MARTINITE, A NEW HYDRATED SODIUM CALCIUM FLUORBOROSILICATE SPECIES FROM MONT SAINT-HILAIRE, QUEBEC: DESCRIPTION, STRUCTURE DETERMINATION AND GENETIC IMPLICATIONS

ANDREW M. MCDONALD§

Mineral Exploration Centre and Department of Earth Sciences, Laurentian University, Sudbury Ontario P3E 2C6, Canada

GEORGE Y. CHAO¶

Ottawa–Carleton Geoscience Centre, Department of Earth Sciences, Carleton University, Ottawa Ontario K1S 5B6, Canada

ABSTRACT

Martinite, ideally (Na, Ca)₂Ca₃(Si,S,B)₄B₂O₉(OH,Cl)₂F₂·4H₂O, is a new mineral species from the Poudrette quarry, Mont Saint-Hilaire, Quebec. The mineral arose through the interaction of highly fractionated, hyperalluminous fluids with sodalite xenoliths. Martinite develops both as single crystals and as rosettes of triangular to roughly hexagonal plates varying from 50 μm to a maximum of about 1 mm across. Individual crystals are typically <10 μm in thickness and dominated by (001), and colorless to mauve to purple in color. Associated minerals include aegirine, albite, erdite, eudialyte-group minerals, galena, langite, lueshite, luzonite-group minerals, molybdenite, posnjakite, rasvumite, sérandite, sazhinite-(Ce), sphalerite, terskite, ussingite, villiaumite, wurtzite and a number of unknown minerals, including several Cu₂–S minerals (UK55 group), UK53a, UK73, UK82, UK91 and a wollastonite-like mineral. The mineral has a vitreous luster, is transparent, has a white streak and shows no fluorescence in either short- or long-wave ultraviolet radiation. It has a Mohs hardness of 4; the crystals are inelastic, and have a perfect cleavage on (001). It is brittle with an uneven fracture. The calculated density is 2.51 g/cm³. Martinite is non-pleochroic, optically biaxial (+), with α 1.529(1), β 1.549(1), γ 1.551(1) (for λ = 590 nm), 2V meas = 38(1)°, 2V calc = 35(1)°; no dispersion was noted. The optical orientation is X ≈ c. On average, 19 electron-microprobe analyses gave: Na₂O 17.70, MgO 0.03, CaO 16.71, MnO 0.07, B₂O₃ (calc.) 5.02, SiO₂ 48.85, TiO₂ 0.06, SO₃ 2.30, F 2.01 (F1.84OH0.16) 2•4H₂O. The principal absorption bands in the infrared spectrum include 3437, 1634, 1382, 1081, 898 and 862 cm⁻¹. The mineral is triclinic, space group P̅1, a 9.5437(7), b 9.5349(6), c 14.0288(10) Å, α 108.943(1), β 74.154(1), γ 119.780(1)°, V 1038.1(1) Å³, Z = 2. The strongest seven lines in the X-ray powder-diffraction pattern [d in Å(hkl)] are: 13.18(100)(001), 6.58(43)(002), 2.968(37)(130), 2.908(27)(323), 2.800(17)(212), 2.800(17)(212). The structure of martinite has been re

Keywords: martinite, new mineral species, layered borosilicate, reyerite–gyrolite group, crystal structure, Mont Saint-Hilaire, Quebec, Canada.

SOMMAIRE

La martinite, de composition idéale (Na, Ca)₂Ca₃(Si,S,B)₄B₂O₉(OH,Cl)₂F₂·4H₂O, est une nouvelle espèce minérale découverte à la carrière Poudrette, au mont Saint-Hilaire, Québec. Ce minéral s’est formé suite à l’interaction de fluides hyperalluminiques fortement évolués avec des xénolithes de syénite à sodalite. La martinite se présente en monocristaux ou bien en
Martinite was rst encountered in September, 1991 in sodalite syenite xenoliths (SSX) from the sixth bench in the extreme southern part of the Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec, Canada. The material used to completely characterize the species in this study was obtained from two proximal xenoliths found in situ, one discovered by M. Haineault and the other by Dr. Peter Tarassoff and Mr. Laszló Horváth. To the authors' knowledge, martinite has not been found in any SSX subsequently exposed in the quarry, nor in any of the other geological micro-environments at Mont Saint-Hilaire. The particular xenolith found by Haineault is estimated to be 30 cm across, and that by Tarassoff and Horváth, approximately 1 m in diameter. Sodalite syenite xenoliths consist predominantly of coarse-grained sodalite with lesser amounts of analcime and microcline with rare and unusual "secondary" minerals like martinite, occurring in small cavities (typically <1 cm). P. Tarassoff (pers. commun.) notes that the dominant mineralogy of the xenolith examined

Mots-clés: martinite, nouvelle espèce minérale, borosilicate stratifié, groupe de la réyerite–gylroite, structure cristalline, Mont Saint-Hilaire, Québec, Canada.

