6)Å
	V	602(1)Å³	V	601(1)Å³
Optical Data:	α	1.535(2)	α	1.538(2)
	β	1.542(2)	β	1.549(2)
	γ	1.545(2)	γ	1.551(2)
	$2Vm$	62(5)°	$2Vm$	56(5)°

* Powder-diffractometer data, Ni-filtered Cu Kα radiation.

symmetry for edingtonite from either locality. With a powder diffractometer and Cu$K\alpha$ radiation, there was sufficient resolution of peaks to distinguish the orthorhombic symmetry and hence to determine unique a and b cell dimensions. Silicon was used as an internal standard for the cell refinement (Table 1). There is a greater difference between a and b for the Brunswick mine edingtonite than for that from Ice River. The fact that the Ice River edingtonite is dimensionally closer to a tetragonal cell may explain its propensity for twinning.

OPTICAL PROPERTIES

Optical properties of edingtonite from both localities are presented in Table 1. Principal indices of refraction and optic angles were measured on grains illuminated with a sodium vapor lamp ($\lambda = 589$ nm).

The epitactic overgrowth discussed above and shown in Figure 3 has a lower birefringence than the core (first-order grey to black in comparison to first-order cream to yellow in the (001) section). As the mineral approaches a uniaxial indicatrix, it is likely becoming more nearly tetragonal in symmetry. This is discussed further under Chemical Composition.

pearance, but careful inspection of the doubly terminated crystals shows the true noncentrosymmetric point-group 222. Crystals are generally complexly intergrown and twinned, with a thin transparent epitactic overgrowth on a cloudy core. Two twin laws have been identified: lamellar (110) and penetration [001] with individuals at 90° (Fig. 2). The overgrowth, as seen in thin section, has a fine lamellar twinning and is oriented with {110} parallel to {110} of the core (Fig. 3). A good {110} cleavage was noted.

Edingtonite crystals from the Brunswick No. 12 mine are very well-formed pseudotetragonal prisms attaining dimensions of 45x10x10 mm. They are white and opaque to colorless and transparent with smooth lustrous surfaces. The morphology of these crystals is more complex than those of Ice River, but no twinning was observed. Forms present include prisms $m\{110\}$ and $n\{101\}$, disphenoids $o\{111\}$, $p\{1\bar{1}1\}$ and $r\{2\bar{1}1\}$, and the basal pinacoid $c\{001\}$ (Fig. 1b). This edingtonite also has a good {110} cleavage.

Single-crystal X-ray precession-camera patterns were not suitable for distinguishing orthorhombic

TABLE 2. CHEMICAL* AND DENSITY DATA FOR EDINGTONITE

	Ice River NMNS #40378 (average of 7 analyses on 3 grains)	Brunswick mine GSC #14899 (average of 6 analyses on 2 grains)	Ideal
SiO2	36.3	35.9	35.51
Al2O3	20.6	20.8	20.08
BaO	28.6	29.6	30.21
K2O	0.32	0.11	----
H2O	12.8	12.5	14.20
Total	98.62	98.91	100

Numbers of ions based on 28 oxygen atoms

Si	6.23	6.20	6
Al	4.17	4.23	4
Ba	1.92	2.00	2
K	0.07	0.02	----
H2O	7.34	7.22	8
D_{obs} g/cm³	2.73(2)	2.78(2)	----
D_{calc} g/cm³	2.75	2.76	2.80

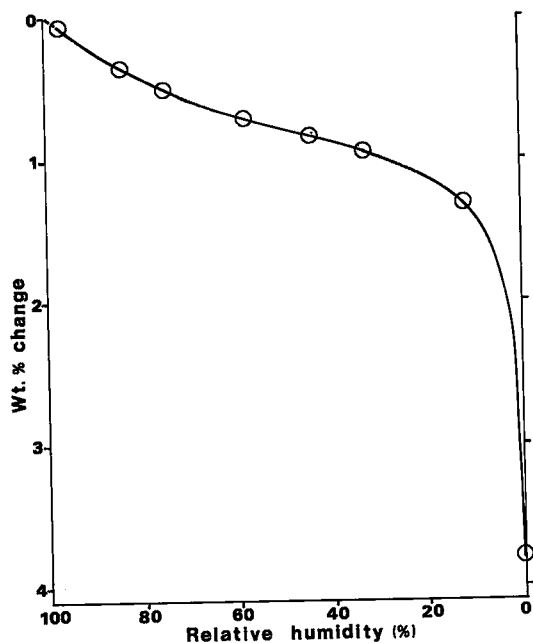* Analysts: M. Bonardi, Geological Survey of Canada (microprobe), R. Ramik, Royal Ontario Museum (H2O by TGA).

