

## HAINEAULTITE, A NEW HYDRATED SODIUM CALCIUM TITANOSILICATE FROM MONT SAINT-HILAIRE, QUEBEC: DESCRIPTION, STRUCTURE DETERMINATION AND GENETIC IMPLICATIONS

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### ABSTRACT

Haineaultite, ideally  $(\text{Na,Ca})_5\text{Ca}(\text{Ti,Nb})_5(\text{Si,S})_{12}\text{O}_{34}(\text{OH,F})_8 \cdot 5\text{H}_2\text{O}$ , is a new mineral species found predominantly in altered marble xenoliths at the Poudrette quarry, Mont Saint-Hilaire, Quebec. The mineral arose through the interaction of incompatible-element-rich late-stage fluids with marble xenoliths. At least some marble xenoliths were derived from limestones of Silurian, rather than Grenvillian, age. Crystals of haineaultite are generally lemon-yellow and more rarely tan, off-white or pale orange. The mineral occurs as either isolated, prismatic crystals, or fan-like aggregates of more tabular crystals, elongate along [001], with a maximum length of 6 mm. Associated minerals include pectolite, fluorapophyllite, vesuvianite, tainiolite, albite (pink), fluorite, calcite, microcline, aegirine and, to a lesser extent, analcime, steacyite, monteregianite-(Y), leucosphenite, mangan-neptunite, ancylite-(Ce), an alkali amphibole, a eudialyte-group mineral, sodalite, stillwellite-(Ce), vinogradovite, götzenite, pyrite, molybdenite, galena, sphalerite, and hibschite. The mineral has a vitreous luster, is transparent to translucent, has a white streak and shows no fluorescence in either short- or long-wave ultraviolet radiation. It has a Mohs hardness of 3 to 4, with distinct to good cleavages on {100}, {010} and {001}. It is brittle with a blocky to splintery fracture. The calculated density is  $2.28 \text{ g/cm}^3$ . Haineaultite is optically biaxial (+), with  $\alpha 1.599(1)$ ,  $\beta 1.610(1)$ ,  $\gamma 1.696(1)$ ,  $2V_{\text{meas}} = 38(1)^\circ$ ,  $2V_{\text{calc}} = 41(1)^\circ$ , and non-pleochroic. The optical orientation is  $X = b$ ,  $Y = c$  and  $Z = a$ . Sixteen electron-microprobe analyses gave, on average,  $\text{Na}_2\text{O}$  4.70,  $\text{K}_2\text{O}$  2.09,  $\text{MgO}$  0.07,  $\text{CaO}$  9.99,  $\text{MnO}$  0.25,  $\text{FeO}$  0.49,  $\text{SiO}_2$  42.70,  $\text{TiO}_2$  18.86,  $\text{ZrO}_2$  0.31,  $\text{Nb}_2\text{O}_5$  5.56,  $\text{SO}_3$  2.60,  $\text{F}$  0.17 and  $\text{H}_2\text{O}$  (calc.) 10.11,  $\text{O}=\text{F}$  -0.07, total 97.83 wt.%. The principal absorptions in the infrared include 3392, 1620, 1100, 985, 900, 720, 470  $\text{cm}^{-1}$ , indicative of both OH and  $\text{H}_2\text{O}$  in the structure. The mineral is orthorhombic, space group  $C222$ ,  $a$  7.204(2),  $b$  23.155(5),  $c$  6.953(2) Å,  $V$  1159.8(1) Å<sup>3</sup>,  $Z = 1$ . The strongest seven lines in the X-ray powder-diffraction pattern [ $d$  in Å(I)( $hkl$ )] are: 11.564(100)(020), 6.932(90)(001,110), 3.052(75)(240), 2.977(70)(042), 5.258(40)(130), 4.446(40)(041), and 2.582(40)(152,062). The structure of haineaultite was refined to  $R = 5.41\%$ ,  $wR^2 = 18.50\%$ . It consists of eight-membered (8MR) rings of  $\text{SiO}_4$  tetrahedra, linked to adjacent rings to form *vierer* double chains along [001], which are cross-linked by  $\text{TiO}_6$  octahedra to produce a mixed tetrahedron–octahedron titanosilicate framework similar to that found in zorite. Channels running parallel to [100] are occupied by Ca and  $\text{H}_2\text{O}$ , with Na occupying channels parallel to [001]. The mineral possesses an OD structure, exemplified by disordering of both framework and interframework ions. Haineaultite bears a relationship to technologically important synthetic microporous titanosilicates such as ETS-4 and ETS-10.

*Keywords:* haineaultite, new mineral species, microporous, titanosilicate, crystal structure, Mont Saint-Hilaire, Quebec.

### SOMMAIRE

La haineaultite, de composition idéale  $(\text{Na,Ca})_5\text{Ca}(\text{Ti,Nb})_5(\text{Si,S})_{12}\text{O}_{34}(\text{OH,F})_8 \cdot 5\text{H}_2\text{O}$ , est une nouvelle espèce minérale retrouvée surtout dans des xénolithes de marbre altérés dans la carrière Poudrette au mont Saint-Hilaire, Québec. Elle est le résultat de l'interaction de ces xénolithes avec une phase fluide tardive enrichie en éléments incompatibles. Au moins dans certains cas, ces xénolithes seraient dérivés de calcaires d'âge silurien plutôt que grenvillien. Les cristaux de haineaultite sont en général jaune-citron, et plus rarement beige, blanc-crème ou orange pâle. Les cristaux sont soit isolés et prismatiques, soit en agrégats de cristaux tabulaires radiés, allongés le long de [001], et atteignant une longueur maximale de 6 mm. Lui sont associés pectolite, fluorapophyllite, vésuvianite, tainiolite, albite (rose), fluorite, calcite, microcline, aegirine et, à un degré moindre, analcime, steacyite, monterégianite-(Y), leucosphénite, mangan-neptunite, ancylite-(Ce), une amphibole alcaline, un minéral du

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groupe de l'eudialyte, sodalite, stillwellite-(Ce), vinogradovite, götzenite, pyrite, molybdénite, galène, sphalérite, et hibschite. Le minéral possède un éclat vitreux et une rayure blanche; il est transparent à translucide, et ne montre aucune fluorescence, soit en ondes ultraviolettes longues ou courtes. Sa dureté est de 3 à 4, et les clivages {100}, {010} et {001} sont bons. Ce minéral est cassant, avec une fracture en blocs ou en échapes. La densité calculée est 2.28 g/cm<sup>3</sup>. La haineaultite est optiquement biaxe (+), avec  $\alpha$  1.599(1),  $\beta$  1.610(1),  $\gamma$  1.696(1),  $2V_{\text{mes}}$  38(1)°,  $2V_{\text{calc}}$  41(1)°, et non pléochroïque. L'orientation optique est  $X = b$ ,  $Y = c$  et  $Z = a$ . Seize analyses avec une microsonde électronique ont donné, en moyenne, Na<sub>2</sub>O 4.70, K<sub>2</sub>O 2.09, MgO 0.07, CaO 9.99, MnO 0.25, FeO 0.49, SiO<sub>2</sub> 42.70, TiO<sub>2</sub> 18.86, ZrO<sub>2</sub> 0.31, Nb<sub>2</sub>O<sub>5</sub> 5.56, SO<sub>3</sub> 2.60, F 0.17 and H<sub>2</sub>O (calc.) 10.11, O=F -0.07, pour un total de 97.83% (poids). Les absorptions principales du spectre dans l'infrarouge sont 3392, 1620, 1100, 985, 900, 720, 470 cm<sup>-1</sup>, indications de la présence de OH et de H<sub>2</sub>O dans la structure. Le minéral est orthorhombique, groupe spatial C222,  $a$  7.204(2),  $b$  23.155(5),  $c$  6.953(2) Å,  $V$  1159.8(1) Å<sup>3</sup>,  $Z = 1$ . Les sept raies les plus intenses du spectre de diffraction, méthode des poudres [ $d$  en Å(I)( $hkl$ )], sont: 11.564(100)(020), 6.932(90)(001,110), 3.052(75)(240), 2.977(70)(042), 5.258(40)(130), 4.446(40)(041), et 2.582(40)(152,062). La structure de la haineaultite a été affinée jusqu'à un résidu  $R$  de 5.41% ( $wR^2 = 18.50\%$ ). Elle consiste d'anneaux de tétraèdres SiO<sub>4</sub> à huit membres agencés à des anneaux adjacents pour former des chaînes doubles de type *vierer* le long de [001], avec liaisons transversales assurées par des octaèdres TiO<sub>6</sub> pour produire une trame titanosilicatée contenant un mélange de tétraèdres et d'octaèdres semblable à ce que l'on trouve dans la zorite. Les canaux le long de [100] contiennent Ca et H<sub>2</sub>O, et ceux le long de [001] contiennent le Na. Le minéral possède une structure OD, manifestée par un désordre impliquant la trame et les ions interstitiels à la trame. La haineaultite montre un lien avec les titanosilicates microporeux synthétiques technologiquement importants, tels ETS-4 et ETS-10.