INTRODUCTION

Martinite, ideally (Na8Ca2)3Ca3(Si,S,B)14B2O38 (OH,Cl)2F4•4H2O, is a new mineral species and member of the reyerite–gylroite group, discovered in sodalite syenite xenoliths (SSX) at the Poudrette Quarry, Mont Saint-Hilaire, Rouville County, Quebec. It was rst encountered in 1991 as a thin, hexagonal plate found in a sample submitted by M. Gilles Haineault to one of us (GYC) for identiﬁcation. The mineral macroscopically resembles a colorless mica, but was found to give a distinct X-ray powder pattern that did not match any known one. In light of this ﬁnding, the mineral was considered as a potentially new species and was temporarily assigned the label UK92. It has been named martinite after Robert François Martin (né en 1941), professeur de géologie à l’université McGill, et rédacteur en chef de la revue The Canadian Mineralogist de longue date.

Canadian Museum of Nature, Aylmer, Quebec, Canada (catalogue number CMNMC 83719).

OCURRENCE

Martinite was rst encountered in September, 1991 in sodalite syenite xenoliths (SSX) from the sixth bench in the extreme southern part of the Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec, Canada. The material used to completely characterize the species in this study was obtained from two proximal xenoliths found in situ, one discovered by M. Haineault and the other by Dr. Peter Tarassoff and Mr. Laszló Horváth. To the authors’ knowledge, martinite has not been found in any SSX subsequently exposed in the quarry, nor in any of the other geological micro-environments at Mont Saint-Hilaire. The particular xenolith found by Haineault is estimated to be 30 cm across, and that by Tarassoff and Horváth, approximately 1 m in diameter. Sodalite syenite xenoliths consist predominantly of coarse-grained sodalite with lesser amounts of analcime and microcline with rare and unusual “secondary” minerals like martinite, occurring in small cavities (typically <1 cm). P. Tarassoff (pers. commun.) notes that the dominant mineralogy of the xenolith examined
by Horváth and Tarassoff is similar to that from which the species nalipoite was first described (Chao & Ercit 1991), i.e., 75 modal % sodalite, 15% analcime and 10% microcline. Martinite is clearly a rare species, although the xenolith discovered by Haineault yielded approximately three dozen crystals, all in small cavities ranging in size from 0.2 to 0.5 cm. Associated minerals include aegirine, albite, erdite, eudialyte-group minerals, galena, langite, lueshite, lovozerite-group minerals, molybdenite, posnjakite, rasvumite, sérandite, sazhinite-(Ce), sphalerite, terskite, ussingite, villiaumite, wurtzite and a number of unknown minerals, including several Cu2–S minerals (UK55 group), UK53a, UK73, UK82, UK91, and a löllingite-like mineral.

ORIGIN

A large number (>110) of late-stage, rare minerals (e.g., ussingite, vuonnemeite, rasvumite) have been discovered in SSX at Mont Saint-Hilaire (Horváth & Pfenninger 2000), including several new to science [e.g., abenakiite-(Ce), rouvilleite, lukechangite-(Ce)]. Most are characteristically enriched in alkalis and alkaline earths, are silica-poor, hydrous, and in many cases contain essential Ti, Zr, Nb, REE and F. Many are unstable under normal conditions of humidity, either decrepitating [e.g., thomasclarkeite-(Y); Grice & Gault 1998] or being converted to a white efflorescence when exposed to air (e.g., thermonatrite, revdite). In fact, the minerals and mineral assemblages found in the SSX very closely resemble those found in the hyperagpaitic pegmatites and hydrothermally affected rocks found in the Khibina and Lovozero massifs (Horváth & Pfenninger 2000). In view of the fact that the rare and unusual minerals in the SSX at Mont Saint-Hilaire typically occur in cavities between coarse-grained crystals of sodalite, and given their unusual chemical signatures, we contend that they are late-stage products arising through the interaction of highly evolved hyperagpaitic fluids and sodalite syenite xenoliths. The chemical composition and occurrence of martinite are consistent with its crystallization from such a fluid under similar conditions.

Most of the SSX found at Mont Saint-Hilaire have been found in a 30 m² area in the southeast portion of the Poudrette quarry over the period 1983–1991. However, the bulk of the unusual minerals found in such rocks were discovered in the late 1980s from a portion of this area measuring approximately 3 m². This area, commonly referred to as the “corner rock”, was found to be very rich in SSX, most of which were positioned quite close to a large block of biotite – muscovite – quartz hornfels. Given the low porosity and dense nature of the block of hornfels, it could have acted as a cap, trapping late-stage, hyperalkaline fluids, inhibiting the release of volatiles and facilitating both the crystallization and stabilization of a large number of unusual minerals (Van Velthuizen 1990). As many of the rare minerals found associated with martinite were also noted in SSX from the 1980s find and because the xenolith in which martinite occurs is proximal to this area, the implication is that martinite crystallized from a hyperagpaitic fluid similar to that which produced the minerals found in the 1980s discovery.

