TUNDRITE-(Ce) FROM MONT SAINT-HILAIRE, QUEBEC: CRYSTAL-STRUCTURE ANALYSIS AND SPECIES CHARACTERIZATION

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ABSTRACT

Tundrite-(Ce), ideally Na\(_2\)Ce\(_2\)TiO\(_2\)(SiO\(_4\))(CO\(_3\))\(_2\), has been found recently in the Mont Saint-Hilaire quarry, Quebec. It occurs as yellow-green, bladed, singly terminated crystals up to 9 mm in length. Minerals associated with tundrite-(Ce) are aegirine, analcime, an astrophyllite-group mineral, catapleiite, a eudialyte-group mineral, gonnardite, mangan-neptunite, monazite-(Ce), natrolite, rhodochrosite, sphalerite and vinogradovite. Tundrite-(Ce) is triclinic, space group \(\text{P} \sigma\), with the following unit-cell parameters, refined from powder-diffraction data: \(a = 7.5702(6)\) Å, \(b = 13.949(2)\) Å, \(c = 5.0235(5)\) Å, \(\alpha = 100.19(1)\) \(^\circ\), \(\beta = 101.26(1)^{\circ}\), \(\gamma = 100.19(1)\) \(^\circ\), \(V = 487.91(6)\) Å\(^3\) and \(Z = 2\). Crystals are tabular on \(\{100\}\) and elongate on \(\{001\}\), with pinacoid forms: \{100\}, \{010\}, \{201\} and \{101\}. Electron-microprobe analyses give the average and ranges: Na\(_2\)O 9.44 (9.07–9.66), CaO 0.34 (0.16–0.42), La\(_2\)O\(_3\) 16.12 (15.26–17.95), Ce\(_2\)O\(_7\) 27.01 (25.41–28.56), Pr\(_2\)O\(_3\) 2.13 (1.72–2.38), Nd\(_2\)O\(_3\) 6.16 (5.61–6.58), Sm\(_2\)O\(_3\) 0.38 (0.18–0.73), TiO\(_2\) 11.17 (10.73–11.93), Nb\(_2\)O\(_5\) 2.30 (1.14–3.11), Ta\(_2\)O\(_5\) 0.07 (0.00–0.15), SiO\(_2\) 9.32 (9.10–9.54), CO\(_2\) 13.91 (TGA), H\(_2\)O 0.36 (TGA), for a total of 98.80 (97.43–100.17) wt. %. The empirical formula based on the crystal-structure analysis, ideally showing 24 oxygen atoms, is \(2[\text{Na}^{1.906}\text{Ca}^{0.039}\text{La}^{0.621}\text{Nd}^{0.229}\text{Pr}^{0.081}\text{Sm}^{0.014}]\text{Ce}^{1.976}\text{Ti}^{0.875}\text{Nb}^{0.093}\text{Ta}^{0.006}\text{O}_{2.250}\text{Si}^{0.976}\text{O}_{3.998}\text{O}_{2.3}]\). The structure has been refined to an \(R\) index of 2.7% for 2827 unique reflections. The structure has three chemically distinct layers parallel to \(\{010\}\): (1) a Na–Ti–Si–O slab, (2) a Ce–C–O slab and (3) a Na–O slab. Slabs are cross-linked by independent [CO\(_3\)]\(^{\text{f}}\) and [SiO\(_4\)]\(^{\text{f}}\) groups. Minor amounts of OH are present to ensure charge balance as a result of the substitutions Nb \(\leftrightarrow\) Ti and Ca \(\leftrightarrow\) REE.

Keywords: tundrite-(Ce), crystal structure, rare-earth elements, chemical composition, infrared spectroscopy, hydrogen, Mont Saint-Hilaire, Quebec.