(Traduit par la Rédaction)

*Mots-clés:* haineaultite, nouvelle espèce minérale, microporeux, titanosilicate, structure cristalline, mont Saint-Hilaire, Québec.

## INTRODUCTION

Haineaultite, ideally (Na,Ca)<sub>5</sub>Ca(Ti,Nb)<sub>5</sub>Si<sub>12</sub>O<sub>34</sub>(OH,F)<sub>8</sub>•5H<sub>2</sub>O, is a new mineral species discovered in altered marble xenoliths at the Poudrette Quarry, Mont Saint-Hilaire, Rouville County, Quebec. In was first encountered on June 22, 1986, by Dr. Peter Tarassoff, who submitted a sample of the unknown mineral (PT 189, UK61) to one of us (GYC) for identification. The mineral was found to give an X-ray powder-diffraction pattern similar to that of zorite [Na<sub>2</sub>Ti(Si,Al)<sub>3</sub>O<sub>9</sub>• $n$ H<sub>2</sub>O; Mer'kov *et al.* 1973] but with noticeably smaller values of  $d$ . Subsequent qualitative chemical analyses indicated it to be significantly enriched in Ca relative to zorite. A complete, detailed study of the mineral was undertaken, the results of which have clearly demonstrated that the mineral is indeed new. It has been named *haineaultite* (pronounced *ā n̄ ō ite*) after Mr. Gilles Haineault (b. 1946) of St-Mathieu de Beloeil, Quebec, a well-known collector and dealer of minerals from Mont Saint-Hilaire who has for many years contributed to the development of a knowledge base about the mineralogy of Mont Saint-Hilaire. In light of its crystal-chemical relationship with zorite, haineaultite may be considered a Cadominant analogue of Na<sub>2</sub>Ti(Si,Al)<sub>3</sub>O<sub>9</sub>• $n$ H<sub>2</sub>O. Both the mineral and mineral name were approved by the Commission on New Minerals and Mineral Names, IMA (IMA 97-015). The holotype material is housed in the collection of the Canadian Museum of Nature, Ottawa (catalogue no. CNMNM 81547).

## OCCURRENCE

Mont Saint-Hilaire is one of ten east-west-trending alkaline intrusions of early Cretaceous age collectively referred to as the Monteregian Hills (Adams 1903). The

Poudrette quarry is located in the peralkaline East Hill Suite, the youngest of three intrusive suites that constitute Mont Saint-Hilaire (Currie *et al.* 1986). The East Hill Suite is mineralogically the most complex; to facilitate mineralogical and geochemical discussions, a microenvironment nomenclature has been informally adopted and is in common usage (*e.g.*, Piilonen *et al.* 1998). This nomenclature utilizes a combination of petrological features and mineralogical assemblage to characterize each microenvironment. As both may be broadly similar for different microenvironments, the scheme can be somewhat limited in its application. Haineaultite was first encountered in 1986 (PT 189) in what may be an unusual altered marble xenolith or breccia with an extremely dark matrix. At this point, the actual lithological or microenvironment classification of the sample remains unresolved, despite our petrographic study. Since then, similar material has been infrequently encountered at Mont Saint-Hilaire, with some of the best specimens having been found in 2000 on level 8 near the east corner of the quarry. The area of interest is situated between nepheline and sodalite syenite, proximal to the margin of a large block of hornfels. It is rich not only in altered marble xenoliths, but also contains significant quantities of igneous breccia and sodalite syenite xenoliths. Haineaultite is clearly a late-stage mineral whose origin is likely related to fluids that moved through solidified or partially solidified rocks.

Crystals of haineaultite from the unusual breccia or altered marble xenolith (henceforth, type 1) are tabular with somewhat complex, stepped terminations. Associated minerals include quartz, a labuntsovite-group mineral, calcite, a sodic amphibole and another unknown mineral, temporarily designated UK75 (possibly the Ti-dominant analogue of lemoynite). The majority of the haineaultite recovered to date has been from vugs in

what are clearly altered marble xenoliths. These crystals (henceforth, type 2) are prismatic to tabular or bladed and occur as part of a complex assemblage, the dominant minerals of which include pectolite, fluorapophyllite, vesuvianite, tainiolite, albite (pink), fluorite, calcite (in yellow, equant crystals), microcline and aegirine, along with the minor phases analcime, steacyite, monteregianite-(Y), leucosphenite, manganneptunite, ancylite-(Ce), an alkali amphibole, a eudialyte-group mineral, sodalite, stillwellite-(Ce), vinogradovite, götzenite, pyrite, molybdenite, galena, sphalerite, and hibschite.

#### ORIGIN OF MARBLE XENOLITHS

Given the fact that most haineaultite has come from marble xenoliths, a discussion of the origin of these xenoliths with respect to the formation of the mineral seems appropriate. Marble xenoliths at Mont Saint-Hilaire have been briefly described by a number of investigators, including Currie *et al.* (1986), Mandarino & Anderson (1989) and Horváth & Gault (1990). In general, they are white to pale green in color, ranging in size from a few centimeters to a maximum of about five meters across, averaging one to two meters. In some cases, the xenoliths are angular, and their contacts with the nepheline syenite are sharp, with the adjacent rock unaltered, whereas in others, the blocks are quite rounded with distinctly metasomatized contacts (with euhedral vesuvianite, meionite and grossular). Individual grains of calcite may be fine- or coarse-grained, and this, in conjunction with some of the observed contact-relationships, suggests that the xenoliths have, to a certain extent, undergone partial recrystallization. In spite of this, relict bedding and folding have been noted in some xenoliths. The xenoliths are predominantly composed of calcite and diopside, with lesser amounts of phlogopite and sulfides (pyrite, pyrrhotite). However, to date, more than 85 distinct minerals have been found in such material (Horváth & Gault 1990), some of them being extremely rare [*e.g.*, monteregianite-(Y), steacyite, penkvilksite, sugilite], and others possibly new to science (*e.g.*, UK39, UK75; Chao *et al.* 1990). Many of the exotic minerals are characterized by compositions enriched in REE, Zr, Ti, Li, F and Na [*e.g.*, eudialyte-group minerals, sérandite, magadiite, ancylite-(Ce), tainiolite]. In general, most of the exotic minerals occur in vugs 10–15 cm in diameter, found at the core of xenoliths. The vugs are typically lined with euhedral crystals of pectolite nucleating on a thin rind of purple fluorite, along with black amphibole that is typically richterite in composition (Taylor 1999). They also commonly contain a distinctly yellow, platy calcite, which is interpreted to be of a later generation.