PHYSICAL AND OPTICAL PROPERTIES

Crystals of martinite develop as thin, subhedral to euhedral plates, typically measuring <10 µm in thickness and varying from 50 µm to maximum of about 1 mm across (Fig. 1). The crystals, dominated by {001}, are colorless to mauve to purple in color (those with a pinkish hue are most commonly associated with erdite). They develop both as single crystals and as rosettes of triangular to roughly hexagonal plates. No twinning was observed by optical microscopy or by single-crystal X-ray-diffraction methods. The mineral has a vitreous luster, a white streak, is transparent, and shows no fluorescence in either short- or long-wave ultraviolet radiation. It has a Mohs hardness of 4 and a perfect {001} cleavage. It is brittle with an uneven fracture. Cleavage fragments are quite inelastic, a characteristic

![Fig. 1](image-url)
useful in distinguishing martinite from similar-looking colorless micas. The density could not be determined owing to a dearth of material. The calculated density is 2.51 g/cm³, determined using the empirical chemical formula and the unit-cell parameters derived from the crystal-structure analysis.

Martinite is non-pleochroic, biaxial negative, with \( \alpha = 1.529(1) \), \( \beta = 1.549(1) \), \( \gamma = 1.551(1) \) (for \( \lambda = 590 \) nm). \( V_{\text{max}} = 38(1)^{\circ} \), \( V_{\text{calc}} = 35(1)^{\circ} \); no dispersion was noted. The optical orientation is \( X \approx c \). A Gladstone–Dale calculation gave a compatibility index of \(-0.031\), which is classed as excellent (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 μm. Energy-dispersion spectra (EDS) were collected using the following standards: wollastonite (CaO), synthetic MnTiO₃ (MnO, TiO₂), periclase (MgO) and celestine (SrO). In addition, wavelength-dispersion data were collected using tugtupite (NaK, SiK, ClK, FKo) as a standard. No other elements were indicated by qualitative EDS scans. Also sought, but not detected, were Al, K, Fe and P. Nineteen elements were indicated by qualitative EDS scans. Also pite (Na wavelength-dispersion data were collected using tugtupite (MgK, F), synthetic MnTiO₃ (MnK, TiK) and celestine (SrK). In addition, wavelength-dispersion data were collected using tugtupite (NaK, SiK, ClK, FKo) as a standard. The empirical formula, based on 46 anions, is: (Na₉.19Ca₉.02Mn₀.03Mg₀.01)₂(Si₁₃.₀₈S₀.₄₆B₀.₄₅F₀.₂₂O₃₈(OH)₁₂Mn₀.₀₂Mg₀.₀₁)₂₂.00 (F₁.₈₄OH₀.₀₂)₂•H₂O or, ideally, (Na, Ca)₁₂Ca₄(Si, S, B)₄O₃₂(OH, Cl)₂F₂•4H₂O. The mineral does not effervesce in 1:1 HCl at room temperature.

**INFRARED ANALYSIS**

The infrared spectrum of martinite (Fig. 2) 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 was mounted in a Spectra-Tech low-pressure diamond-anvil microsample cell. The spectrum, a sum total of 200 co-added scans, was obtained over the range 4000–400 cm⁻¹. Absorption bands were identified using the data of Farmer (1974). The spectrum shows a broad band centered at the 3437 cm⁻¹ region (O–H stretching), and a relatively weak, broad band at 1634 cm⁻¹ (H–O–H bending). The spectrum also shows a strong, sharp band at 1011 cm⁻¹, with shoulders at 1137, 1081, 986 and 862 cm⁻¹ (asymmetric O–Si–O, O–B–O stretching) and five sharp, weak to moderately strong bands in the region 786–498 cm⁻¹ (symmetric Si–O–Si, O–B–O stretching; Farmer 1974). As the ranges in the frequency modes for BO₄ and SiO₄ tetrahedra overlap [asymmetric stretching: 1100–850 cm⁻¹ for BO₄ versus 1200–900 cm⁻¹ for SiO₄; symmetric stretching: 850–700 cm⁻¹ for BO₄ versus 800–400 cm⁻¹ for SiO₄; Farmer (1974)], it is not possible to unequivocally assign absorption bands in these regions.

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

X-ray powder-diffraction data (Table 1) were collected with a Debye–Scherrer camera 114.6 mm in diameter employing Ni-filtered CuKα radiation (\( \lambda = 1.5418 \) Å). Interplanar spacing and intensity data were determined using a scanned X-ray film. 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).