CHEMICAL COMPOSITION

Analyses of the two specimens (Table 2) were
made by microprobe in the laboratories of the
Geological Survey of Canada, and the H_2O content
was determined by thermogravimetric analysis in the
Royal Ontario Museum laboratory. Electron-
microprobe analyses were obtained using a Materials
Analysis Company instrument (energy-dispersion
mode) operating at 20 kV, with a specimen current
of ~ 10 nA (measured on kaersutite) and a count-
ing time of 100 seconds. Because edingtonite loses
water readily when heated, samples were mounted
in cold-setting epoxy resin. Also, to minimize loss
of water due to electron bombardment and high
vacuum, a broad, defocused beam of electrons was
utilized in analysis. The following analytical stan-
dards were used: kyanite (Al), kaersutite (Si,K) and
barite (Ba). The simultaneous thermogravimetric –
evolved-gas analyses (TGA, EGA) were made on
55-mg samples from each locality with a Mettler
TA–1 Thermoanalyzer coupled to an Inficon IQ 200
quadrupole mass-spectrometer.

Table 2 also lists the observed and calculated den-
sities, which agree within the limits of error.

Like other analyzed specimens of edingtonite
(Ismagilov 1977, Hey 1934, Novák 1970), the Cana-
dian samples are essentially barium–aluminum

silicate hydrates with very little substitution of other
cations. On the basis of an edingtonite formula deriv-
ed from a whole-rock composition, Ismagilov (1977)
calculated that edingtonite from the southern Urals
contains 4.35 wt.% CaO. In that calculation, it was
assumed the plagioclase present is pure albite. No
data were given to justify this assumption; therefore,
the composition reported must be held in doubt for
the present. Both Heddle (1855) and Hey (1934) in-
dicated the presence of calcium in one edingtonite
specimen from Old Kilpatrick, but the amount of
material was insufficient for a full chemical analysis.
The full analysis of Old Kilpatrick edingtonite lists
only a "trace" of calcium (Heddle 1855).

In the present study, analyses independent of those
given in Table 2 were done by D. Smith, University
of Alberta, also using a microprobe with an energy-
dispersion spectrometer. There was no significant in-
homogeneity in the edingtonite from the Brunswick
mine, but a significant, although small, variance was
found in the Ice River crystals between the white core
and the clear overgrowth discussed above (Fig. 3).
The core contains between 0 and 0.07% K_2O,
whereas the overgrowth varies from 0.65 to 0.71%
K_2O. The chemical transition is sharp at the
overgrowth boundary. This minor amount of
potassium appears to affect the crystal structure of
the edingtonite overgrowth, making it more nearly
tetragonal (i.e., almost optically uniaxial as discussed
above). This shift in crystal symmetry is in keeping
with the findings of Taylor (1935) for synthetic
potassium-edingtonite, which is tetragonal.

Analysis of water in edingtonite has always
presented problems. In the literature, the proportion
of H_2O in edingtonite ranges from 6.68 to 7.81 H_2O
molecules, with the majority of results close to seven.
The crystal-structure refinement (Galli 1976) in-
dicated that there are ideally eight H_2O molecules.
The problem of low content of reported water was
studied by R. Waller, National Museum of Natural
Sciences, Ottawa and his results are given in Figures
4 and 5.

Figure 4 shows the relationship between loss or
gain of H_2O vs. relative humidity (RH) at 23°C. A
sample of Brunswick No. 12 edingtonite, crushed to
− 40 + 100 and weighing ~ 300 mg, was placed in
a series of desiccators containing saturated salt solu-
tions. The weight of the sample was reproducible for
either increasing or decreasing steps. Similar samples
of natrolite and quartz served as controls to deter-
mine whether adsorption of water onto surfaces was
significant. The effect of adsorption was negligible
until almost 100% RH, at which point the control
samples of quartz and natrolite began to gain weight.
The graph shows how readily edingtonite loses or
gains structural water even at room temperature. The
significance of these results is that any laboratory
with less than 80% RH should correct edingtonite

analytical data for dehydration. Below 10% RH, water loss becomes drastic, and reliable corrections would be difficult. The water contents reported in Table 2 were determined at ~ 30% RH, which means a loss of 1.0 wt.% H_2O prior to TGA. If this correction is added to Table 2, the resultant formulas
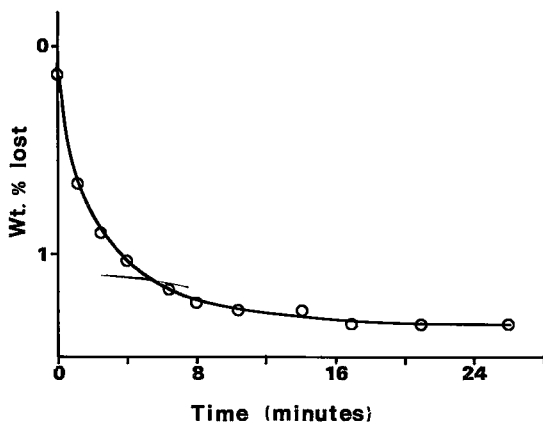

FIG. 5. Edingtonite from Brunswick No. 12 mine. Weight % H_2O lost from a sample conditioned to 97% RH then allowed to desorb in 20% RH (at 22°C), plotted *versus* time.