The origin of the marble xenoliths is unclear, and has not been dealt with extensively in the literature. Some investigators have suggested that the marble represents Precambrian basement (probably Grenvillian in

age, *i.e.*, 1.3–1.0 Ga) that was ripped up and incorporated into the ascending magma; they cite evidence that includes recrystallization features along with relict bedding and folding (Horváth & Gault 1990). This hypothesis is untenable for two reasons: 1) fossils (brachiopods, corals) have been found associated with some of the xenoliths, and 2) the majority of the Grenvillian rocks that likely underlie MSH are part of the Morin terrane of the Central Granulite Terrane (Davidson 1989), which is dominantly composed of gabbro, anorthosite, monzonite and quartzofeldspathic gneiss, rather than marble. With respect to 1), a fine example of a fossilized brachiopod, completely replaced by a combination of pectolite (predominantly) and a sodic amphibole (an assemblage characteristic of the vugs found in the marble xenoliths), was collected at MSH and now resides at the Canadian Museum of Nature (A1995.0029). The sample has been identified by Prof. P. Copper (Laurentian University) as a Spiriferid, likely belonging to the *Striispirifer* genus, which is of Wenlock or Llandovery age (early Silurian). In addition, a sample of a rugose coral has also been noted in what appears to be a marble xenolith. It has been identified (by Prof. P. Copper) as an *Atrypa sp.* in a broad sense, likely Silurian, but possibly Devonian in age. Thus the fossil evidence clearly indicates that at least some of the marble xenoliths must be younger than Grenvillian in age. With respect to 2), while the true basement lithology underlying MSH is obscured by overlying Paleozoic rocks, that located less than 60 km to the north is composed of ultramafic, mafic and felsic intrusives, and in some cases, their metamorphic equivalents, which occupy the Morin terrane (*e.g.*, Davidson *et al.* 2002). In this terrane, marble is volumetrically insignificant, constituting less than 2% of the total rock package (M. Easton, pers. commun.). The marble present in this terrane exhibits no relict bedding and is typically found associated with clasts of gneiss, paragneiss or quartzite, features inconsistent with the observations made on marble xenoliths at MSH. In summary, there is strong evidence to suggest that the marble xenoliths MSH are unlikely to be Grenvillian in age.

As the three suites that constitute MSH were clearly intruded into limestones of the originally overlying Ordovician Lorraine and Richmond groups (Currie *et al.* 1986), it is conceivable that a certain amount of limestone of Silurian age (subsequently eroded away) was also intruded. The implication is thus that different blocks from all the overlying carbonates may have been rafted down into the magma during emplacement, rather than incorporated from below during magma ascent.

The unusual assemblage of minerals associated with haineaultite reflects an enrichment in incompatible elements (Ti, Zr, REE, Li, *etc.*) in the late-stage fluid. It is not clear, however, to what extent its interaction with the primary minerals of the xenoliths has influenced the composition and assemblage of secondary minerals. To test for differences in the composition of what are inter-

puted to be primary green *versus* late-stage yellow calcite, a comparative LAM-ICP-MS study of their REE contents was undertaken. Whereas both exhibit noticeable Eu anomalies, there are significant differences in the distribution of REE over their entire range (Fig. 1). In particular, the late-stage yellow calcite shows pronounced enrichments in the LREE and MREE relative to primary green calcite. These enrichments are noteworthy, as the late-stage yellow calcite commonly occurs in an assemblage containing a number of LREE-enriched minerals, including ancylite-group minerals, tadhikite-group minerals, tundrite-(Ce), and stillwellite-(Ce). Whereas it may be premature to speculate on the reasons for the absolute differences in the REE patterns for the two types of calcite, we conclude that there were significant geochemical differences in the source fluids for the two, and that the REE distribution in the late-stage yellow calcite is consistent with a LREE-rich fluid.

It is worthy of note that many of exotic minerals associated with haineaultite [*e.g.*, eudialyte-group minerals, sérandite, magadiite, ancylite-(Ce), tainiolite] are also found in other microenvironments at MSH (*e.g.*, late-stage pegmatites, sodalite syenite xenoliths, igneous breccias *etc.*). The fluids from which all these minerals were derived may well have had strong chemical similarities, and differences in the exotic mineral assemblages between the various microenvironments may be more a function of the interaction between host lithology and fluid rather than differing fluid compositions. It is interesting to note that the majority of marble xenoliths containing exotic minerals have been found near the southeastern corner of the Poudrette quarry, in an area recognized for containing many unusual late-stage minerals, including several new to science (Horváth & Pfenninger 2000). The implication is that the crystallization of the numerous exotic minerals may principally be a function of proximity to incompatible-element-rich

late-stage fluids, rather than the primary mineralogical composition of the xenolith. Zorite (to which haineaultite is closely related) and other related, synthetic titanosilicates have been synthesized (*e.g.*, Anderson *et al.* 1994) from alkaline fluids at a relatively low temperature (<250°C), which provides some basic information on the conditions of haineaultite formation. However, the true nature and origin of the late-stage fluids still remain unknown; a more in-depth study on the origin and metamorphic history of the xenoliths is planned to investigate these outstanding questions.

#### PHYSICAL AND OPTICAL PROPERTIES

Crystals of haineaultite are typically prismatic, tabular or bladed, elongate on [001], with a maximum length of 6 mm. Type-1 haineaultite occurs as pale orange, tabular crystals, bounded by the pinacoids {100} and {010}. Such crystals possess complex terminations that have a stepped-like nature, the indices for which could not be unambiguously determined, but are likely low-order prisms {0kl}. Type-2 haineaultite occurs as either isolated, blocky crystals, or fan-like aggregates of more tabular crystals, which are generally lemon-yellow, and more rarely, tan or off-white. Their morphology is relatively simple: crystals are bounded by the major pinacoids {100} and {010}, the minor pinacoid {001} and prism {011} (Fig. 2). Indexing of the faces was facilitated by comparing calculated interfacial angles and those measured from photomicrographs of the mineral obtained by scanning electron microscopy. No twinning was observed in type-2 material; however, attempts to refine the crystal structure of type-1 material were not successful, one explanation for which may be the presence of previously unrecognized twinning. The mineral has a vitreous luster, is transparent to translucent, has a white streak and shows no fluorescence in either short- or long-wave ultraviolet radiation. It has a Mohs hard-

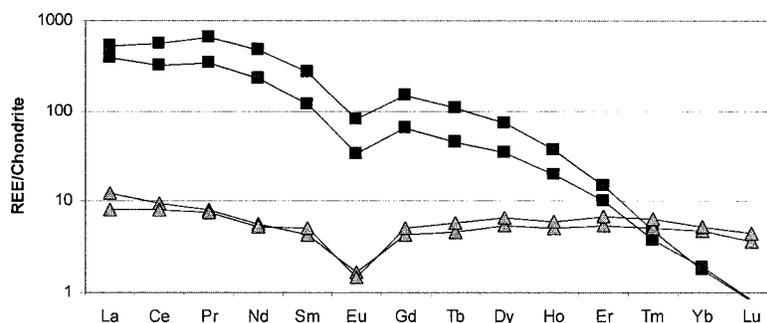


FIG. 1. A chondrite-normalized REE plot of calcite from marble xenoliths. The pale green calcite (triangles), is interpreted to be primary, and the yellow calcite (squares) to be secondary, possibly arising from late-stage fluids interacting with the marble xenolith.

ness of 3 to 4, and distinct to good cleavages on {100}, {010} and {001}. It is brittle with a blocky to splintery fracture. The calculated density is 2.28 g/cm<sup>3</sup>. Measurements of density were found to be highly erratic, likely owing to significant but variable concentrations of inclusions, which include albite (identified by Gandolfi PXRD and qualitative energy-dispersion analyses) and hedenbergite (identified solely from EDS data); an accurate value could not be determined.