A single crystal mounted approximately parallel to \( c^* \) was used for the collection of X-ray intensity data. These were collected on a fully automated Enraf–Nonius CAD4 four-circle diffractometer operated at 50 kV, 26 mA, with graphite-monochromated MoKα radiation. It should be noted that the unit cell given herein has been transformed from that originally referenced (IMA #2001–059, so as to adhere to the IUCr convention, \( c < a < b \)), in order to emphasize the relationship between martinite and minerals of the reyerite group. A full sphere of X-ray intensity data out to 20 = 56.7°...
was collected using a 6:20 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 measurement and reduction (Lorentz, polarization, background, scaling) were carried out using the NRCVAX set of computer programs (Gabe et al. 1989). No absorption correction was applied to the data, given the low μ value for the mineral. 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 Sheldrick–93 package of programs (Sheldrick 1993). The crystal structure was solved using direct methods, with scattering curves and anomalous dispersion coefficients taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. Preliminary X-ray precession photographs indicated $P^\tau$ diffraction symmetry. Phasing of a set of normalized structure-factors gave a mean value of $\bar{E}^2 = 1$ equal to 0.972 (predicted values: 0.968, centrosymmetric, 0.736, non-centrosymmetric); on this basis, $P^\tau$ was selected, and proved to be the correct space-group. Phase-normalized factors were calculated and used to produce an $E$-map on which were located Ca, along with several Si and O sites. The remaining Na and O sites were located on subsequent Fourier-difference maps. Results from this model indicated one of the tetrahedrally coordinated sites [B(1)] to have excessively short Si–O bond distances in the range 1.45–1.50 Å, and the other to have relatively short Si–O bond distances of 1.50–1.58 Å [Si(7)]. Refinement of the electron scattering (assuming Si) in the first site gave 4.9(1) electrons and for the second, 9.7(1) electrons. In light of this finding, a qualitative wavelength-dispersion scan was made, which confirmed the presence of B in the mineral. On the basis of these data, the B has been assigned to one site, and a mixed (Si,B) occupancy to the other. Determination of those O sites likely occupied by OH or H$_2$O was made on the basis of bond-valence calculations in conjunction with charge-balance considerations. Anisotropic refinement of this model indicated that the Na$_2$, Na$_3$, Na$_6$ and Ca$_2$ sites have lower-than-ideal site-occupancy factors (SOF; Table 3). Attempts at refining the Na$_2$, Na$_3$ and Na$_6$ sites with mixed (Na,Ca) occupancies were not successful, and the assumption was thus made that these sites are partially vacant. In the case of Na$_6$, further refinement suggested pronounced elongation in the [001] direction, and the site was subsequently split into two partially occupied sites (Na$_{6a}$, Na$_{6b}$). In the case of the Ca$_2$ site, the refinement was conducted assuming a mixed (Ca,Na) occupancy. Final least-squares refinement of this model gave residuals of $R = 6.30$ and $wR^2 = 13.82\%$, with maximum and minimum electron-densities of +2.54 and –0.94 e/Å$^3$.

Table 3 contains the final positional and displacement parameters, with selected interatomic distances in Table 4, and bond-valence sums in Table 5. Observed and calculated structure-factors are available at the Depository of Unpublished Data on the MAC web site [document Martinite CM45_xxx].

**CRYSTAL-STRUCTURE DESCRIPTION**

Martinite is strongly layered perpendicular to [001]; it consists of sheets of tetrahedra (T), octahedra (O) and...
interlayer cations (X). The S layers (S for silicate) are composed of six-membered, pseudohexagonal rings of SiO$_4$ tetrahedra that are linked by [(Si,B)O$_4$ and (BO$_4$) tetrahedra (Fig. 3) to complete the sheet. The apices of the SiO$_4$ tetrahedra in these rings all point in a common direction toward the O sheet ([001]), but deviate slightly away from [001] owing to geometrical restrictions resulting from linkages made with overlying O sheets. This deviation contributes to a reduction in the overall symmetry of the mineral, although a strong pseudohexagonal character is retained. In general terms, the Si–O bond distances involving oxygen atoms in the plane of these rings (i.e., the a–b plane) are rather normal (~1.61–1.64 Å), whereas those involving apical atoms of oxygen (O1 → O6, corresponding to bridging atoms of oxygen that link to O sheets) are noticeably shorter (1.58–1.60 Å). The (Si,B)O$_4$ and BO$_3$(OH) tetrahedra that interconnect the pseudohexagonal silicate rings in
the α–β plane are oriented such that their apices point away from the O sheets, toward the interlayer region of the structure. Neither of these bridging tetrahedra directly link to like tetrahedra in adjacent T sheets (along [001]), a feature consistent with that in related minerals (e.g., federite; Mitchell & Burns 2001). The sheets of tetrahedra in martinite resemble the double sheets of SiO₄ and AlO₄ tetrahedra observed in minerals like reyerite and gyrolite. These are referred to as S₂ sheets by Merlino (1988a, b), which differ in shape and possible condensation relative to those referred to as S₁ sheets. The designation of sheets of tetrahedra using the symbol S is most unfortunate, as T is considerably more accurate (they represent sheets of tetrahedra) and avoids unnecessary confusion (e.g., S is present in the sheets of tetrahedra found in martinite). Thus, whereas there may be other examples describing the crystal structures of related phases using the S notation to represent sheets of tetrahedra present in the literature, we have chosen to refer to such sheets using the term T. Thus, in martinite, the sheets of tetrahedra present are T₂ sheets.