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SOMMAIRE

Nous avons trouvé récemment des cristaux de tundrite-(Ce), dont la formule idéale est Na\(_2\)Ce\(_2\)TiO\(_2\)(SiO\(_4\))(CO\(_3\))\(_2\), à la carrière dans le flanc du mont Saint-Hilaire, Québec. Elle se présente en cristaux jaune-verts, en lames terminées atteignant une longueur de 9 mm. Lui sont associés aegirine, analcime, un minéral du groupe de l’astrophyllite, catapleiite, un minéral du groupe de l’eudialyte, gonnardite, mangan-neptunite, monazite-(Ce), natrolite, rhodochrosite, sphalerite et vinogradovite. Tundrite-(Ce) est triclinique, groupe spatial \(\text{P} \sigma\), avec les paramètres réticulaires suivants, affinés avec les données en diffraction X obtenues sur poudre: \(a = 7.5702(6)\) Å, \(b = 13.949(2)\) Å, \(c = 5.0235(5)\) Å, \(\alpha = 100.19(1)\) \(^\circ\), \(\beta = 101.26(1)^{\circ}\), \(\gamma = 100.19(1)\) \(^\circ\), \(V = 487.91(6)\) Å\(^3\) et \(Z = 2\). Les cristaux sont tabulaires sur \(\{100\}\) et allongés selon \(\{010\}\), avec formes pinacoidales \{100\}, \{010\}, \{201\} et \{101\}. Les analyses effectuées avec une microsonde électronique ont donné les valeurs moyennes et les intervalles suivants: Na\(_2\)O 9.44 (9.07–9.66), CaO 0.34 (0.16–0.42), La\(_2\)O\(_3\) 16.12 (15.26–17.95), Ce\(_2\)O\(_7\) 27.01 (25.41–28.56), Pr\(_2\)O\(_3\) 2.13 (1.72–2.38), Nd\(_2\)O\(_3\) 6.16 (5.61–6.58), Sm\(_2\)O\(_3\) 0.38 (0.18–0.73), TiO\(_2\) 11.17 (10.73–11.93), Nb\(_2\)O\(_5\) 2.30 (1.14–3.11), Ta\(_2\)O\(_5\) 0.07 (0.00–0.15), SiO\(_2\) 9.32 (9.10–9.54), CO\(_2\) 13.91 (TGA), H\(_2\)O 0.36 (TGA), pour un total de 98.80 (97.43–100.17) % (poids). La formule empirique fondée sur les résultats de l’analyse structurale, totalisant de façon idéale 24 atomes d’oxygène, est \(2[\text{Na}^{1.906}\text{Ca}^{0.039}\text{La}^{0.621}\text{Nd}^{0.229}\text{Pr}^{0.081}\text{Sm}^{0.014}]\text{Ce}^{1.976}\text{Ti}^{0.875}\text{Nb}^{0.093}\text{Ta}^{0.006}\text{O}_{2.250}\text{Si}^{0.976}\text{O}_{3.998}\text{O}_{2.3}]\). Nous en avons affiné la structure jusqu’à un résidu \(R\) de 2.7% en utilisant 2827 réflexions uniques. La structure est faite de trois couches distinctes parallèles à \(\{010\}\): (1) un Na–Ti–Si–O, (2) un Ce–C–O, (3) un Na–O. Les couches sont interconnectées par des groupes [CO\(_3\)]\(^{\text{f}}\) et [SiO\(_4\)]\(^{\text{f}}\) indépendants. Des quantités mineures de OH assurent la neutralité des charges qui résultent des substitutions Nb \(\leftrightarrow\) Ti et Ca \(\leftrightarrow\) REE.

(Mots-clés: tundrite-(Ce), structure cristalline, terres rares, composition chimique, spectroscopie infrarouge, hydrogène, Mont Saint-Hilaire, Québec.

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(Traduit par la Rédaction)
INTRODUCTION