Haineaultite is non-pleochroic, biaxial positive,  $\alpha$  1.599(1),  $\beta$  1.610(1),  $\gamma$  1.696(1) (for  $\lambda = 590$  nm),  $2V_{\text{meas}} = 38(1)^\circ$ ,  $2V_{\text{calc}} = 41(1)^\circ$ ; no dispersion was noted. The optical orientation is  $X = b$ ,  $Y = c$  and  $Z = a$ . A Gladstone–Dale calculation gave a compatibility index of 0.075, which is classed as fair (Mandarino 1981).

#### CHEMICAL COMPOSITION

Chemical analyses were conducted on a CAMEBAX SX50 electron microprobe using an operating voltage of 15 kV, a beam current of 10 nA and a beam diameter of approximately 10  $\mu\text{m}$ . Energy-dispersion data were collected using the following standards: wadeite (SiK $\alpha$ , ZrL $\alpha$ , KK $\alpha$ ), wollastonite (CaK $\alpha$ ), synthetic MnTiO<sub>3</sub> (MnK $\alpha$ , TiK $\alpha$ ), periclase (MgK $\alpha$ ), sphalerite (ZnL $\alpha$ ) and synthetic hematite (FeK $\alpha$ ). In addition, wavelength-dispersion data were collected using albite (NaK $\alpha$ ), synthetic FeNb<sub>2</sub>O<sub>6</sub> (NbL $\alpha$ ) and synthetic BaF<sub>2</sub> (FK $\alpha$ ) as standards. No other elements were indicated by qualitative EDS scans. Also sought, but not detected, were Al and Hf. Sixteen analyses of two type-2 crystals gave as an average (range): Na<sub>2</sub>O 4.70 (3.64–6.44), K<sub>2</sub>O 2.09 (1.62–2.83), MgO 0.07 (0–0.24), CaO 9.99 (8.64–10.78), MnO 0.25 (0–0.56), FeO 0.49 (0.11–1.00), SiO<sub>2</sub> 42.70 (41.80–43.55), TiO<sub>2</sub> 18.86 (18.08–19.45), ZrO<sub>2</sub>

0.31 (0–0.75), Nb<sub>2</sub>O<sub>5</sub> 5.56 (4.63–6.98), SO<sub>3</sub> 2.60 (1.71–3.43), F 0.17 (0–0.39) and H<sub>2</sub>O (calc.) 10.11 (9.94–10.23), O=F –0.07 (0–0.16), total 97.83 wt.%. The presence of H<sub>2</sub>O was confirmed by infrared spectroscopy (see below) and results of the crystal-structure analysis, the latter serving as the basis for calculation of the stoichiometric proportion of H<sub>2</sub>O. The empirical formula based on 47 anions is: (Na<sub>2.41</sub>Ca<sub>1.83</sub>K<sub>0.71</sub>) $\Sigma$ <sub>4.95</sub>Ca (Ti<sub>3.76</sub>Nb<sub>0.67</sub>Fe<sub>0.11</sub>Mn<sub>0.06</sub>Zr<sub>0.04</sub>Mg<sub>0.03</sub>) $\Sigma$ <sub>4.67</sub>(Si<sub>11.30</sub>S<sub>0.52</sub>) $\Sigma$ <sub>11.82</sub>O<sub>34</sub>(OH<sub>7.86</sub>F<sub>0.14</sub>) $\Sigma$ <sub>8</sub>•5H<sub>2</sub>O or, ideally, (Na,Ca)<sub>5</sub>Ca(Ti,Nb)<sub>5</sub>(Si,S)<sub>12</sub>O<sub>34</sub>(OH,F)<sub>8</sub>•5H<sub>2</sub>O. The low analytical total may be due to a combination of element migration under the electron beam and the presence of vacancies in the crystal structure. Owing to the paucity of material, no analyses of type-1 crystals were made. The mineral does not effervesce in 1:1 HCl at room temperature.

#### INFRARED ANALYSIS

The infrared spectrum of haineaultite (Fig. 3) was obtained using a Bomem Michelson MB–120 Fourier transform infrared spectrometer equipped with a mercury–cadmium telluride (MCT) detector. A single crystal of material from the altered marble xenoliths was mounted in a Spectra–Tech low-pressure diamond-anvil microsample cell and the spectrum, using a total of 200 co-added scans, was obtained over the range 4000–400 cm<sup>–1</sup>. The spectrum shows a broad band centered on the 3392 cm<sup>–1</sup> region (O–H stretching), and a relatively sharp band at 1620 cm<sup>–1</sup> (H–O–H bending), confirming the presence of H<sub>2</sub>O as molecular water. The spectrum also shows a strong, sharp band at 985 cm<sup>–1</sup> with two shoulders at 1100 and 900 cm<sup>–1</sup> (asymmetric O–Si–O stretching) and four sharp, moderately strong bands in the region 712–470 cm<sup>–1</sup> (symmetric Si–O–Si stretching; Farmer 1974).

#### X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

Precession photographs show haineaultite to be orthorhombic, diffraction symmetry  $2/m 2/m 2/m$ , with  $C222$ ,  $Cmm2$  and  $Cmmm$  as possible choices of the space group. X-ray powder-diffraction data (Table 1) were collected with a 114.6 diameter Debye–Scherrer camera employing Ni-filtered CuK $\alpha$  radiation ( $\lambda = 1.5418$  Å). Intensities were visually estimated. Whether or not an  $hkl$  plane contributed to a reflection was determined from the powder pattern calculated using the atom parameters determined in the crystal-structure analysis and the program *POWDERCELL* (Nolze & Kraus 1998).

The single crystal used for the collection of intensity data measures 0.16  $\times$  0.12  $\times$  0.07 mm. X-ray intensity data were collected on a fully automated Siemens P3 four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated MoK $\alpha$  radiation. A full

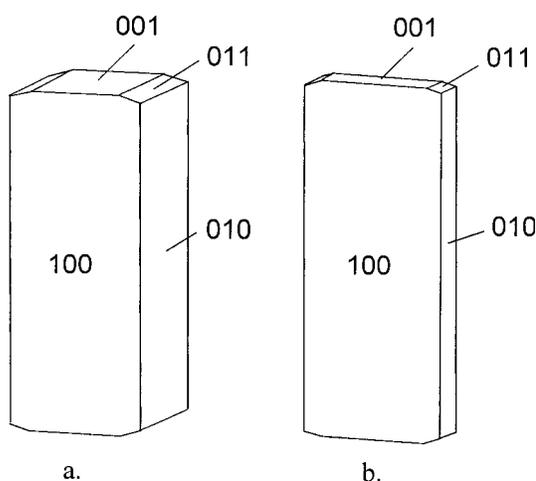


FIG. 2. Crystal drawings of type-2 haineaultite showing three pinacoids and a prism: a. prismatic habit; b. bladed habit.

