LETTER

# Incorporation of sodium into the chlorite structure: the crystal structure of glagolevite, Na(Mg,Al)$_6$[Si$_3$AlO$_{10}$](OH,O)$_8$

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## ABSTRACT

The crystal structure of glagolevite, Na(Mg,Al)$_6$[Si$_3$AlO$_{10}$](OH,O)$_8$, a new mineral from the Kovdor alkaline massif, Kola peninsula, Russia, has been solved and refined to $R_1 = 0.117$, calculated from 1503 unique observed reflections ($F_o \geq 4\sigma F_o$), and to $R_1 = 0.118$ for all 1550 unique reflections. The specimen contained several polytypes; the crystal studied yielded triclinic space group $C1$, $a = 5.3580(11)$, $b = 9.2810(19)$, $c = 14.574(3)$ Å, $\alpha = 90.00(3)$, $\beta = 97.08(3)$, $\gamma = 90.00(3)°$, $V = 719.2(3)$ Å$^3$. Glagolevite is the first mineral of the chlorite group that contains Na atoms located between the 2:1 layers and the interlayer octahedral sheets. The Na atoms are in sevenfold coordination. The Na(O,OH)$_7$ polyhedron is a trigonal prism with one of the triangular bases extended to a square. The tetrahedral sheets show disorder owing to polytype intergrowths. Tetrahedral site occupancies correlate with the occupancies of the Na sites. The polytypic composition of the crystal studied is estimated at 57% II$b$-6, 31% II$b$-2, and 12% II$b$-4.

## INTRODUCTION

Chlorite-group minerals are hydrous phyllosilicates with structures based upon alternating tetrahedral-octahedral 2:1 layers and interlayer hydroxide octahedral sheets. Bailey (1988) noted that, for common rock-forming chlorites, incorporation of large cations such as Na and Ca into sites located between the 2:1 layer and the interlayer sheet is unlikely. Dunn et al. (1987) described franklinfurnaceite, Ca$_2$Fe$^{2+}$Mn$_3^{2+}$Mn$^{3+}$[Zn$_2$Si$_2$O$_{10}$](OH)$_8$, a tri-dioctahedral zincosilicate intermediate between chlorite and mica. Peacor et al. (1988) reported a crystal-structure determination for franklinfurnaceite, and demonstrated that the Ca atoms are in octahedral coordination between the 2:1 layers and the interlayer sheets. According to Peacor et al. (1988), this type of Ca incorporation into the chlorite structure is possible only if the structure type is II$a$, the interlayer sheet is dioctahedral, and if substitutions of substantial Al and/or Fe$^{3+}$ occur in the 2:1 layer. The Ca-bearing tri-dioctahedral chlorite was also reported by Makarov (1971).

Recently, during mineralogical investigations of the Kovdor Phlogopite quarry, Kovdor massif, Kola peninsula, Russia, Seredkin et al. (2003) found a colorless platy mineral that forms, together with vesuvianite, large lenses within altered melilitic rocks. The mineral has the chlorite structure but contains 4.40 wt% Na$_2$O. Its simplified formula is Na(Mg,Al)$_6$[Si$_3$AlO$_{10}$](OH,O)$_8$; the Na content corresponds to 0.76 atoms per formula unit (apfu). Comparison of unit-cell data derived from X-ray powder diffraction showed that this mineral is distinct from clinochlore, (Mg,Al)$_6$[(Si,Al)$_4$O$_{10}$](OH)$_8$, as the $c$ parameter of ~14.6 Å is larger than that of clinochlore, which has $c$ parameter ranging from 14.20 to 14.40 Å (Rule and Bailey 1987; Zheng and Bailey 1989; Joswig and Fuess 1990; Smyth et al. 1997; Guggenheim and Zhan 1999). This new species, and the name glagolevite, were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (CNMMN IMA) (Seredkin et al. 2003). Here we report the structure of glagolevite, which includes the first demonstration of Na in a chlorite structure between the 2:1 layer and the interlayer octahedral sheet. In contrast to franklinfurnaceite, glagolevite is a tri-trioctahedral chlorite mineral.