(calculated on the basis of 28 oxygen atoms) are: $(Ba_{1.89}K_{0.06})_{\Sigma 1.95}Al_{4.08}Si_{6.11}O_{20.25} \cdot 7.75H_2O$ (Ice River) and $(Ba_{1.97}K_{0.02})_{\Sigma 1.99}Al_{4.16}Si_{6.08}O_{20.37} \cdot 7.63H_2O$ (Brunswick mine), *i.e.,* close to 8 molecules H_2O.

In order to observe the rate at which structural water is lost, a sample of the Brunswick mine edingtonite was conditioned to 97% RH at 22°C until stable with respect to weight. The sample was then allowed to desorb in 20% RH at 22°C. Figure 5 shows the results: the water loss approaches equilibrium in ten minutes.

The TGA curves (Fig. 6a, b) give additional information on the water in edingtonite. For both localities, the curves are similar, showing that most of the water was lost in three stages. Approximately four molecules of H_2O were lost under vacuum at 25°C. An additional two molecules of H_2O were lost between 50 and 150°C, and the final two molecules were lost between 150 and 200°C. The general features of this TGA curve resemble those of Van Reeuwijk (1972), but the intervals of desorption temperatures given in Figure 6 are considerably lower since the heating experiment was performed under vacuum. Van Reeuwijk (1972) reported 3.0, 2.5 and 1.75 H_2O molecules lost for each of the three intervals of temperature. The EGA curves (relative amounts of evolved H_2O recorded on a mass spectrometer) (Fig. 6a, b) also show approximately equal splitting of the four water molecules
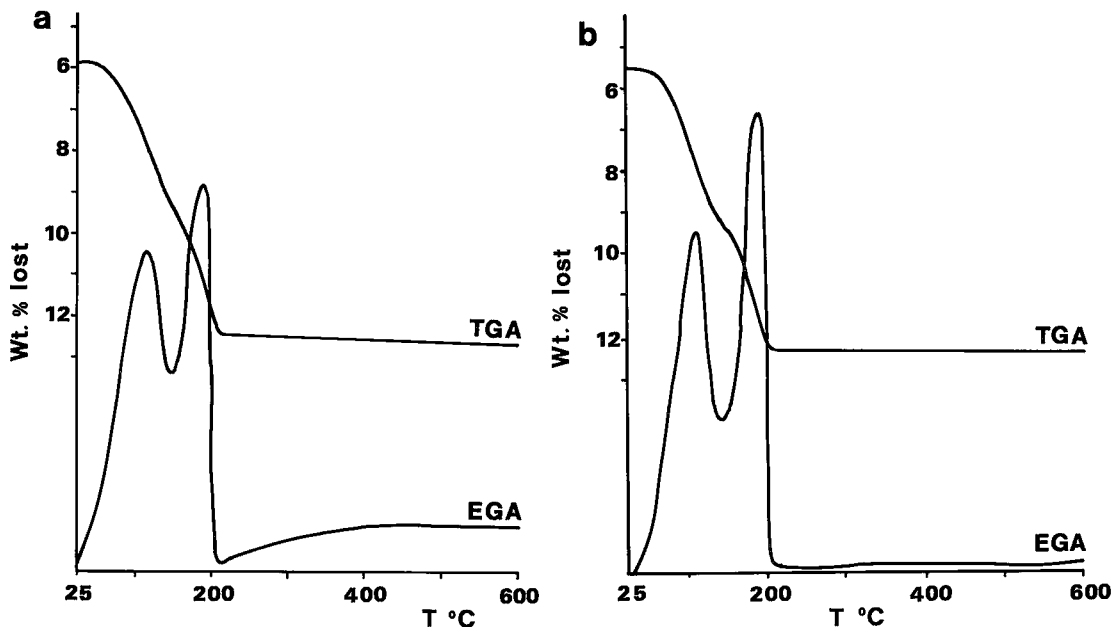

FIG. 6. Thermal analyses of edingtonite: thermal gravimetric analysis (TGA) and relative intensity (arbitrary units, measured on a mass spectrometer) of H_2O gas evolved (EGA). a) Ice River, b) Brunswick No. 12 mine.

that are structurally more tightly bonded. In the structure refinement, Galli (1976) noted the existence of two distinct H_2O sites, each with a multiplicity of four. One H_2O site has fewer ligands and a larger barium–water bond length than the other H_2O site (2.832 vs. 2.808 Å). No doubt the H_2O more loosely bonded to barium will account for the four molecules lost under vacuum below 25°C. The observation that the four more strongly bonded H_2O molecules are lost in two stages leads to the conclusion that they are not structurally equivalent, which contradicts the results of the recent refinement (Galli 1976), or that there is a structural change in edingtonite upon heating. The current neutron-diffraction studies of edingtonite at various temperatures by Å. Kvick and J.V. Smith (pers. comm., 1983) might find a solution to this problem.

ACKNOWLEDGEMENTS

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