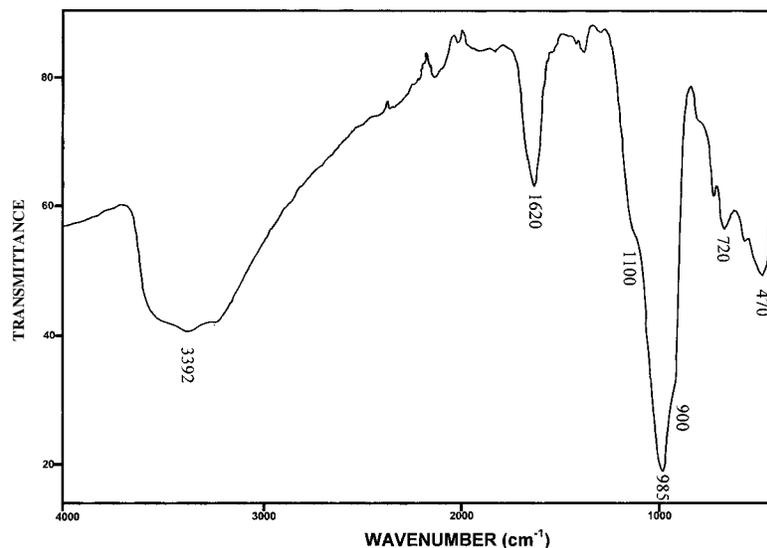


FIG. 3. Infrared spectrum of haineaultite.

TABLE 1. HAINEAULTITE: X-RAY POWDER-DIFFRACTION DATA

<i>l</i>	<i>d</i> <sub>obs</sub> (Å)	<i>d</i> <sub>calc</sub> (Å)	<i>hkl</i>	<i>l</i>	<i>d</i> <sub>obs</sub> (Å)	<i>d</i> <sub>calc</sub> (Å)	<i>hkl</i>
100	11.564	11.578	020	1	2.020	2.038	351
90	6.932	6.953	001			2.021	1110
		6.879	110	3	1.984	1.987	063
20	5.949	5.961	021	10	1.965	1.969	312
10	5.763	5.789	040	10	1.926	1.928	0102
40	5.258	5.266	130	5	1.890	1.893	282
40	4.446	4.449	041	10	1.872	1.876	2101
5	4.184	4.198	131	3	1.826	1.817	352
35	3.593	3.602	200	15	1.793	1.801	400
35	3.433	3.439	220	10	1.774	1.780	282
10	3.367	3.374	061	25	1.736	1.739	004
30	3.172	3.198	201	20	1.697	1.699	2102
75	3.052	3.058	240	5	1.667	1.675	193
70	2.977	2.981	042			1.669	441
25	2.896	2.902	132	3	1.635	1.638	0103
20	2.755	2.759	171			1.630	333
35	2.630	2.632	260	10	1.583	1.584	422
40	2.582	2.594	152	15	1.538	1.542	442
		2.583	062	10	1.525	1.528	2122
15	2.499	2.502	202	3	1.507	1.509	1150
10	2.435	2.445	222	3	1.503	1.503	2140
5	2.420	2.423	190	5	1.4890	1.4935	481
5	2.289	2.296	242	3	1.4722	1.4774	462
3	2.272	2.274	172	10	1.4491	1.4508	264
1	2.222	2.225	082	10	1.4122	1.4168	0161
8	2.147	2.152	043			1.4163	530
10	2.125	2.132	350	10	1.3788	1.3811	443
5	2.096	2.099	262			1.3797	2142

TABLE 2. MISCELLANEOUS INFORMATION FOR HAINEAULTITE

Space group	C222 (# 21)	Diffractometer	Siemens P3
<i>a</i> (Å)	7.204(2) *	Radiation	MoK $\alpha$ (50 kV, 40 mA)
<i>b</i>	23.155(5) *	Monochromator	Graphite
<i>c</i>	6.953(2) *	Crystal shape	Blocky, elongate on [001]
<i>V</i> (Å <sup>3</sup> )	1159.8(1)	Crystal size	0.16 × 0.12 × 0.07 mm
<i>Z</i>	1	$\mu$ (MoK $\alpha$ )	1.23 mm <sup>-1</sup>
Chemical Formula	(Na,Ca) <sub>2</sub> Ca(Ti,Nb) <sub>2</sub> (Si,S) <sub>12</sub> O <sub>32</sub> (OH,F) <sub>8</sub> ·5H <sub>2</sub> O	Intensity-data collection	$\theta$ : $2\theta$ scan mode
2 $\theta$ limit	60°	Number of unique reflections	1712
Number of observed reflections	1418	Number of observed reflections	1418
Criterion for observed	$F_o > 4\sigma(F_o)$	GoF	1.251
Final <i>R</i> for all observed reflections	5.41%	Final <i>wR</i> <sup>2</sup> for all observed reflections	18.50%

\* values refined from four-circle diffractometer data.

sphere of X-ray intensity data out to  $2\theta = 60^\circ$  was collected using a  $\theta$ : $2\theta$  scan-mode, with scan speeds inversely proportional to intensity. With these operating conditions, no decrepitation was evident in the final analysis of the reflections used as intensity standards. Data reduction (Lorentz, polarization, background, scal-

ing) was carried out using the program SAINT. An ellipsoidal absorption-correction was applied using 30 intense diffraction-maxima in the range of 6 to  $31^\circ 2\theta$ , following the method of North *et al.* (1968). The merging *R* for the  $\psi$ -scan data set (328 reflections) decreased from 2.02% before the absorption correction to 1.47% after the absorption correction. Information pertinent to the data collection and structure determination is provided in Table 2.

Solution and refinement of the crystal structure were accomplished using the SHELX-93 package of programs (Sheldrick 1993). The crystal structure was solved using direct methods, with scattering curves taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. Phasing of a set of nor-

malized structure-factors gave a mean value of  $|E^2 - 1|$  equal to 0.896 (predicted values: 0.968, centrosymmetric, 0.736, non-centrosymmetric). Space-group *C222* was selected on the basis of the low calculated combined figure of merit (0.082 versus 0.136 for *Cmmm* and 0.532 for *Cmm2*). Phase-normalized factors were calculated and used to produce an *E*-map on which were located *Ti*, *Si* and several *O* sites. The remaining *Na*, *Ca* and *O* sites were located on subsequent Fourier-difference maps. Determination of those *O* sites likely occupied by O, OH or H<sub>2</sub>O was made on the basis of calculations of bond-valence sums. Anisotropic refinement of this model indicated that several sites, namely *Na*, *Ca*, *Ti2*, *Si2* and *OW10* sites have lower-than-ideal site-occupancy factors (SOF). For *Ca*, *Ti2*, *Si2*, the refined SOF are, curiously, almost exactly 1/4 or 1/2 of their theoretical values: 0.118(4) versus 0.5 (*Ca*; Wyckoff symbol 4*k*), 0.130(2) versus 0.25 (*Ti2*; 4*k*), and 0.464(8) versus 1 (*Si2*; 8*l*). The low refined SOF values are enigmatic, but reviews of the crystal structures of zorite (Sandomirskii & Belov 1979) and those of related, synthetic titanosilicate counterparts, such as *ETS-10* and *ETS-4* (Anderson *et al.* 1994), reveal that such vacancies are the norm in these minerals and materials. Sandomirskii & Belov (1979), for example, considered zorite to have an order-disorder (OD) type of structure. Additional evidence supporting disorder in haineaultite includes the presence of streaking along *a*\* and *c*\*, and of weak superlattice reflections (doubling the repeat along *a* and *c*) observed in precession photographs, and the results of the present crystal-structure refinement, which indicate the presence of two symmetrically equivalent *Si2* atoms separated by 1.384(4) Å. In light

of these data, the SOF for *Ca*, *Ti2*, *Si2* were fixed at 0.125, 0.125 and 0.5, respectively. Further refinement indicated the SOF for *Na* [0.63(1)] and *OW10* [0.12(1)] also to be significantly lower than predicted if fully occupied (*i.e.*, 1 and 1/2, respectively), likely owing to vacancies in these sites. Final least-squares refinement of this model gave residuals of *R* = 5.41 % and *wR*<sup>2</sup> = 18.50 %, with maximum and minimum electron-densities of +1.23 and -0.61 e/Å<sup>3</sup>. Refinement of haineaultite was also attempted in the centrosymmetric space-group *Cmmm*. Similar, lower-than-ideal SOF for the same sites were noted, but the residuals obtained for this model were found to be slightly higher (*R* = 6.00 % and *wR*<sup>2</sup> = 18.70 %). It should be noted that given the intermediate value for  $|E^2 - 1|$  obtained in this study, along with the propensity of the mineral to disorder, there does exist the possibility that extent of the disorder is variable, such that small increases in a single crystal could result in a centrosymmetric structure. Hence the possibility of *Cmmm* being the true space-group for haineaultite cannot be discounted. In addition, another unidentified mineral, temporarily designated UK61a on the basis of its close similarity to haineaultite (formerly UK61), has also been found at Mont Saint-Hilaire. This phase may in fact be a more highly disordered polymorph of (Na,Ca)<sub>5</sub>Ca (Ti,Nb)<sub>5</sub>(Si,S)<sub>12</sub>O<sub>34</sub>(OH,F)<sub>8</sub>•5H<sub>2</sub>O; further studies are ongoing.