## EXPERIMENTAL METHODS

Many crystals of glagolevite were examined by single-crystal X-ray diffraction, but proved unsuitable for structural analysis owing to broad and ill-defined diffraction peaks, and the presence of substantial diffraction streaking. Eventually a specimen was obtained that contained a large but visually undistorted crystal of glagolevite. The crystal was carefully separated from the matrix and mounted on a Bruker three-circle diffractometer equipped with a 1K CCD (charge-coupled device) detector with a crystal-to-detector distance of 5.4 cm. Initial diffraction data contained various deleterious features, but the data collected was ultimately sufficient for solution and partial refinement of the structure. More than a hemisphere of data was collected using monochromated MoK$\alpha$ X-radiation and framewidths of 0.3° in ω. The unit-cell dimensions (Table 1) were refined on the basis of 564 strong reflections using least-squares techniques. The data were corrected for Lorentz, polarization, background, and absorption effects ($R_{int} = 0.039$). Additional information pertinent to the data collection is given in Table 1. Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from *International Tables for X-ray Crystallography,* Ibers and Hamilton (1974). The Bruker SHELXTL Version 5 system of programs was used for determination and

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refinement of the structure. Initially, we attempted to refine the structure on the basis of atomic coordinates for $C\bar{1}$ clinochlore II$b$-4 (Zheng and Bailey 1989). However, it was not possible to refine this model below an $R_1$ index of 0.25. Reducing the symmetry to space group $C1$ lowered $R_1$ to ~0.14. The model included the octahedral and tetrahedral sheets of the 2:1 layer. Analysis of the difference-Fourier maps revealed several additional positions between the 2:1 layer and the interlayer sheets, and also at the level of Si atoms of the tetrahedral sheets. The latter peaks were included in the refinement as Si atoms, and tetrahedral sheets on both sides of the octahedral sheet of the 2:1 layer were modeled as split over two sets. The electron-density residues between the 2:1 layer and interlayer sheet were designated Na. During the refinement, soft constraints were imposed on the Si-O distances of the tetrahedral sheets, which exhibited positional disorder. Isotropic displacement parameters of the O atoms were constrained to be equal for different tetrahedral sheets. The structure was refined on the basis of $F^2$ for all unique data, and converged to $R_1 = 0.117$ for the 1503 unique observed reflections ($F_o > 4\sigma F_o$), and to $R_1 = 0.118$ for all 1550 unique reflections. Although the $R_1$ value is high, this is probably the best X-ray data that can be obtained for glagolevite from the Kovdor massif. Final atomic positional and displacement parameters, and selected interatomic distances are in Tables 2 and 3, respectively.

## RESULTS

The structure of glagolevite (Fig. 1a) is distinct from the structures of common rock-forming chlorites in that it contains Na sites between the 2:1 layer and interlayer octahedral sheet. The Na atoms are coordinated by three hydroxl groups from the adjacent interlayer octahedral sheet, and four O atoms from the overlying tetrahedral sheet (Fig. 1b). The Na(O,OH)$_7$ polyhedron may be described as a trigonal prism, in which one of the triangular bases is extended into a square. The Na-O,OH distances vary from 2.28 to 2.93 Å. The site-occupancy refinement for the Na positions produced site-occupancy factors of 0.30(4), 0.10(3), and 0.18(3) for the Na1, Na2, and Na3 sites, respectively. This accounts for 0.58(10) apfu Na, which is in good agreement with the average chemical analysis of 0.76 apfu (Seredkin et al. 2003). Incorporation of Na into the sites between the 2:1 layers and interlayer octahedral sheets accounts for the increase of the $c$ parameter by ~0.2 Å as compared to Na-free clinochlore. This value can be easily calculated using arguments developed by Nelson and Guggenheim (1993). The average $z$ coordinate of the OH atoms is approximately 0.07 (i.e., OH20, OH21, and OH23; average $z = 0.0707$), whereas the average $z$ coordinate for the O atoms on the alternative side of the space is approximately $z = 0.27$ (i.e., O9-O15; average $z = 0.27055$). The difference is $0.27055 - 0.0707 = 0.19985$. The distance between the sheets can be determined as $0.19985 \times c\sin\beta = 2.8904$ Å. For the other side of the interlayer, the similar distance is 2.955 Å. For the "average" chlorite structure [clinochlore studied by Nelson and