Four distinct cations (Na₁ in a special position at the inversion center, Na₅, Ca₁ and Ca₂ in general positions) occur in the sheets of octahedra (O). The O sheets consist of a closest-packed arrangement of seven edge-sharing \( \text{M}_{\text{H}}\text{O}_6 \) octahedra (\( \text{M} = \text{Na}, \text{Ca}; \text{H}: \text{unspecified ligand} \)) (Fig. 4). These sheets are joined to the T₂ layers through apical atoms of oxygen from the SiO₄ tetrahedra of the pseudohexagonal rings (Fig. 5). The O sheets are effectively sandwiched between two symmetrically equivalent T₂ layers (T₁T₂), producing a strongly bonded T–O–T unit (Fig. 6). The \( \text{Si}, \text{B} \text{O}_4 \) and \( \text{BO}_3(\text{OH}) \) tetrahedra (i.e., those tetrahedra not part of the six-membered rings of SiO₄ tetrahedra) have their apical directions oriented along [001], away from the T–O–T unit and toward an interlayer component (X) that houses poorly ordered Na polyhedra and H₂O molecules. The bonding between polyhedra in the X component and the adjacent T₂ sheets is weak, and likely involves considerable H-bonding (although the intensity data were not of sufficient resolution to discern H positions). For example, the apex of the \( \text{BO}_3(\text{OH}) \) tetrahedron, \( \text{[OH}_2\text{]} \), corresponds to (OH); for the \( \text{Si}, \text{B} \text{O}_4 \) tetrahedra, the lower-than-ideal bond-valence sum (1.406 \( \text{v}_\text{u} \); Table 5) is suggestive of significant O²– \( \equiv \) (OH) disorder. In any event, weak bonding between the T₂ sheet and the X layer is the most plausible factor responsible for the perfect \{001\} cleavage observed in the mineral.

**TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN MARTINITE**

<table>
<thead>
<tr>
<th>Cation</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₁</td>
<td>2.383 (3)</td>
</tr>
<tr>
<td>Na₂</td>
<td>2.304 (5)</td>
</tr>
<tr>
<td>Na₅</td>
<td>2.476 (4)</td>
</tr>
<tr>
<td>O₁</td>
<td>2.23 (2)</td>
</tr>
<tr>
<td>O₂</td>
<td>2.272 (5)</td>
</tr>
<tr>
<td>O₄</td>
<td>2.235 (5)</td>
</tr>
<tr>
<td>O₅</td>
<td>2.449 (6)</td>
</tr>
<tr>
<td>O₆</td>
<td>2.639 (6)</td>
</tr>
<tr>
<td>Ca₁</td>
<td>2.382</td>
</tr>
<tr>
<td>Ca₂</td>
<td>2.593 (4)</td>
</tr>
<tr>
<td>Ca₅</td>
<td>2.304 (4)</td>
</tr>
<tr>
<td>Ca₁₁</td>
<td>2.20 (1)</td>
</tr>
<tr>
<td>Si₁</td>
<td>2.471 (5)</td>
</tr>
<tr>
<td>Si₂</td>
<td>2.410</td>
</tr>
<tr>
<td>Si₄</td>
<td>1.587 (4)</td>
</tr>
<tr>
<td>Si₅</td>
<td>1.623 (4)</td>
</tr>
<tr>
<td>Si₆</td>
<td>1.634 (3)</td>
</tr>
<tr>
<td>Si₇</td>
<td>1.637 (3)</td>
</tr>
<tr>
<td>Si₈</td>
<td>1.635 (4)</td>
</tr>
<tr>
<td>Si₉</td>
<td>1.617</td>
</tr>
<tr>
<td>Si₁₀</td>
<td>1.479 (3)</td>
</tr>
</tbody>
</table>

**FIG. 3.** A plan view of the T₂ layer of tetrahedra in martinite. The six-membered silicate rings are cross-linked by Si(7) O₄ (orange) and by BO₃(OH) (blue) tetrahedra.
Fig. 4. A plan view of the closest-packed O layer in martinite. The four types of edge-sharing \( M_{\text{H}_{92}} \) octahedra are defined in terms of the central cation: \( Na1 \) (yellow), \( Na5 \) (purple), \( Ca1 \) (red) and \( Ca2 \) (orange). Green spheres represent F.