Table 3 contains the final positional and displacement parameters, selected interatomic distances in Table 4, and bond-valence sums in Table 5. Observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National

TABLE 3. POSITIONAL AND DISPLACEMENT PARAMETERS FOR HAINEAULTITE

	<i>x</i>	<i>y</i>	<i>z</i>	SOF	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>eq</sub>
Na	-0.002(1)	0.1378(2)	0.2853(6)	0.63(1)	0.005(1)	0.024(2)	0.054(2)	-0.016(2)	-0.012(4)	0.014(4)	0.028(1)
Ca	1/4	1/4	-0.011(2)	0.125	0.039(4)	0.053(4)	0.018(3)	0	0	0.016(3)	0.035(2)
Ti1	3/4	3/4	0.4982(4)	0.40(1)	0.0220(5)	0.0127(4)	0.0101(4)	0	0	0.0088(3)	0.0149(3)
Nb				0.10(1)							
Ti2	0	0	1/2	0.125	0.014(1)	0.009(11)	0.090(3)	0	0	0	0.038(1)
Si1	0.0013(7)	0.33863(4)	0.2296(2)	1.00	0.0135(5)	0.0119(5)	0.0068(4)	0.0001(4)	-0.001(1)	0.000(2)	0.0105(4)
Si2	0.0961(3)	0.43539(9)	0.495(1)	0.50	0.012(1)	0.0079(9)	0.017(1)	-0.002(3)	0.006(3)	-0.0013(7)	0.0122(5)
O1	0.186(1)	0.3064(5)	0.304(1)	1.00	0.005(3)	0.044(6)	0.027(4)	0.016(4)	0.001(3)	0.008(3)	0.025(2)
O2	0.014(2)	0.4044(2)	0.3103(6)	1.00	0.046(4)	0.014(1)	0.019(2)	-0.007(1)	0.003(3)	-0.009(4)	0.026(2)
O3	0	0.3459(2)	0	0.50	0.050(3)	0.028(2)	0.008(2)	0	0.010(7)	0	0.028(1)
O4	0	1/2	1/2	0.25	0.026(3)	0.006(2)	0.031(3)	0	0	0	0.021(1)
O5	-0.185(2)	0.3061(4)	0.291(1)	1.00	0.024(4)	0.023(4)	0.039(4)	0.028(4)	-0.005(4)	-0.002(4)	0.028(2)
O6	1/2	0.7197(2)	1/2	0.50	0.008(2)	0.014(2)	0.023(2)	0	-0.007(6)	0	0.0150(8)
OH7	0	0.1993(5)	0	0.50	0.124(9)	0.069(6)	0.061(6)	0	-0.02(2)	0	0.084(3)
OH8	0.316(1)	0.4372(4)	0.471(3)	0.50	0.013(3)	0.018(3)	0.06(1)	-0.006(5)	0.004(5)	-0.002(2)	0.033(5)
OW9	-0.069(5)	1/2	0	0.50	0.28(6)	0.22(2)	0.14(2)	0.13(2)	0	0	0.21(2)
OW10	0	0	0.218(4)	0.12(1)	0.03(2)	0.02(1)	0.06(2)	0	0	0.02(4)	0.03(1)

SOF: site-occupancy factor.

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CRYSTAL-STRUCTURE DESCRIPTION  
AND RELATED STRUCTURES

Haineaultite contains two crystallographically distinct tetrahedra, Si(1)O<sub>4</sub> and Si(2)O<sub>3</sub>OH, that are linked into eight-membered rings (8MR; Fig. 4). Bond distances in Si(1)O<sub>4</sub> tetrahedra are typical (1.598–1.610 Å), with one elongate bond (1.626 Å) representing a bridging atom of oxygen with Si(2)O<sub>4</sub>. The Si(2)O<sub>3</sub>OH tetrahedra are considerably more irregular, with bond distances ranging from 1.588 [O shared with Ti(1)] to 1.722 Å [bridging O with Si(2)]. The effective pore-size of the 8MR ring (using the terminology of Kuznicki *et al.* 2001) varies from  $D_1 = 6.953$  (*i.e.*, *c* repeat) to  $D_2 =$

7.139 to  $D_3 = 6.190$  Å (Fig. 4). In haineaultite, adjacent silicate rings are linked *via* Si(2)O<sub>3</sub>OH tetrahedra to form chains running parallel to [001]; in this manner, the mineral may be classed as an unbranched silicate composed of *vierer* double chains (Liebau 1985).

Adjacent 8MR along [100] are linked *via* isolated Ti(1)(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> (effectively TiO<sub>6</sub>) octahedra. The double silicate chains are joined along [010] by chains of Ti(2)O<sub>6</sub> octahedra (Fig. 5). Weak bonding between the Tiφ<sub>6</sub> octahedra (φ: unspecified ligand) and the double silicate chains presumably leads to the perfect {100} and {010} cleavages observed in the mineral. The two types of Tiφ<sub>6</sub> octahedra are both relatively regular, with axial bonds being generally longer than equatorial ones (Table 4).

Haineaultite may be considered as having a three-dimensional, mixed tetrahedron–octahedron (heteropolyhedral) framework. This configuration produces large channels, which are occupied by a combination of Na, Ca and molecules of H<sub>2</sub>O. Both Ca and H<sub>2</sub>O are located in channels parallel to [100], H<sub>2</sub>O in the center of channels formed by the 8MR silicate rings, and Ca in channels of 6MR formed between Ti(2)O<sub>6</sub> octahedra and the Si(1)O<sub>4</sub> tetrahedra from adjacent *vierer* double chains (Fig. 6). The Na atoms are located in complex channels oriented parallel to [001]. These channels are formed in the centers of 7MR bounded by one Ti(1)φ<sub>6</sub> and two Ti(2)O<sub>6</sub> octahedra, along with two Si(1)O<sub>4</sub> and two Si(2)O<sub>3</sub>OH tetrahedra (not shown in figures).