Guggenheim (1993)], the analogous distance is 2.810 Å. The differences of the interlayer distances in glagolevite from those observed in the average chlorite structure are 0.08 and 0.145 Å, i.e., 0.225 Å in total, in good agreement with the increase in the $c$ parameter of glagolevite in comparison with Na-free clinochlore.

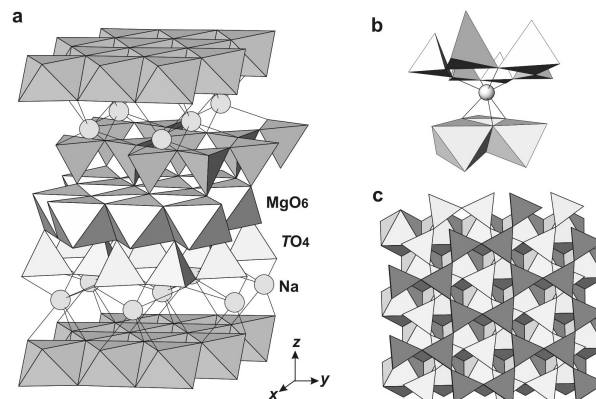Analysis of the stacking arrangement for glagolevite using



**FIGURE 1.** The crystal structure of glagolevite (**a**), coordination of the Na1 site (**b**) and view from the top onto the 2:1 layer with disordered tetrahedral sheets.