Tundrite was first described by Semenov (1963) from three nepheline syenite pegmatites on Mt. Nepkha, Lovozero complex, Kola Peninsula, Russia. The mineral was described as being triclinic and having the formula \(\text{Ce}_2\text{Ti}((\text{Si},\text{P})_4)\text{O}_{20}\text{OH})\cdot 4\text{H}_2\text{O}\). The crystallography, both optical and X-ray, are in good agreement with descriptions of other tundrite-group minerals that have been described subsequently, but the chemical data are in error. Semenov et al. (1967) described another occurrence of tundrite-group minerals from the Ilmaaussaq complex, South Greenland. Cerium-dominant members, previously named “tundrite”, were renamed tundrite-(Ce), and Nd-dominant compositions were described as the new mineral species tundrite-(Nd). The authors recognized the presence of major amounts of sodium by chemical analysis. The formulae were given as \(\text{Na}_2\text{Ce}_2\text{Ti}((\text{Si},\text{Nb})_4)\text{SiO}_{20}\text{OH}\) (Z = 2) or \(\text{Na}_2\text{Ce}_2\text{Ti}((\text{Si},\text{Nb})_4)\text{SiO}_{20}\text{OH}\) (Z = 1). Not until the work of Shlyukova et al. (1973) was the presence of carbonate discovered in tundrite-group minerals, given the revised formula \((\text{Na},\text{K})_3(\text{REE},\text{Ca})_4(\text{Ti},\text{Nb})_2(\text{SiO}_4)_2(\text{CO}_3)_2\text{O}_4(\text{OH})_2\text{H}_2\text{O}\). The proportion of the rare-earth elements was not given, so it is not certain whether this was tundrite-(Ce) or tundrite-(La). This material was good enough for a crystal-structure analysis by Shumyatskaya et al. (1976), which led to the formula \(\text{Na}_2\text{Ce}_2\text{Ti}((\text{Si},\text{Nb})_4)\text{SiO}_{20}\text{OH}\). This crystal-structure analysis, with a rather large degree of uncertainty, having an \(R\) index of 7%, was not supported by chemical analyses, and its variance with the data of Shlyukova et al. (1973) was not explained. A detailed study of tundrite-(Ce) from the Ilmaaussaq complex, South Greenland, was published by Karup-Møller (1982), who gave the formula \(\text{Na}_3,1,7(\text{Ce}_{1,76}\text{Nd}_{0,73}\text{La}_{0,06})\text{Pr}_{0,25}\text{Sm}_{0,16}\text{Gd}_{0,04}\text{Ca}_{0,16}\text{S}_{3,71}(\text{Nb}_{0,31}\text{Ti}_{1,83})\text{X}_{2,14}\text{O}_{1,25}(\text{SiO}_2)_2(\text{CO}_3)_2\text{Si}_{2,27}\). The disparity in results among these reports warranted a restudy of tundrite-(Ce), especially in view of the availability of newly discovered, well-crystallized material.

OCCURRENCE

In May, 2006, Dr. R. Peter Richards of Oberlin, Ohio, noted the presence of a mineral, later identified as tundrite-(Ce), in an isolated boulder in Mont Saint-Hilaire, Quebec. He relayed the information to Willow and Quintin Wight, who located the boulder, in use as a road marker. The boulder, approximately one meter high and one-and-a-half meters long, is a pegmatitic segregation that clearly did not originate within the hornfels unit where it presently rested. Its origin must lie somewhere in the pegmatitic segregation associated with the block of igneous breccia in the higher (southwesterly) portion of the quarry. Externally, the boulder appeared barren of interesting minerals, but a trial blow knocked off a large fragment, revealing a cluster of golden-yellow tundrite-like blades embedded in analcime. The analcime host was like a plug, blocking the entrance to a larger cavity beneath. There was no trace of tundrite-group minerals within the cavity itself. A search of the dislodged material located further fragments of the original portion removed by the hammer blow. Minerals associated with tundrite-(Ce) are aegirine, albite, analcime, an astrophylite-group mineral, catapleiite, a eudialyte-group mineral, gonnardite, mangan-neptunite, monazite-(Ce), natrolite, quartz, rhodochrosite, sphenelite and vinogradovite.

Material is housed in the collection of the Canadian Museum of Nature, Ottawa under catalogue number CMNMC 85866.

PHYSICAL AND OPTICAL PROPERTIES

Tundrite-(Ce) belongs to the triclinic pinacoidal class, \(\bar{1}\). The crystals are bladed on \{010\}, elongate on \{001\}, up to 9 mm in length (Fig. 1). The following pinacoid forms were measured and drawn (Fig. 2): \{100\}, \{010\}, \{201\} and \{101\}. No twinning was observed, and \{100\} faces are heavily striated owing to the \{010\} platy nature of the crystals. The crystals are translucent, pale yellow in color, with a white streak and a vitreous luster. There is no fluorescence with either short-wave or long-wave ultraviolet light. The mineral has an approximate hardness of 3 (Mohs scale), is brittle and splintery, with a perfect \{010\} cleavage. The density, 4.08 g/cm\(^3\), measured by the Berman balance method, agrees well with the calculated density, 4.19 g/cm\(^3\).

