

## Crystal structure refinement and chemical formula of prosopite, $\text{CaAl}_2\text{F}_4[(\text{OH})_{4-x}\text{F}_x]$ $x = 0.0\text{--}1.0$

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Prosopite is an alumino-fluoride of calcium mineral. The chemical compositions of prosopite samples obtained from Zacatecas (Mexico), Ivigtut (Greenland), and Katugin deposit (Eastern Siberia, Russia) were determined using scanning electron microscopy and energy-dispersive X-ray spectroscopy. The fluorine content (in apfu) was between 4 and 5, and those less than 4 were not observed. The empirical formula derived as a mean of chemical compositions of multiple grains from Ivigtut is  $(\text{Ca}_{0.96}\text{Sr}_{0.04})\text{Al}_{2.00}\text{F}_4[(\text{OH})_{3.72}\text{F}_{0.28}]$ . The crystal structure of prosopite [monoclinic;  $a = 6.7103(3)$  Å,  $b = 11.1619(5)$  Å,  $c = 7.3741(3)$  Å,  $\beta = 94.919(2)^\circ$ ; space group  $C2/c$ ;  $Z = 4$ ] was analyzed using single-crystal X-ray diffraction and was refined to the  $R$  value of 0.0185 ( $wR2 = 0.0554$ ) using 791 unique reflections with  $|F_o| > 4\sigma(|F_o|)$ . The positions of hydrogen atoms were determined at the position where residual electron density peaks appeared using the difference Fourier method.  $\text{F}^-$  and  $\text{O}^{2-}$  ions are distributed at each F and O site in order. The chemical structural formula,  $\text{Ca}_{0.964(2)}\text{Sr}_{0.036}\text{Al}_2\text{F}_4(\text{OH})_4$ , obtained from the refinement of Ivigtut sample is approximately consistent with the result of chemical analysis. During the chemical analysis (Zacatecas, Ivigtut, and Katugin deposit samples) and refinement (Ivigtut sample), we assume that  $(\text{OH})^-$  dissolution into F sites does not occur (but substitution of  $\text{F}^-$  in (OH) sites slightly occurs) and propose that the chemical structural formula of prosopite is expressed as  $\text{CaAl}_2\text{F}_4[(\text{OH})_{4-x}\text{F}_x]$  ( $x = 0.0\text{--}1.0$ ). The crystal structure of prosopite consists of two types of  $\text{AlF}_2(\text{OH})_4$  octahedra and one kind of  $\text{CaF}_6(\text{OH})_2$  dodecahedra. The size difference between F sites and (OH) sites can be observed in Ca dodecahedra and Al2 octahedra; however, evident differences in Al-F and Al-O distances are not observed in Al1 octahedral sites. Two hydrogen bonds ( $\text{O1-H1}\dots\text{O2}$  and  $\text{O2-H2}\dots\text{F2}$ ) are confirmed using bond valence sum calculations.

**Keywords:** Prosopite, Structure refinement, Crystal chemistry, Bond valence sum calculation, Hydrogen bonding

### INTRODUCTION

Prosopite,  $\text{CaAl}_2(\text{F},\text{OH})_8$ , an alumino-fluoride of calcium mineral, commonly occurs in association with aluminum fluoride minerals such as cryolite,  $\text{Na}_3\text{AlF}_6$ , and thomsonolite,  $\text{NaCaAlF}_6 \cdot (\text{H}_2\text{O})$ , in granitic, alkaline intrusive, or volcanic environments, and is an alteration product after F-rich greisenization and hydrothermal processes (e.g., Scheerer, 1857; Palache et al., 1951; Bailey, 1980; Young et al., 1997). Prosopite usually appears in a variety of colors such as turquoise or pale red owing to the presence