**TABLE 2.** Atomic coordinates and isotropic displacement parameters (Å$^2$) for glagolevite

| Atom | s.o.f. | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|---|
| M1 | Mg$_{1.00}$ | 0.242(1) | 0.5794(8) | 0.4995(6) | 0.0075(7)* |
| M2 | Mg$_{1.00}$ | −0.259(1) | −0.586(1) | −0.4995(6) | 0.0075(7)* |
| M3 | Mg$_{1.00}$ | 0.246(1) | 0.2457(9) | 0.4986(6) | 0.0075(7)* |
| M4 | Mg$_{1.00}$ | 0.243(1) | 0.7495(9) | 0.0011(6) | 0.0075(7)* |
| M5 | Mg$_{1.00}$ | 0.247(1) | 0.4145(9) | 0.9999(6) | 0.0075(7)* |
| M6 | Mg$_{1.00}$ | −0.253(1) | −0.4189(9) | −0.9991(6) | 0.0075(7)* |
| Na1 | 0.30(4) | −0.512(7) | 0.751(4) | 0.805(3) | 0.035(10)† |
| Na2 | 0.10(3) | −0.556(18) | −0.735(11) | −0.793(7) | 0.035(10)† |
| Na3 | 0.18(3) | 0.414(11) | −0.426(7) | −0.803(6) | 0.035(10)† |
| T1 | Si$_{1.00}$ | −0.0333(9) | 0.5797(6) | 0.6897(4) | 0.0063(7)‡ |
| T2 | Si$_{0.199(9)}$ | 0.488(4) | 0.738(2) | 0.6758(11) | 0.0063(7)‡ |
| T3 | Si$_{0.801(9)}$ | 0.4876(11) | 0.4198(7) | 0.6921(4) | 0.0063(7)‡ |
| T4 | Si$_{1.00}$ | 0.0194(9) | −0.5837(6) | −0.6897(4) | 0.0063(7)‡ |
| T5 | Si$_{0.383(9)}$ | −0.457(2) | −0.411(1) | −0.6878(8) | 0.0063(7)‡ |
| T6 | Si$_{0.617(9)}$ | −0.5006(12) | −0.7581(8) | −0.6930(5) | 0.0063(7)‡ |
| O1 | 1 | −0.059(3) | 0.582(2) | 0.5764(9) | 0.0106(8)§ |
| O2 | 0.801(9) | 0.253(2) | 0.516(2) | 0.7300(12) | 0.0106(8)§ |
| O3 | 0.801(9) | −0.038(3) | 0.747(2) | 0.7316(12) | 0.0106(8)§ |
| O4 | 0.801(9) | −0.237(3) | 0.479(2) | 0.7357(12) | 0.0106(8)§ |
| O5 | 0.199(9) | 0.256(5) | 0.641(6) | 0.710(4) | 0.0106(8)§ |
| O6 | 0.199(9) | −0.039(10) | 0.4050(19) | 0.710(10) | 0.0106(8)§ |
| O7 | 0.199(9) | −0.266(6) | 0.661(6) | 0.729(3) | 0.0106(8)§ |
| O8 | 1 | 0.430(3) | 0.748(2) | 0.5664(9) | 0.0106(8)§ |
| O9 | 0.383(9) | 0.263(4) | −0.490(3) | −0.720(2) | 0.0106(8)§ |
| O10 | 0.383(9) | −0.248(4) | −0.509(3) | −0.731(2) | 0.0106(8)§ |
| O11 | 0.383(9) | 0.070(6) | −0.747(2) | −0.726(2) | 0.0106(8)§ |
| O12 | 1 | 0.058(3) | −0.584(2) | −0.5780(9) | 0.0106(8)§ |
| O13 | 0.617(9) | 0.223(3) | −0.687(2) | −0.734(2) | 0.0106(8)§ |
| O14 | 0.617(9) | 0.033(4) | −0.423(2) | −0.735(2) | 0.0106(8)§ |
| O15 | 0.617(9) | −0.256(3) | −0.658(2) | −0.731(2) | 0.0106(8)§ |
| O16 | 1 | −0.447(3) | −0.752(2) | −0.5785(8) | 0.0106(8)§ |
| O17 | 1 | 0.436(3) | 0.414(2) | 0.5719(10) | 0.0106(8)§ |
| O18 | 1 | −0.447(3) | −0.420(2) | −0.5782(10) | 0.0106(8)§ |
| OH19 | 1 | 0.409(2) | 0.584(2) | 0.9286(10) | 0.0106(8)§ |
| OH20 | 1 | −0.378(2) | −0.585(2) | −0.9307(10) | 0.0106(8)§ |
| OH21 | 1 | 0.116(2) | 0.583(2) | 0.0709(10) | 0.0106(8)§ |
| OH22 | 1 | −0.092(2) | −0.587(2) | −0.0735(10) | 0.0106(8)§ |
| OH23 | 1 | 0.619(2) | 0.751(2) | 0.0719(10) | 0.0106(8)§ |
| OH24 | 1 | −0.598(2) | −0.748(2) | −0.0690(11) | 0.0106(8)§ |

Note: s.o.f. = site occupation factor.
*,†,‡,§ constrained to be equal during refinement.