Fig. 5. Linkages between the O and \( T_2 \) sheets in martinite projected on the \( ab \) plane in (a), and inclined to this plane in (b). The legend for the tetrahedra as in Figure 3, and all the \( M_{\text{H}_{92}} \) octahedra in grey (for the sake of simplicity, no distinction is made between the individual types of octahedra).
The inelastic, brittle nature of the cleavage fragments observed in martinite (an important diagnostic feature of the mineral) can be explained by the presence of Na polyhedra of low coordination in the X layer, producing an interlayer of quasi-octahedra, similar to that found in brittle micas or in chlorite-group minerals.

**RELATED PHASES**

Martinite is a member of the so-called reyerite–gyrolite group (Bonaccorsi & Merlino 2005), which consists of a number of layered alkali and alkaline-earth silicate and aluminosilicate hydrates having a trigonal or strongly pseudotrigonal symmetry (Table 6). The crystal structures of these phases contain sheets of octahedra (O), tetrahedra (T), a variety of interlayer components (X), along with symmetry equivalents of all three (indicated by a “bar” e.g., D) using the terminology of Merlino (1988a). The sheets of octahedra are all closest packed (brucite-like), occupied either solely by Ca or by a combination of Ca, Na or Mn. Two different sheets of tetrahedra are present in minerals belonging to this group, each with the composition $T_8O_{20}^7$: tetrahedrally coordinated cation, Si, Al, B or, in trace

![Fig. 6. The $OT_2T_2O$ module in martinite. Legend as in Figures 3 and 4, with $H_2O$ (green spheres), $Na_2$ and $Na_6$ (blue spheres), $Na_3$ (red spheres) and $Na_4$ (purple spheres).](image-url)

| Table 5. Empirical Bond-Valences (v) for Martinite* |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Na1       | Na2⁺      | Na3⁺      | Na4       | Na5       | Na6⁺      | Na6b⁺     | Ca1       | Ca2⁺      | Si1       | Si2       | Si3       | Si4       | Si5       | Si6       | Si7⁺      | B         | ΣBV       |
| F 0.148¹⁺  | 0.154 0.226 0.297 1.082 1.944 | 0.140¹⁺  | 0.245 0.295 0.262 1.084 1.886 | 0.161¹⁺  | 0.212 0.262 1.117 1.844 | 0.253 0.255 1.105 2.017 | 0.235 0.269 1.129 1.955 | 0.233 0.397 1.111 1.947 | 0.118 0.984 0.963 | 0.128 0.973 0.965 | 0.212 0.971 0.981 | 0.141 0.971 0.981 | 0.12 0.035 0.133 0.989 0.958 | 0.113 0.992 0.979 | 0.220 1.041 0.708 1.969 | 0.212 0.085 0.029 1.000 1.853 | 0.144 0.064 1.005 0.984 | 0.17 0.019 0.871 2.065 | 0.19 0.052 0.037 1.076 1.406 | 0.159 0.082 0.016 0.786 1.188 | 0.145 0.014 0.072 | 0.168 0.037 | 0.195 | 0.886 0.912 1.040 1.357 0.238 0.154 1.970 1.559 4.099 4.036 4.115 4.043 4.087 4.082 3.745 3.130 | 0.325 |

amounts as seen in martinite, S). The first sheet, referred to as $T_1$, has four tetrahedra whose vertices point in one direction and four tetrahedra with vertices pointing in the opposite direction, this sheet being connected to sheets of octahedra (O) on both sides. The second sheet, referred to as $T_2$, has six tetrahedra whose vertices point in one direction (toward a sheet of octahedra) and two whose vertices point in the other. All members of the reyerite–gyrolite group possess $T_2$ layers, although only some members possess both $T_1$ and $T_2$ layers (e.g., reyerite itself).

The $T_2$ layers present in phases belonging to the reyerite–gyrolite group may or may not be condensed through shared vertices along [001]. In cases where they are, as in fedorite, double layers, $T_2T_2$, of composition $T_{16}O_{38}$, are formed. These double layers also result in the development of large channels, within which ions of large radius (K, Na) and $H_2O$ can be accommodated. In situations where the double layers are not condensed, as in gyrolite, an interlayer component containing ions of large radius coordinated by $H_2O$ is formed. Such interlayer components can be highly variable in terms of thickness and content (cf. martinite versus gyrolite); they also play an important role in the industrial applications of these minerals (and their related synthetic counterparts), as they are expandable and in some cases, the expansion is reversible (e.g., gyrolite; Garbev et al. 2004).