of a small amount of transition metal ions. The chemical formula of prosopite is considered  $\text{CaAl}_2(\text{F},\text{OH})_8$  (e.g., Giacobozzo and Menchetti, 1969; Young et al., 1997) or  $\text{CaAl}_2\text{F}_4(\text{OH})_4$  (e.g., Pudovkina et al., 1973). The crystal structure of prosopite was determined based on the results of X-ray diffraction interpretation for the first time by Giacobozzo and Menchetti (1969). Pudovkina et al. (1973) performed single-crystal structure analysis of prosopite and refined the structure with distinction of F and (OH) sites as  $\text{CaAl}_2\text{F}_4(\text{OH})_4$ . However, they did not report the possible position of hydrogen atoms, and therefore, the details of hydrogen bonding and anionic site preference were not elucidated. In this study, we determined the chemical compositions of prosopite using scanning elec-

tron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDS) and analyzed the crystal structure of prosopite including the position of hydrogen atoms in detail using single-crystal X-ray diffraction. We investigated the relation between the substituted quantity of  $F^-$  for  $(OH)^-$  in prosopite and the structure of prosopite in order to clarify the state of the solid solution and/or the relation of order-disorder between  $F^-$  and  $(OH)^-$  in prosopite.

## EXPERIMENTS

### Chemical analysis

The prosopite samples used for the measurement were obtained from Zacatecas in Mexico (sample No. 1), Ivigtut in Greenland (Kingdom of Denmark, sample Nos. 2 and 3) and Katugin deposit in Eastern Siberia (Russia, sample No. 4). The chemical compositions were determined with multiple grains of each sample using JEOL SEM (JSM-7001F operated by 15 kV, 0.5 nA) equipped with Oxford EDS (INCA SYSTEM). The number of grains analyzed and analytical points were 3 and 19 (sample No. 1), 5 and 54 (sample No. 2), 5 and 31 (sample No. 3) and, 2 and 29 (sample No. 4), respectively. The following standard materials were employed:  $CaF_2$  for F,  $Al_2O_3$  for Al,  $CaSiO_3$  for Ca, copper metal for Cu, and  $SrTiO_3$  for Sr. The chemical formula was determined considering that the total number of charges (w.r.t.  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Al^{3+}$ , and  $Cu^{2+}$ ) is eight, and the unanalyzed

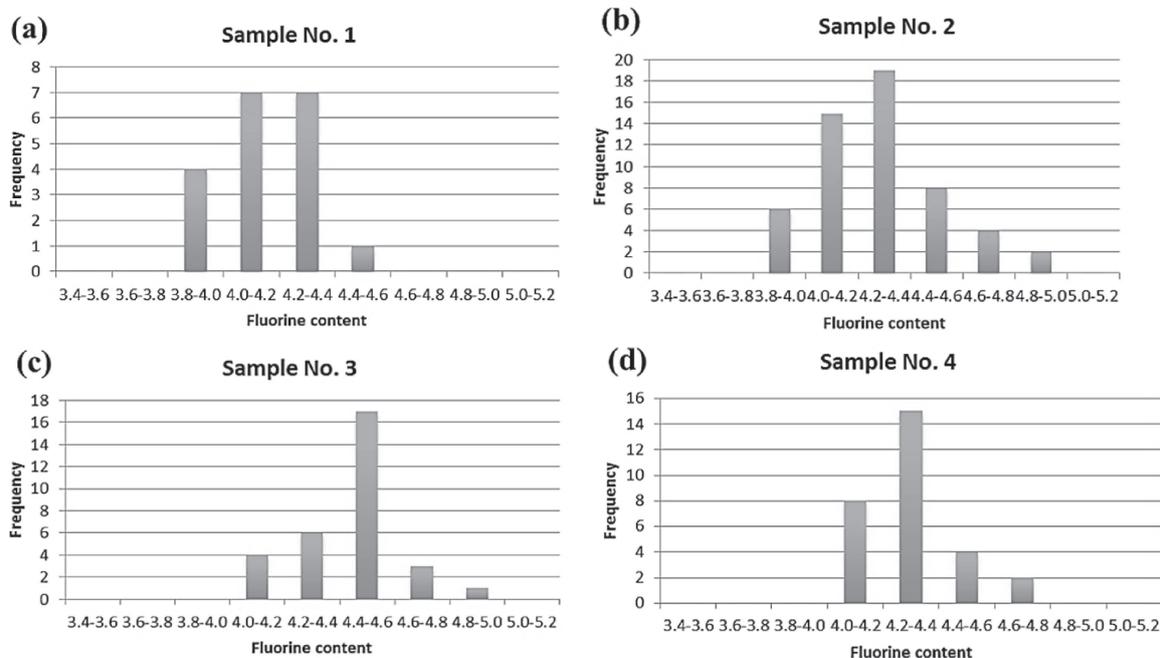
anions are assumed to be  $(OH)^-$ .