**TABLE 1.** Crystallographic data and refinement parameters for glagolevite

| | | | |
|---|---|---|---|
| $a$ (Å) | 5.3580(11) | $\mu$ (cm$^{-1}$) | 8.03 |
| $b$ (Å) | 9.2810(19) | $D_{calc}$ (g/cm$^3$) | 2.61 |
| $c$ (Å) | 14.574(3) | Crystal size (mm) | 0.68 × 0.56 × 0.16 |
| $\alpha$ (°) | 90.00(3) | Radiation | Mo$K\alpha$ |
| $\beta$ (°) | 97.08(3) | Total Ref. | 1803 |
| $\gamma$ (°) | 90.00(3) | Unique Ref. | 1550 |
| $V$ (Å$^3$) | 719.2(3) | Unique $|F_o| \geq 4\sigma_F$ | 1503 |
| Space group | $C1$ | $R_1$ | 0.117 |
| $F_{000}$ | 569 | $wR_2$ | 0.325 |
| $Z$ | 2 | $S$ | 1.147 |
| Empirical chemical formula: | | Na$_{0.76}$(Mg$_{5.50}$Al$_{0.46}$Fe$_{0.03}$Mn$_{0.01}$)$_{\Sigma6.00}$ | |
| | | (Si$_{2.90}$Al$_{1.10}$O$_{10}$)(OH$_{7.88}$O$_{0.12}$)$_{\Sigma8.00}$·0.85H$_2$O. | |
| Idealized chemical formula: | | NaMg$_6$[Si$_3$AlO$_{10}$](OH,O)$_8$·H$_2$O | |

*Notes:* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where $n$ is the number of reflections and $p$ is the number of refined parameters.

**TABLE 3.** Selected bond lengths (Å) in the structure of glagolevite

| Tetrahedral sheets | | | | | | | |
|---|---|---|---|---|---|---|---|
| sheet I′ | | sheet I″ | | sheet II′ | | sheet II″ | |
| T1–O7 | 1.63(2) | T1–O1 | 1.64(1) | T4–O12 | 1.62(1) | T4–O12 | 1.62(1) |
| T1–O1 | 1.64(1) | T1–O4 | 1.64(1) | T4–O10 | 1.63(2) | T4–O14 | 1.64(2) |
| T1–O5 | 1.65(2) | T1–O3 | 1.67(1) | T4–O11 | 1.64(2) | T4–O13 | 1.65(1) |
| T1–O6 | 1.65(2) | T1–O2 | 1.68(1) | T4–O9 | 1.67(2) | T4–O15 | 1.67(1) |
| <T1–O> | 1.64 | <T1–O> | 1.66 | <T4–O> | 1.64 | <T4–O> | 1.65 |
| | | | | | | | |
| T2–O8 | 1.59(2) | T3–O4 | 1.63(1) | T5–O18 | 1.59(2) | T6–O16 | 1.66(1) |
| T2–O7 | 1.61(2) | T3–O2 | 1.69(1) | T5–O10 | 1.63(2) | T6–O14 | 1.66(2) |
| T2–O6 | 1.64(2) | T3–O3 | 1.72(2) | T5–O11 | 1.63(2) | T6–O13 | 1.67(2) |
| T2–O5 | 1.66(2) | T3–O1 | 1.74(2) | T5–O9 | 1.68(2) | T6–O15 | 1.75(2) |
| <T2–O> | 1.63 | <T3–O> | 1.70 | <T5–O> | 1.64 | <T6–O> | 1.69 |
| **Octahedral sheet of the 2:1 layer** | | | | | | | |
| M1–O8 | 2.04(2) | M2–O8 | 2.02(2) | M3–O8 | 2.06(2) | | |
| M1–O17 | 2.07(2) | M2–O17 | 2.05(2) | M3–O17 | 2.09(2) | | |
| M1–O12 | 2.07(2) | M2–O18 | 2.10(2) | M3–O1 | 2.09(2) | | |
| M1–O1 | 2.08(2) | M2–O16 | 2.10(2) | M3–O16 | 2.10(2) | | |
| M1–O16 | 2.12(2) | M2–O1 | 2.12(2) | M3–O18 | 2.10(2) | | |
| M1–O18 | 2.12(2) | M2–O12 | 2.16(2) | M3–O12 | 2.11(2) | | |
| <M1–O> | 2.08 | <M2–O> | 2.09 | <M3–O> | 2.09 | | |
| **Interlayer octahedral sheet** | | | | | | | |
| M4–OH20 | 1.98(2) | M5–OH22 | 1.99(2) | M6–OH19 | 1.98(2) | | |
| M4–OH24 | 1.98(2) | M5–OH23 | 2.01(2) | M6–OH20 | 1.99(2) | | |
| M4–OH21 | 2.02(2) | M5–OH21 | 2.05(2) | M6–OH23 | 2.05(2) | | |
| M4–OH22 | 2.12(2) | M5–OH24 | 2.04(2) | M6–OH21 | 2.11(2) | | |
| M4–OH19 | 2.12(2) | M5–OH19 | 2.13(2) | M6–OH24 | 2.11(2) | | |
| M4–OH23 | 2.14(2) | M5–OH20 | 2.14(2) | M6–OH22 | 2.14(2) | | |
| <M4–OH> | 2.06 | <M5–OH> | 2.06 | <M6–OH> | 2.06 | | |
| **Na positions** | | | | | | | |
| Na1–OH22 | 2.41(4) | Na2–O11 | 2.34(10) | Na3–OH21 | 2.28(6) | | |
| Na1–OH19 | 2.46(4) | Na2–OH23 | 2.47(10) | Na3–O14 | 2.38(6) | | |
| Na1–O4 | 2.58(4) | Na2–OH20 | 2.72(11) | Na3–OH20 | 2.72(6) | | |
| Na1–O2 | 2.68(4) | Na2–O10 | 2.75(11) | Na3–OH23 | 2.78(6) | | |
| Na1–OH24 | 2.70(4) | Na2–O9 | 2.74(11) | Na3–O13 | 2.87(6) | | |
| Na1–O3 | 2.87(4) | Na2–OH21 | 2.85(10) | Na3–O13 | 2.86(7) | | |
| Na1–O3 | 2.89(4) | Na2–O10 | 2.93(11) | Na3–O15 | 2.90(7) | | |
| <Na1–O,OH> | 2.66 | <Na2–O,OH> | 2.69 | <Na3–O,OH> | 2.68 | | |