Overall, the crystal structure of haineaultite is consistent with that of zorite (Fig. 7a; Sandomirskii & Belov 1979), although there are minor differences between the two in terms of space-group symmetry (*Cmmm* for zorite *versus* *C222* for haineaultite), respective channel occupants and in the Ti polyhedra that cross-link the silicate chains (in zorite, these are disordered TiO<sub>5</sub> polyhedra, and in haineaultite, ordered Tiφ<sub>6</sub> octahedra). Furthermore, there are similarities between the crystal

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN HAINEAULTITE

NaO <sub>4</sub> polyhedron			CaO <sub>4</sub> polyhedron		
Na	–O6	2.414 (5)	Ca	–OH7 × 2	2.151 (6)
	–OH7	2.442 (8)		–O5 × 2	2.382 (16)
	–OH8	2.542 (14)		–O1 × 2	2.594 (16)
	–O5	2.601 (12)		–O3 × 2	2.860 (4)
	–O1	2.620 (12)	<Ca	–O>	2.497
	–OH8'	2.756 (16)			
<Na	–O>	2.562			
Ti(1)O <sub>6</sub> octahedron			Ti(2)O <sub>6</sub> octahedron		
Ti1	–O6 × 2	1.933 (2)	Ti2	–OW10 × 2	1.963 (30)
	–O1 × 2	1.935 (8)		–OH8 × 4	1.976 (9)
	–O5 × 2	2.015 (8)	<Ti2	–O>	1.970
<Ti1	–O>	1.961			
Si(1)O <sub>4</sub> tetrahedron			Si(2)O <sub>4</sub> tetrahedron		
Si1	–O5	1.598 (9)	Si2	–O2	1.588 (10)
	–O3	1.605 (1)		–OH8	1.598 (10)
	–O1	1.610 (8)		–O4	1.649 (2)
	–O2	1.626 (4)		–O2'	1.722 (10)
<Si1	–O>	1.610	<Si2	–O>	1.639

TABLE 5. EMPIRICAL BOND-VALENCES (*v.u.*) FOR HAINEAULTITE\*

	Na	Ca	Ti1/Nb	Ti2	Si1	Si2	Σ <i>V</i>
O1	0.110	0.178 <sup>*21</sup>	0.757 <sup>*21</sup>		1.047		1.919
O2					0.989	1.099, 0.774	1.926
O3		0.090 <sup>*21 -</sup>			1.053 <sup>*2 -</sup>		2.128
O4						0.937 <sup>*4 -</sup>	1.874
O5	0.113	0.336 <sup>*21</sup>	0.621 <sup>*21</sup>		1.067		1.844
O6	0.189		0.774 <sup>*21 -</sup>				1.669
OH7	0.176 <sup>*2 -</sup>	0.610 <sup>*21 -</sup>					0.530
OH8		0.134, 0.077		0.679 <sup>*41</sup>		1.070	1.010
OW10				0.647 <sup>*21</sup>			0.324
Σ <i>V</i>	0.799	2.428	4.304	4.001	4.156	3.880	

\* Parameters from Brese & O'Keeffe (1991). Note: all sums calculated using the SOF presented in Table 3.

structures of haineaultite and minerals belonging to the so-called rhodesite group (Ferraris *et al.* 2004), which includes the new mineral seidite-(Ce)  $[\text{Na}_4(\text{Ce},\text{Sr})_2\{\text{Ti}(\text{OH})_2(\text{Si}_{18}\text{O}_{18})\}(\text{O},\text{OH},\text{F})_4\cdot 5\text{H}_2\text{O}]$ ; Ferraris *et al.* 2003]. Minerals of the rhodesite group have crystal structures characterized by double silicate layers (themselves having eight-membered rings), linked by either isolated  $\text{MO}_6$  octahedra or similar octahedra in edge-sharing chains or continuous layers. Ferraris *et al.* (2003) suggested that the crystal structure of haineaultite (formerly UK61) is closer to that of seidite-(Ce) than of zorite, although a clear basis for this conclusion was not provided. In any event, the hypothesis is not correct. Whereas a similarity in the crystal structures of seidite-(Ce) and zorite exists, *i.e.*, both contain double silicate layers linked by isolated  $\text{TiO}_6$  octahedra, there are important differences between them. In seidite-(Ce), the  $\text{SiO}_4$  tetrahedra are linked through shared corners along [010] and [001] and partially along [100] to form a true double silicate layer (Fig. 7b); in zorite, the  $\text{SiO}_4$  tetrahedra are linked into chains that are cross-linked by a  $\text{TiO}_5$  pyramid to form a mixed layer. In this regard, the crystal structure of haineaultite is actually closer to that of zorite than to that of seidite-(Ce).

#### IMPLICATIONS FOR MATERIAL SCIENCES

Haineaultite, zorite and some other Ti-bearing minerals [*e.g.*, vinogradovite,  $(\text{Na},\text{Ca},\text{K})_4\text{Ti}_4\text{AlSi}_6\text{O}_{23}(\text{OH})\cdot 2\text{H}_2\text{O}]$  are all related to a family of technologically significant, zeolite-like materials referred to as inorganic microporous titanosilicates. The latter have three-dimensional framework structures composed of both tetrahedrally and octahedrally coordinated atoms, unlike most zeolite-like silicates, aluminosilicates and aluminophosphates, whose frameworks are solely composed of tetrahedrally coordinated atoms. The first phase in this family, *ETS-4* (Engelhard Corporation Titanosilicate) was initially described by Kuznicki (1989) and the best-known phase, *ETS-10*, has been described by Anderson *et al.* (1994). Other synthetic equivalents have been termed *GTS* (Chapman & Roe 1990) or [Ti]ZSM (Tuel & Ben Taarit 1994). All of these materials are of significant technological interest, owing to their application in areas ranging from catalysis to adsorption to ion exchange (Kuznicki *et al.* 2001). Their significance in these applied settings is a function of their overall structural flexibility: the effective pore-sizes in these materials can be systematically reduced through dehydration-induced contraction of the *8MR* *via* heating. Carefully controlled heating experiments have been conducted over the range from room temperature to 350°C (Kuznicki *et al.* 2001). In this manner, the *8MR* pore-sizes are strictly controlled or “tuned”, allowing these materials to be effectively employed as molecular sieves. They have been found to be particularly useful in separating gas mixtures containing molecules of similar size in the range of 3–4 Å, including  $\text{N}_2$ – $\text{CH}_4$ , Ar–

$\text{O}_2$  and  $\text{N}_2$ – $\text{O}_2$ . It is also noteworthy that in both uncontrolled experiments up to 200°C and controlled experiments beyond 350°C, the crystal structures of these materials have been observed to collapse completely, possibly owing to the loss of structural  $\text{H}_2\text{O}$  (Kuznicki *et al.* 2001). Materials such as *ETS-10* have been synthesized at temperatures up to 200°C (above this *T*, anatase may precipitate: Tuel & Ben Taarit 1994) using gels formed predominantly from a sodium silicate solution containing small amounts NaOH, KOH, NaCl and others, to which seed crystals were added (Anderson *et al.* 1994). Other investigators have produced what they consider to be synthetic analogues of zorite and vinogradovite using Ti-silicate gels [produced by mixing  $\text{Ti}(\text{OC}_2\text{O}_5)$  and colloidal silica] reacted with a variety of hydroxides (*e.g.*, NaOH, KOH, EtOH, CsOH) or bicarbonates at a low temperature (~200°C; Chapman & Roe 1990). Whereas some of these compounds are industrially produced on the multi-tonne scale (*e.g.*, *ETS-4*), the crystals formed are very small, generally with particle sizes of ~5 µm. The small size of the crystallites could in part be due to the rapidity with which the reactions occur (typically 24 to 64 h).

The crystal structures of both Na- and Sr-dominant *ETS-4*, along with that of *ETS-10*, have been solved (*cf.* Kuznicki *et al.* 2001), principally *via* Rietveld refinement of both powder X-ray and neutron-diffraction data. Results indicate that best-fit agreement is greatest with the space-group *Cmmm*, consistent with interpretation made for zorite (Sandomirskii & Belov 1979), but slightly different than the space-group *C222* preferred for haineaultite. It is also of interest to note that *ETS* materials exhibit high degrees of disorder, consistent with that observed in haineaultite, and data from a large number of experimental techniques (HRTEM, MAS-NMR, electron diffraction, *etc.*) have been employed to elucidate and more completely characterize their crystal structures (*e.g.* Anderson *et al.* 1994).