The specimens included a small amount of Cu and Sr as the substituents of Al and Ca, respectively (Table 1). The impurity substitution reaction,  $Al^{3+} + (OH)^- \leftrightarrow Cu^{2+} + H_2O$ , occurs at the cation sites. The empirical formulae as the means of chemical compositions are  $Ca(Al_{1.98}Cu_{0.03})F_4[(OH)_{3.84}F_{0.16}]$  (Zacatecas sample No. 1),  $(Ca_{0.96}Sr_{0.04})Al_{2.00}F_4[(OH)_{3.72}F_{0.28}]$  (Ivigtut sample No. 2),  $(Ca_{0.93}Sr_{0.04})Al_{2.02}F_4[(OH)_{3.56}F_{0.44}]$  (Ivigtut sample No. 3), and  $Ca_{0.98}Al_{2.01}F_4[(OH)_{3.70}F_{0.30}]$  (Katugin sample No. 4). Figure 1 shows the histograms of the measured amount (frequency) of fluorine content as apfu (atoms per formula unit). Textural and compositional variations such as chemical zoning were not observed in the analysis of the multiple analytical points in a grain of each sample. As shown in Figure 1, the frequency distri-

**Table 1.** Mean of chemical compositions as apfu of all prosopite samples (No. 1 to No. 4)

	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4
F	4.16	4.28	4.44	4.30
Al	1.98	2.00	2.02	2.01
Ca	1.00	0.96	0.93	0.98
Cu	0.029	—	—	—
Sr	—	0.04	0.04	—
$OH^*$	3.84	3.72	3.56	3.70

\* Unanalyzed anion content obtained by subtracting F content from that of eight anions is assumed to be that of  $(OH)^-$ .



**Figure 1.** Histograms of measured amount (frequency) of fluorine content as apfu of the four prosopite samples. (a) Zacatecas, Mexico. (b) Ivigtut, Greenland. (c) Ivigtut, Greenland. (d) Katugin deposit, Eastern Siberia, Russia.

bution of fluorine content is not a normal distribution. Thus, the chemical compositions are obtained from the arithmetic average values and the errors are not considered (Table 1). The ratio of Ca and Al, which are cations in the empirical formula, as the means of chemical compositions of four samples is almost the same as that of the ideal chemical formula of prosopite. The fluorine content was between 4 and 5 and the quantity of maximum substitution of  $F^-$  for  $(OH)^-$  in prosopite was estimated to be 25% (Table 1 and Fig. 1).

### Crystal structure refinement

The crystal structure of prosopite (sample No. 2) was analyzed using single-crystal X-ray diffraction. The crystal-line qualities of the single-crystal specimens were evaluated using a four-circle diffractometer at the BL-10A beam line of the Photon Factory, High Energy Accelerator Research Organization, KEK, Japan, using high-resolution monochromatized synchrotron X-ray radiation. The structure refinement was performed using reflection intensity data obtained using a Rigaku X-ray diffractometer (Vari-MAX-RAPID) with an imaging plate (graphite-monochromatized  $MoK\alpha$  radiation,  $\lambda = 0.71069 \text{ \AA}$ ) and a rotating anode X-ray tube, at Tohoku University. Focused  $MoK\alpha$  radiation was utilized and the conventional oscillation technique was applied. After Lorentz and polarization corrections, an absorption correction was performed by using the integration method based on the shape of the specimen (Higashi, 1995). The space group  $C2/c$  was adopted based on the systematic absence conditions of the observed diffraction intensity data. Accordingly, 2944 reflection intensities were measured. The experimental details and crystallographic data are summarized in Table 2.