the nomenclature proposed by Bailey (1988) indicates that glagolevite is a chlorite II*b* polytype (octahedral sheets of the 2:1 layer and interlayer sheets have opposite orientation; cations of the interlayer sheet form triads symmetrically disposed in projection to the center of the hexagonal ring in the tetrahedral sheet below). According to Bailey (1988), this polytype is the most common in nature, and it has the lowest energy. However, there are several II*b* polytypes that differ in the relative positions of the tetrahedral sheets located above and below the interlayer octahedral sheet. In glagolevite, tetrahedral sheets on either side of the 2:1 layer occupy one of two positions, and these positions are shifted relative to each other by ±*b*/3 (Fig. 2c). The refined occupancies of these sheets differ. The tetrahedral sheets on one side, **I′** and **I″**, are formed by the $Si1O_4$ and $Si2O_4$, and $Si1O_4$ and $Si3O_4$ tetrahedra, respectively. The tetrahedral site occupancies of the **I′** and **I″** sheets are 0.20 and 0.80, respectively. The tetrahedral sheets on the other side of the 2:1 layer, **II′** and **II″**, are made up of $Si4O_4$ and $Si5O_4$, and Si4 and Si6 tetrahedra, respectively. These sheets have tetrahedral site occupancies of 0.38 and 0.62, respectively. Note that the occupancies of the atomic sites in the tetrahedral sheets are different, which may explain in part the non-centrosymmetry of glagolevite. The orientations of tetrahedral sheets relative to the interlayer octahedral sheets (**I′-II′, I′-II″, I″-II′** and **I″-II″**) are shown in Fig. 2. Following Bailey's notations, these orientations correspond to the II*b*-6, II*b*-4, II*b*-2 and II*b*-6 polytypes, respectively. Note that the II*b*-
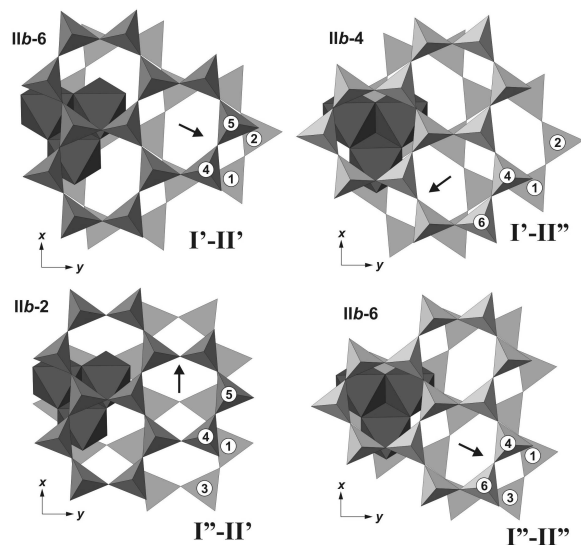