Articulation between the $O$ and $T$ layers is distinctly complicated by the fact that large-radius ions, typically Ca, occupy the $O$ layers. This leads to significant misfit in the $T$ layer as it attempts to link to the $O$ layer. In turn, the misfit results in a lowering of the sheet symmetry from hexagonal or trigonal to triclinic. As discussed by Guggenheim & Eggleton (1987), this type of misfit involving tetrahedra is compensated by modulation or “periodic perturbation” of the sheet, involving reversals in the apical directions of tetrahedra, rotation of individual tetrahedra about an axis normal to the layers, and relative rotation of the sheets of tetrahedra and octahedra about a crystallographic axis (typically c). As is seen in Figure 5, all three of these mechanisms are in operation.

The $T$, $O$ and $X$ structural components in reyerite-group minerals are arranged in a variety of ways to create modules that are stacked perpendicular to [001]; in this regard, they possess crystal structures reminiscent of those found in typical phyllosilicates. For example, the crystal structure of reyerite may be described as having a $T_1OT_2T_1OT_2$ module (Table 6). Within the reyerite–gyrolite group, there is a spectrum of crystal-structure complexity, progressing from

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Crystal-chemical formula</th>
<th>Space group</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\alpha$ (°)</th>
<th>$\beta$ (°)</th>
<th>$\gamma$ (°)</th>
<th>Structural scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fedorite $^1$</td>
<td>(Na,K)$_2$·(Ca,Na)$_4$·(Si,Al)$<em>8$O$</em>{24}$F$_2$·2$H_2$O</td>
<td>$P\bar{1}$</td>
<td>9.6450</td>
<td>9.6498</td>
<td>12.6165</td>
<td>102.427</td>
<td>96.247</td>
<td>119.894</td>
<td>$OT_1T_2O$</td>
</tr>
<tr>
<td>$K$-phase $^2$</td>
<td>Ca,Si$_4$O$_8$($OH$)$_2$</td>
<td>$P\bar{1}$</td>
<td>9.70</td>
<td>9.70</td>
<td>12.25</td>
<td>108.5</td>
<td>78.0</td>
<td>120.0</td>
<td>ibid.</td>
</tr>
<tr>
<td>Reyerite $^3$</td>
<td>(Na,K)$_3$·Ca$_3$Si$_3$Al$<em>4$O$</em>{22}$($OH$)$_2$·6$H_2$O</td>
<td>$P\bar{1}$</td>
<td>9.765</td>
<td></td>
<td>19.067</td>
<td></td>
<td></td>
<td></td>
<td>$T_1OT_2T_1OT_1$</td>
</tr>
<tr>
<td>Trussoctite $^4$</td>
<td>(Ca,Mn)$_2$·Si$_2$O$_6$($OH$)$_2$·2$H_2$O</td>
<td>$P\bar{1}$</td>
<td>9.735</td>
<td></td>
<td>18.83</td>
<td></td>
<td></td>
<td></td>
<td>ibid.</td>
</tr>
<tr>
<td>Martinite $^5$</td>
<td>(Na$<em>{1.5}$·Ca$</em>{7.5}$·Si$<em>3$·S,B)$</em>{3.5}$·O$_{3.5}$ $(OH,Cl)$·$F$·4$H_2$O</td>
<td>$P\bar{1}$</td>
<td>9.5437</td>
<td>9.5349</td>
<td>14.0268</td>
<td>108.943</td>
<td>74.154</td>
<td>119.780</td>
<td>$OT_1XT_1OT_1$</td>
</tr>
<tr>
<td>Z-phase $^6$</td>
<td>Ca,Si$_4$O$_8$($OH$)$_2$[14·x]$H_2$O</td>
<td>?</td>
<td>9.65</td>
<td>9.65</td>
<td>15.3</td>
<td>?</td>
<td>?</td>
<td>120.0</td>
<td>ibid.</td>
</tr>
<tr>
<td>Gyrolite $^7$</td>
<td>Ca$_4$Na$_2$Si$_4$Al$<em>4$O$</em>{22}$($OH$)$_2$·14$H_2$O</td>
<td>$P\bar{1}$</td>
<td>9.74</td>
<td>9.74</td>
<td>22.40</td>
<td>95.7</td>
<td>91.5</td>
<td>120.0</td>
<td>$T_1OT_2XT_1OT_1$</td>
</tr>
<tr>
<td>Tungsite $^8$</td>
<td>Ca$_4$Fe$^3+$·Si$_2$O$_6$($OH$)$_2$</td>
<td>$P\bar{1}$</td>
<td>9.714</td>
<td>9.721</td>
<td>22.09</td>
<td>90.13</td>
<td>98.3</td>
<td>120.0</td>
<td>ibid.</td>
</tr>
<tr>
<td>Orlymanite $^9$</td>
<td>Ca$_4$Mn$_2$Si$_4$O$_8$($OH$)$_2$·2$H_2$O</td>
<td>$P\bar{1}$ or $P\bar{3}$</td>
<td>9.60</td>
<td></td>
<td>35.92</td>
<td></td>
<td></td>
<td></td>
<td>$T_1OT_2OT_1OT_2T_1OT_1$</td>
</tr>
</tbody>
</table>