The crystal structure refinement was carried out using SHELXL97 program (Sheldrick, 1997). The crystal structure of prosopite was refined to the  $R$  value of 0.0185 ( $wR2 = 0.0554$ ) using 791 unique reflections with  $|F_o| > 4\sigma(|F_o|)$ . Scattering factors for neutral atoms and anomalous dispersion coefficients were obtained from International Tables for Crystallography, Volume C (1992). In the structural refinement, the Ca site was considered to be fully occupied by Ca and Sr. Fluorine atoms and oxygen atoms were assigned optionally and the minimum  $R$  value was selected (at approximately 0.3% of the differences). After the least-squares refinements without hydrogen atoms, the  $R$  index ( $= \sum ||F_o| - |F_c|| / \sum |F_o|$ ) was converged at less than 0.03 with anisotropic temperature factors. The position of hydrogen atoms in the structure was determined at the position where residual electron density peaks appeared using the difference Fourier meth-

**Table 2.** Experimental details and crystallographic data of prosopite from Ivigtut, Greenland (sample No. 2)

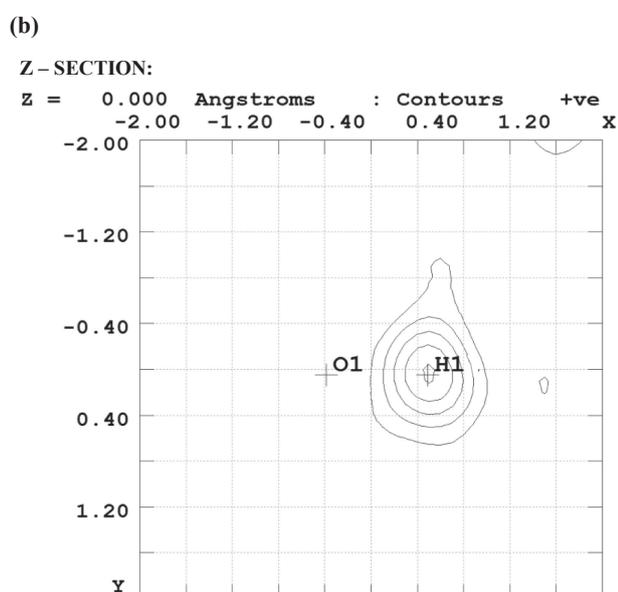
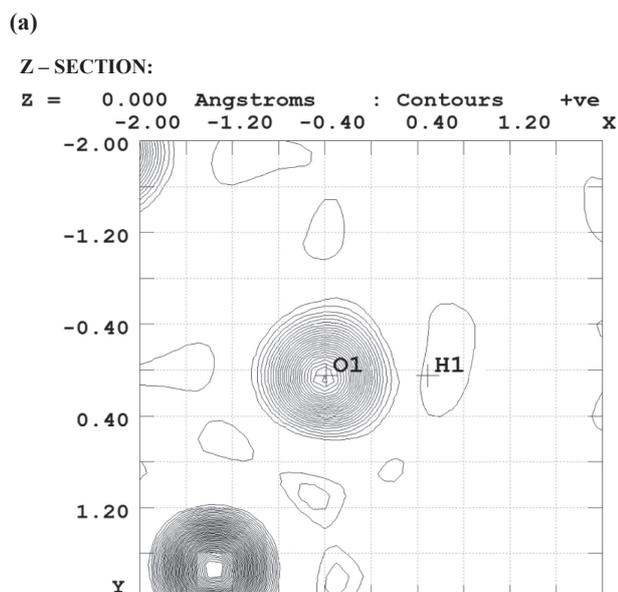
Formula (Sample No. 2: empirical)	$Ca_{0.96}Sr_{0.04}Al_2F_4[(OH)_{3.72}F_{0.28}]$
Formula (refined)	$Ca_{0.964(2)}Sr_{0.036}Al_2F_4(OH)_4$
Space group	$C2/c$
$a$ (Å)	6.7103(3)
$b$ (Å)	11.1619(5)
$c$ (Å)	7.3741(3)
$\beta$ (°)	94.919(2)
Radiation used	$MoK\alpha$
Radiation wavelength (Å)	0.71069
Crystal size (mm)	$0.043 \times 0.048 \times 0.063$
Total reflections	2944
Unique reflections used	791
Final $R$	0.0185
Final $wR2$	0.0554
Goof	1.203