**FIGURE 2.** Mutual orientations of tetrahedral sheets relative to the interlayer octahedral sheet. Arrows indicate shift of the upper tetrahedral sheet relative to the lower sheet. Polytype notations for each type of orientation are given according to Bailey (1988). See text for details.

4 polytype is equivalent to II*b*-6 by a 180° rotation around **b**. These two polytypes have triclinic symmetry, space group $C\bar{1}$. In contrast, the II*b*-2 polytype differs from the II*b*-4 polytype

and has monoclinic symmetry, space group $C2/m$. On the basis of the tetrahedral site occupancies of the tetrahedral sheets, the polytypic composition of the crystal studied is estimated as 57% II$b$-6, 31% II$b$-2, and 12% II$b$-4.

Site occupancies of the tetrahedral sheets and the site occupancies of Na are correlated. The Na1 site [site-occupancy factor (s.o.f.) = 0.30(4)] is between the **I″** tetrahedral sheet (s.o.f = 0.80) and the interlayer octahedral sheet. The Na1 site is presumably empty if the **I′** tetrahedral sheet is occupied (s.o.f. = 0.20). The Na2 and Na3 sites are on the other side of the 2:1 layer. The Na2 site [s.o.f. = 0.10(3)] is between the **II′** tetrahedral sheet (total s.o.f. = 0.38) and the interlayer sheet, whereas the Na3 site [s.o.f. = 0.18(3)] is between the **II″** tetrahedral sheet (s.o.f. = 0.62) and the interlayer sheet. Consequently, the two sides of the 2:1 layer are structurally different on the average over all unit cells as there are two Na sites on one side, and one Na site on the other. This structural feature is consistent with the absence of a center of symmetry in the structure of glagolevite.

In common rock-forming chlorites, the 2:1 layers and interlayer sheets are connected by hydrogen bonds alone. The incorporation of Na provides additional bonding that probably results in replacement of OH groups of the interlayer sheet by $O^{2-}$ anions. Unfortunately, analysis of bond-valence sums corresponding to our structural model is difficult because of the disordered configurations observed in the structure of glagolevite.

The geometrical parameters of the octahedral sheets are in agreement with similar characteristics observed for other minerals of the chlorite groups. The average <Mg-O,OH> bond lengths are in the range of 2.06–2.09 Å. Owing to the relatively low quality of the diffraction data, it is impossible to determine possible Al ordering at the octahedral or tetrahedral positions. However, on the basis of the <T-O> bond lengths listed in Table 3, the Si3 and Si6 sites are more appropriate for Al substitution.

## DISCUSSION

We present the first structural evidence for incorporation of Na into the chlorite structure, with the Na atoms occupying sites between the 2:1 layers and interlayer octahedral sheets. The occurrence of glagolevite as a rock-forming mineral in the Kovdor Phlogopite quarry demonstrates that, under presumable narrow conditions, tri-trioctahedral chlorites may incorporate significant Na. It is apparent that incorporation of Ca into the chlorite structure (e.g., in franklinfurnaceite) is associated with different structural mechanisms, presumably owing to the higher charge of $Ca^{2+}$ cations relative to $Na^+$.

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