Tundrite-(Ce) is biaxial positive, \(2V_{\text{meas}} = 84(5)^\circ\) with \(\beta = 1.80\). The dispersion is strong, with \(r > v\), and pleochroism is weak, with \(Y = \) pale yellow and \(Z = \) greenish yellow. The optical orientation is \(X = \{010\}, Z \approx c\).

CHEMICAL COMPOSITION

Electron-microprobe analysis

Compositions were obtained using a JEOL 733 Superprobe in wavelength-dispersion mode. Operating conditions were 15 kV, 20 nA with a probe diameter of 10 \(\mu\)m. Counts were collected for 25 s or until 0.50% precision was attained. In spite of the high sodium content of this mineral, it proved to be very resistant to beam damage. Monitoring of NaK\(\alpha\) counts over a period of several minutes (longer than the total duration of the analysis) showed no detectable change in count rate. The following X-ray lines and standards were used for analysis: albite (NaK\(\alpha\), SiK\(\alpha\)), fersmite (CaK\(\alpha\)), rutile (TiK\(\alpha\)), manganocolumbite (NbK\(\alpha\)), NiTa\(_2\)O\(_6\) (TaK\(\alpha\)) and synthetic REE phosphates for (LaK\(\alpha\), CeK\(\alpha\), PrK\(\alpha\), NdK\(\alpha\), SmK\(\alpha\)). Raw data were corrected using a PAP correction routine (Pouchou &
TUNDRITE-(Ce) FROM MONT SAINT-HILAIRE, QUEBEC

FIG. 1. Tundrite-(Ce) from Mont Saint-Hilaire, Quebec. (a) Radiating group of crystals 25 mm long (photo: Willow Wight). (b) Prismatic crystal 7 mm long in photograph (photo: Quintin Wight).

Pichoir 1984) as part of the XMQANT package (pers. commun., C. Davidson, CSIRO). In total, 20 analyses were performed on seven separate grains. The amounts of CO₂ and H₂O were determined by thermogravimetric analysis (described below). The analytical results are summarized in Table 1. The empirical formula, based on 24 atoms of oxygen as determined by crystal-structure analysis, is: 2[(Na₁.₉₀₆Ca₀.₀₃₉)₂₁.₉₄₅(Ce₁.₀₃₀La₀.₆₂₁Nd₀.₂₅₉Pr₀.₀₈₁Sm₀.₀₁₄)₂₁.₉₇₅(Ti₀.₈₇₅Nb₀.₁₀₉)₂₀.₉₃₂O₂H₀.₂₅ₒ(Si₀.₉₇₁O₄)(C₀.₉₈₉O₃)₂].

Examination of the data shows a limited extent of substitution of Nb for Ti (Fig. 3).

Thermogravimetric and differential scanning calorimetry analysis

Thermogravimetric (TGA) – differential scanning calorimetry (DSC) analysis was made with a TA Instruments Q600 SDT instrument. A 10.9120 mg powdered sample was heated from room temperature to 800°C at
10°C min⁻¹ with N₂ as a purge gas. The weight losses occurred in two steps: the first loss, a small endothermic peak centered at 50°C, is 0.03887 mg (0.36 wt.%), and the second loss, a large sharp endothermic peak centered at 713°C, is 9.355 mg (13.91 wt.%). The first loss is attributed to H₂O, whereas the second loss is essentially CO₂.

### Infrared analysis

The infrared spectrum of tundrite-(Ce) (Fig. 4) was obtained using a Bomen Michelson MB-120 Fourier-transform infrared spectrometer with a diamond-anvil cell microsampling device. The spectra are well resolved and provide a clear example of the vibration modes for isolated [CO₃]²⁻ and [SiO₄]⁴⁻ groups. The broad (3600 to 2700 cm⁻¹) low peak centered in the 3401 cm⁻¹ region is the O–H or H–O–H stretch frequency, indicating the presence of an [OH]⁻ or an [H₂O] group. The H–O–H bend region (1690–1590 cm⁻¹) does not lead to a clear interpretation of spectral peaks, but from crystal-structure analysis, it is evidently all [OH]. Comparing the remaining complex part of the spectrum to spectra given in Farmer (1974), the following regions of frequency are assigned modes: the two [CO₃]²⁻ groups are both in general atom positions giving rise to several sharp spectral peaks (cm⁻¹): v₂ + v₆: asymmetric stretching in additive combination, 1784 and 1759; v₃: asymmetric stretching, 1535 (plus shoulder), 1435 and 1381; v₁: symmetric stretching, 1081 and 1067; v₄: in-plane bending 719, 704, 694 and 651. The single [SiO₄]⁴⁻ group is also in a general atom position: v₁ + μ₂: symmetric stretching, 949, 897 and 851; v₂ + v₄: in-plane and out-of-plane bending, 555, 501 and 460.