od. Careful examination of the difference Fourier maps indicated two possible hydrogen positions (H1 and H2) near O1 and O2 sites only (Figs. 2 and 3). These hydrogen atoms were involved but their positions were not parameterized in the least-squares cycles. No significant electron density residue was observed around the fluorine atoms. This finding prompted us to select a model where each  $F^-$  and  $O^{2-}$  ion is ordered among four anion sites as shown in Table 3. Pudovkina et al. (1973) also determined the values of the structural parameters of prosopite and indicated an ordered distribution of  $F^-$  and  $O^{2-}$  ions. The chemical structural formula,  $Ca_{0.964(2)}Sr_{0.036}Al_2F_4(OH)_4$ , obtained from the refinement is approximately consistent with the empirical formula,  $(Ca_{0.96}Sr_{0.04})Al_{2.00}F_4[(OH)_{3.72}F_{0.28}]$ , obtained from the chemical analysis. The atomic coordinates and anisotropic atomic displacement parameters for prosopite are listed in Table 3. The selected interatomic distances are presented in Table 4.

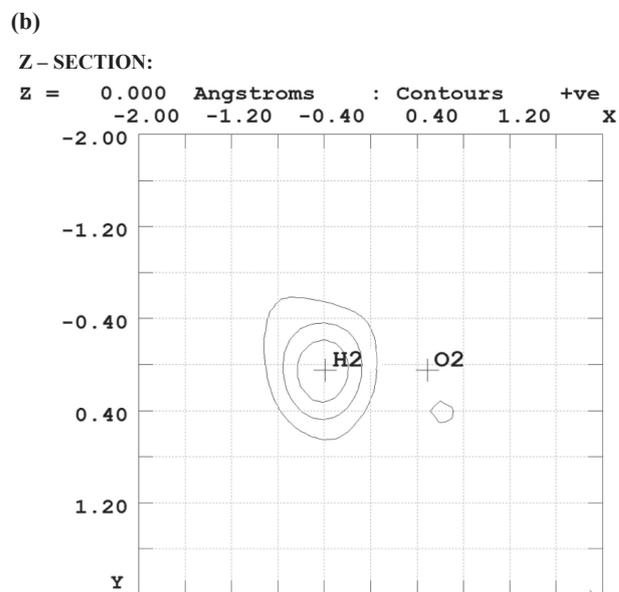
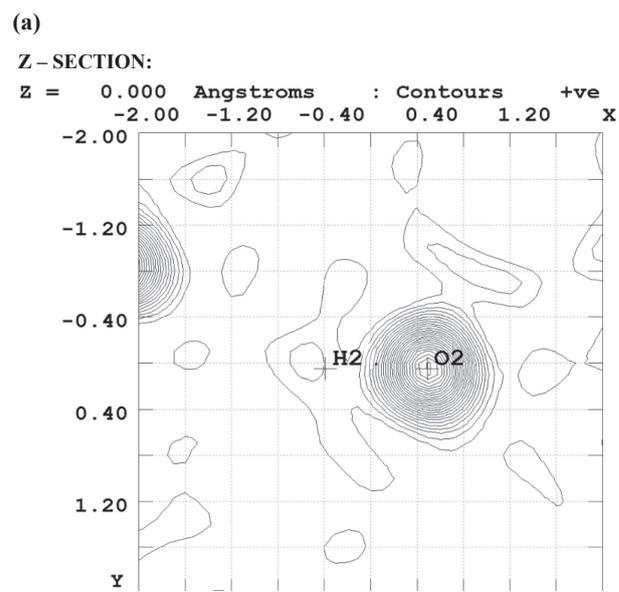
## RESULTS AND DISCUSSION