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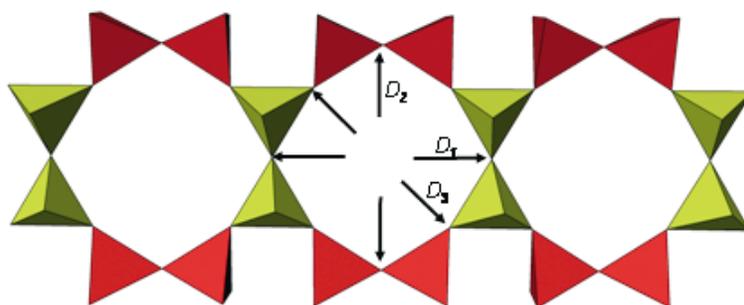


FIG. 4. Eight-membered (8MR) silicate rings and *vierer* chains in haineaultite, projected along [100]. The Si(1)O<sub>4</sub> tetrahedra are shown in red and the Si(2)O<sub>3</sub>(OH) tetrahedra in yellow. Important oxygen-to-oxygen distances, following the terminology of Kuznicki *et al.* (2001), are noted.

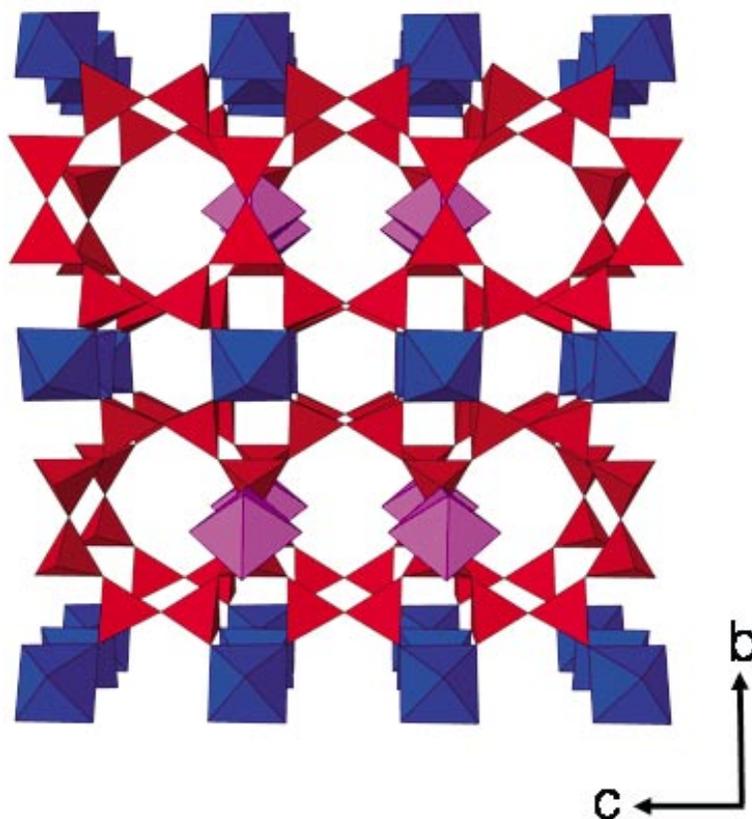


FIG. 5. The octahedron–tetrahedron framework in haineaultite, projected along [100]. The Ti(1)O<sub>6</sub> octahedra are shown in blue, and the Ti(2)O<sub>6</sub> octahedra in lavender. Note that the Ti(2) sites are represented as being fully occupied for the sake of simplicity.

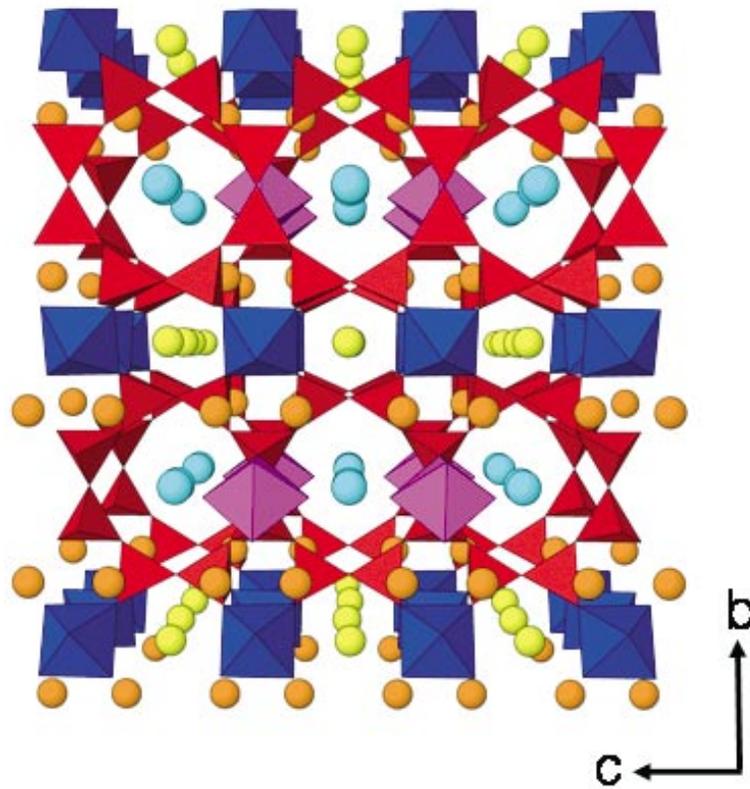


FIG. 6. The channel occupants in the haineaultite structure, projected along [100]. Legend as in Figure 3, with Na atoms shown in orange, Ca atoms in yellow, and O atoms of H<sub>2</sub>O molecules in light blue.

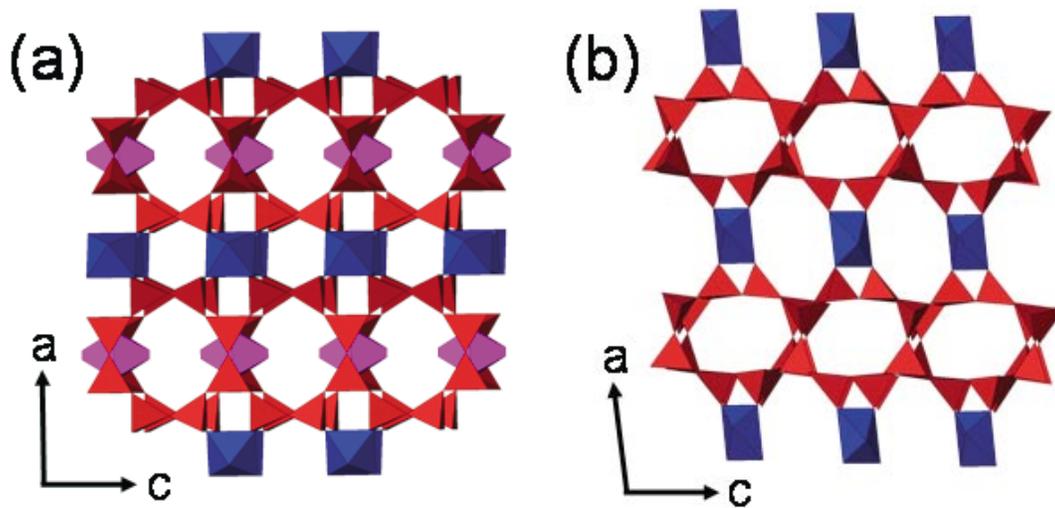


FIG. 7. The tetrahedra–octahedra frameworks as viewed approximately along [010] in (a) zorite and (b) seidite-(Ce). The SiO<sub>4</sub> tetrahedra are shown in red, the TiO<sub>6</sub> octahedra in dark blue, and the TiO<sub>5</sub> pyramids in lavender (note: in zorite, the TiO<sub>5</sub> pyramids are represented as ordered TiO<sub>6</sub> octahedra for the sake of simplicity).

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