#### Table 1. Tundrite: Chemical Composition

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<th>Max</th>
<th>Range</th>
<th>Standard deviation</th>
<th>Theoretical</th>
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* Minimum level of detection based on counting statistics.

** CO₂ and H₂O from TGA analysis. The proportion of cations is calculated on the basis of 24 atoms of oxygen per formula unit (apfu).

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**Fig. 2.** Crystal drawing of tundrite.

**Fig. 3.** Plot of Nb versus Ti in tundrite-(Ce) for all analytical datasets. Dashed line has a slope of minus one.
X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

X-ray powder-diffraction data were collected with a Bruker AXS Discover 8 microdiffractometer using Hi-Star 2-D area detector operated with a GADDS system, CuKα1 radiation at 40 kV, 40 mA, with a sample-to-detector distance of 12 cm (Table 2). The instrument was calibrated with synthetic corundum using a new statistical method of calibration. This method is based on a statistical comparison of changes in Δ2θ error when adjusting the different calibration parameters, consequently allowing an optimization of these parameter values for a minimal Δ2θ error. Indexing of the measured pattern was achieved with the intensities from a powder pattern calculated using atom coordinates determined in the crystal-structure analysis. Diffuse non-diagnostic diffraction was observed in the 75 to 100° range as broad bulging peaks, therefore not usable for cell-refinement data. Differences between measured versus calculated intensities are consistent with what is expected in a triclinic structure, where many hkl planes are contributing to the intensity of one measured peak.

X-ray precession photographs were used to select a single crystal of tundrite-(Ce).Trimming a cleavage fragment of this mineral was found to be difficult owing to its splintery nature, which gives rise to adhering satellite fragments producing streaky X-ray-diffraction reflections. The single crystal chosen for the collection of intensity data measured 0.12 × 0.12 × 0.30 mm. Intensity data were collected on a fully automated Bruker P4 four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated MoKα radiation and a 4K APEX CCD detector mounted at a distance of 6 cm from the crystal. Integrated intensities were collected up to 2θ = 60°, using 10 s frame counts and a frame width of 0.25°. Data pertinent to the intensity-data collection are given in Table 3. The unit-cell parameters for the single crystal were refined using 5523 indexed reflections.

Reduction of the intensity data, structure determination and structure refinement were done with the SHELXTL (Sheldrick 1990) package of computer programs. Data reduction included corrections for background, scaling and Lorentz-polarization factors. An empirical absorption-correction (SADABS, Sheldrick 1998) was applied. The merging R_{(int)} for the dataset...
residuals were found associated with 05 and 06 atoms in the difference-Fourier map in the region of the [Si0

There was an additional weak residual associated with ...

(9606 reflections) decreased from 0.030 before the correction, Assigning phases to a set of normalized ...

calculation, the three Na sites have [6]-coordinated polyhedra, with Na1 and Na3 having almost regular octahedral coordination with O and a refined site-occupancy of 11 e⁻, whereas the coordination of Na2 with O may be described as a bifurcated tetragonal pyramid. This novel Na2 site has slightly higher site-occupancy, 11.9(1) e⁻, indicating that it incorporates heavier atoms such as Ca or the REE. The Ti site has a regular octahedral coordination, and the site-occupancy refinement, 23.8(2) e⁻, agrees very well with the Ti and Nb content of the site, which has 23.9 e⁻. The single Si site and the two C sites have regular tetrahedral and triangular coordination, respectively.

| TABLE 3. TUNDRITE: DATA COLLECTION AND STRUCTURE-REFINEMENT INFORMATION |
|-------------------|------------------|------------------|
| Space group | Measured reflections | 11046 |
| a (Å) | 7.5760(4) | Unique reflections | 2827 |
| b (Å) | 13.9252(7) | Observed reflections | 2803 |
| c (Å) | 5.6290(2) | R(m) (%) | 1.4 |
| β (°) | 90.791(1) | Goodness of fit on F² | 1.22 |
| γ (°) | 100.947(1) | wR² (%) for all data | 7.3 |
| V (Å³) | 486.37(7) | Refinement by full-matrix least squares on F² | |