### Crystal structure of prosopite

From the chemical analysis, the fluorine content was between 4 and 5 and the quantity of maximum substitution of  $F^-$  for  $(OH)^-$  in prosopite was estimated to be 25%. This observation may indicate that fluorine content of more than 4 is common in the prosopite structure. As fluorine and oxygen elements have different proton numbers, the attraction between protons and an electron is different (the origin of chemical shift). The ionic radius (1.33 Å for  $^{VI}F^-$  and 1.40 Å for  $^{VI}O^{2-}$ ) (Shannon, 1976) and polariz-



**Figure 2.** Position of H1 in the prosopite structure. (a) Fourier map near the O1 site; contours are at an interval of  $1.0 \text{ e}/\text{\AA}^3$ . (b) Difference Fourier map near the O1 site; contours are at an interval of  $0.2 \text{ e}/\text{\AA}^3$ .



**Figure 3.** Position of H2 in the prosopite structure. (a) Fourier map near the O2 site; contours are at an interval of  $1.0 \text{ e}/\text{\AA}^3$ . (b) Difference Fourier map near the O2 site; contours are at an interval of  $0.2 \text{ e}/\text{\AA}^3$ .

ability differ even when they are converted to ions. The atomic scattering factors and Coulombic contribution are also different. The  $(\text{OH})^-$  ion with  $\text{H}^+$  ion and the spherical  $\text{F}^-$  ion have different anisotropy in chemical bonding. The replacement of  $\text{F}^-$  in the  $(\text{OH})^-$  sites with large anisotropy is easy. On the contrary, our observation based on both the chemical analysis and structure refinement shows that the substitution of  $(\text{OH})^-$  with large anisotropy for F sites with slight anisotropy hardly occurs. H atoms form hydrogen bonds that require bonding directionality and form Coulomb interaction with the surrounding atoms. An appro-

appropriate site for hydrogen atom is also required. In our structural observation, no significant H site near F sites was observed. Therefore, we assume the model in which  $(\text{OH})^-$  dissolution into F sites does not occur (but the substitution of  $\text{F}^-$  in OH sites slightly occurs) and propose that the chemical structural formula of prosopite is  $\text{CaAl}_2\text{F}_4[(\text{OH})_{4-x}\text{F}_x]$  ( $x = 0.0-1.0$ ).

The crystal structure of prosopite obtained using the refinement is shown in Figure 4. The fundamental framework structure is identical to that reported by Pudovkina et al. (1973), and the present analysis allows us to dem-

**Table 3.** Atomic coordinates and anisotropic atomic displacement parameters for prosopite from Ivigtut, Greenland (sample No. 2)