fedorite with the simplest module (one \(T\) and one \(O\) layer, and no interlayer component), to gyrolite (Table 6). Minehillite, \([K(Na)\text{Ca}_{18}Zn_{2}Al_{4}Si_{40}O_{112}(OH)_{16}]\) space group \(P5c1\), with \(a = 9.777\) and \(c = 33.293\) Å; Dai et al. 1995] has a structure closely related to that of members of the reyerite–gyrolite group, but is not included therein. Whereas it possesses modules that are reminiscent of the \(T_{T}T_{F}\) double layers of tetrahedra, these double layers are in fact composed of pairs of inverted tetrahedra sharing common apices (Si–Al–Si) with AlO₆ octahedra, with an infinite layer being built up through edge-sharing with ZnO₄ tetrahedra (Bonaccorsi & Merlino 2005). Furthermore, although the crystal structure of orlmyanite remains unknown, there is strong evidence that it is indeed related to those of other minerals of the reyerite–gyrolite group (Peacor et al. 1990) and hence, the mineral has been included. Using the terminology of Merlino (1988a), martinite can be described as having a \(OT_{T}XT_{O}\) module. Although such a module is known in synthetic phases (e.g., the \(Z\)-phase; Table 6), martinite represents the first mineral recognized to have it. Martinite is also unique in that it is the first member of the reyerite group found to contain essential boron.

Given the nature and magnitude of the crystal-structure variations possible in minerals of the reyerite–gyrolite group, this group does not strictly constitute a polysomatic series (Ferraris 1997). Rather, the presence of a basic reyerite-like module, with or without a variable interlayer component, suggests that the group represents a merotype series, and hence the term reyerite–gyrolite merotype series (Ferraris 1997) may be most appropriate when combining these minerals into one group based on crystal-structure similarities.

**Genetic Implications**

Minerals of this reyerite–gyrolite group, which now includes martinite, are generally interpreted to be late-stage phases produced through low-\(T\) hydrothermal alteration or metamorphism of mafic rocks (usually alkali basalts). They are most commonly found in vugs in assemblages that include other hydrous low-\(T\) minerals (e.g., zeolites). Owing to the significance of phases present in, and related to, the reyerite–gyrolite group in the cement industry (Taylor 1997) and in the development of radioactive waste repositories (Carroll et al. 1998), a large number of studies involving the syntheses of these minerals has been conducted. These have shown that for calcium silicate hydrate (C–S–H) members of the reyerite group, only a poorly ordered C–S–H gel exists below 120°C, between 140 and 240°C either the poorly defined Z-phase (Assarsson 1957) or gyrolite is stable, and above 200°C, truscottite is stable. Shaw et al. (2002) demonstrated that in the above system over the range 190 to 240°C, the formation of gyrolite involves a three-step process of crystallization: amorphous gel \(\rightarrow\) C–S–H gel \(\rightarrow\) Z-phase \(\rightarrow\) gyrolite. Further heating of gyrolite in the range of 400–600°C results in its conversion to a truscottite-like phase (via dehydration and polymerization of layers of tetrahedra). With continued heating, the truscottite-like phase degrades until 700°C, at which point only an amorphous material remains (Garbev et al. 2004). In the case of the Z-phase \(\rightarrow\) gyrolite conversion, Shaw et al. (2002) opined that the process operates via a continuous, diffusion-controlled mechanism involving the ordering of the silicate layers and an increase in order along \(c\).

They also highlighted the fact that the Z-phase is likely to be unstable and transient (i.e., metastable). The above results have important ramifications for the origin of martinite, as they demonstrate that minerals related to reyerite and martinite can be easily produced at \(T\) less than 250°C. Secondly, as the crystal structure of martinite most closely resembles that of the Z-phase, it suggests that martinite, like the Z-phase, may crystallize through the ordering of a precursor, gel-like material. Lastly, given the crystal-structure similarity of martinite and the Z-phase, the implication is that martinite, like the Z-phase, may effectively be metastable, although there is no evidence of decrepitation of martinite in the samples analyzed in this study.

**Acknowledgements**

Our sincere thanks to Dr. J. Szymański, formerly of CANMET, Ottawa, for assistance with the four-circle diffractometer, Mr. D. Crabtree, of the Ontario Geoscience Laboratory, for help with electron-microprobe analyses, and Dr. P. Tarassoff for discussions regarding the mineral occurrence. We are also most grateful to the reviewers, Drs. J.D. Grice and S. Merlino, and Associate editor D.T. Griffen, for their constructive comments and recommendations, which substantially improved this paper. Financial support, provided through a grant to AMM from the Natural Sciences and Engineering Research Council, is gratefully acknowledged.

**References**


Received July 23, 2006, revised manuscript accepted March 17, 2007.