Ideal unit-cell contents: [Na₉O₂₈Ti₂O₇(SiO₄)₂(OC₃)₃] μ = 11.2 mm⁻¹
TUNDRITE-(Ce) FROM MONT-SAINT-HILAIRE, QUEBEC

Anion OH\textsubscript{13} refined to \(0.11(1) \times 2\) (site multiplicity) for a total of 0.22 oxygen atoms per unit cell. This corresponds to 0.32 wt.% H\textsubscript{2}O, which agrees well with that measured by TGA, 0.36 wt.% H\textsubscript{2}O. Figure 5 shows the location of OH\textsubscript{13}, placed approximately at an equal spacing between the base of the independent [SiO\textsubscript{4}] tetrahedron and the [CO\textsubscript{3}] triangle. Anion OH\textsubscript{13} and its symmetry equivalent OH\textsubscript{13}* are bonded to Ce\textit{l} at 2.65 and 2.67 Å, respectively.

Anon OH\textsubscript{13} refined to \(0.11(1) \times 2\) (site multiplicity) for a total of 0.22 oxygen atoms per unit cell. This corresponds to 0.32 wt.% H\textsubscript{2}O, which agrees well with that measured by TGA, 0.36 wt.% H\textsubscript{2}O. Figure 5 shows the location of OH\textsubscript{13}, placed approximately at an equal spacing between the base of the independent [SiO\textsubscript{4}] tetrahedron and the [CO\textsubscript{3}] triangle. Anion OH\textsubscript{13} and its symmetry equivalent OH\textsubscript{13}* are bonded to Ce\textit{l} at 2.65 and 2.67 Å, respectively.
The role of hydrogen in tundrite

Since the first description of tundrite by Semenov (1963), the amount of H$_2$O and its speciation in the mineral have been in considerable doubt and have led to many erroneous conclusions. The H$_2$O contents reported have varied from 15 wt.% (Semenov 1963) to 0 wt.% (Shumyatskaya et al. 1976). Much more realistic analyses are given by Shlyukova et al. (1973), 3.75 wt.%, and Karup-Møller (1982), 2.2 wt%. From the present study, which includes IR spectra, TGA analysis and crystal-structure analysis, it is evident that there is hydrogen present as [OH]$^-$, and possibly as H$_2$O. The hydroxyl anions may be in the O5 and O6 sites that are bonded only to Ti. The ratio of O$^{2-}$ : OH$^-$ is dependent on the Ti$^{4+}$ : Nb$^{5+}$ ratio in these two O sites. Additional [OH]$^-$ or [H$_2$O] can also be bonded to Ce, and it would lie between the silicate and carbonate polyhedra. The spatial fit is tight between these two polyhedra, with O–O distances of 1.7 to 2.7 Å (Fig. 5a). The actual mechanism of the site occupancy is not yet discernable, but one could imagine that an increase in the site occupancy of OHI3 could correspond to a...
FIG. 7. Layers in the tundrite-(Ce) structure: (a) Na1-, Ti- and Si-centered polyhedra; (b) Ce- and C-centered polyhedra; (c) Na2- and Na3-centered polyhedra. The [TiO₆] polyhedra are brown, the [SiO₄] tetrahedra are red, the [CO₃] triangles are grey, Ce atoms in orange, Na atoms in yellow and OH¹³ in blue.

decrease in the amount of either, or both, [CO₃]²⁻ or [SiO₄]⁴⁻ groups.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the cooperation of, and samples provided by, Dr. Pete Richards. The authors thank Dr. Frank Hawthorne, University of Manitoba, for the use of his four-circle diffractometer, Elizabeth Moffatt of the Canadian Conservation Institute, for the infrared spectrum, and Dr. Hazel Hunter, Natural History Museum. Helpful comments from Dr. Frédéric Hatert as a reviewer, one anonymous reviewer, and Dr. Robert F. Martin, improved the quality of the manuscript.

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Received June 12, 2007, revised manuscript accepted December 15, 2007.