	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<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>
Ca	0.964(2)	0	0.46044(3)	1/4	0.00798(17)	0.00816(17)	0.00959(17)	0	0.00281(11)	0
Sr	0.036	0	0.46044(3)	1/4	0.00798(17)	0.00816(17)	0.00959(17)	0	0.00281(11)	0
Al1	1/4	1/4	0	0.0073(3)	0.0081(3)	0.0071(3)	0.00029(19)	0.0020(2)	-0.00004(19)	
Al2	0	0.14076(5)	1/4	0.0077(3)	0.0071(3)	0.0086(3)	0	0.0025(2)	0	
F1	0.07624(12)	0.38085(7)	0.96143(11)	0.0125(4)	0.0105(4)	0.0113(4)	0.0015(3)	0.0021(3)	0.0028(3)	
F2	0.18263(13)	0.02445(7)	0.28587(12)	0.0122(4)	0.0115(4)	0.0202(4)	0.0042(3)	0.0060(3)	0.0044(3)	
O1	0.19954(14)	0.26342(8)	0.24864(12)	0.0074(4)	0.0108(4)	0.0072(4)	0.0003(3)	0.0002(3)	-0.0014(3)	
O2	0.02486(14)	0.15354(8)	0.99625(12)	0.0095(4)	0.0091(4)	0.0088(4)	-0.0024(3)	0.0020(3)	-0.0015(3)	
H1*	0.2999	0.2661	0.3325							
H2*	0.0338	0.0890	0.9298							

\* Hydrogen position is not refined.

The maximum peak position in the differential Fourier synthesis was considered as each hydrogen position.

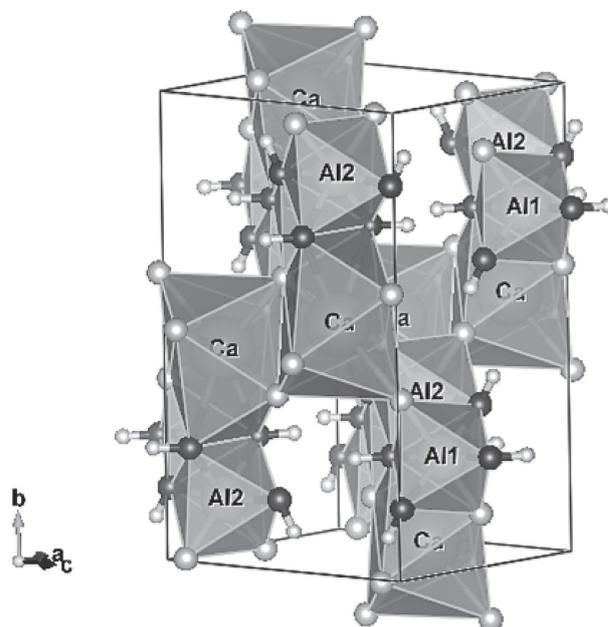
**Table 4.** Selected interatomic distances (Å)

CaF <sub>6</sub> O <sub>2</sub> dodecahedra	Al1F <sub>2</sub> O <sub>4</sub> octahedra	Al2F <sub>2</sub> O <sub>4</sub> octahedra	
Ca-F1[×2]	Al1-F1[×2]	Al2-F2[×2]	
2.4012(8)	1.8752(8)	1.7893(9)	
Ca-F1 <sup>-</sup> [×2]	Al1-O1[×2]	Al2-O1[×2]	
2.3863(8)	1.8987(9)	1.9156(10)	
Ca-F2[×2]	Al1-O2[×2]	Al2-O2[×2]	
2.2831(9)	1.8535(9)	1.8982(9)	
Ca-O1[×2]			
2.5751(10)			
Ave.	2.4114	1.8758	1.8677
Max.	2.5751	1.8987	1.9156
Min.	2.2831	1.8535	1.7893
Max.-Min.	0.2920	0.052	0.1263

onstrate a model where F<sup>-</sup> and O<sup>2-</sup> anions preferentially reside at each F and O site together with the hydrogen positions bonded to O1 and O2. The crystal structure of prosopite consists of two types of AlF<sub>2</sub>(OH)<sub>4</sub> octahedra and one kind of CaF<sub>6</sub>(OH)<sub>2</sub> dodecahedra. The octahedra and dodecahedra form a block unit and large voids are formed between the block units. The voids are filled with hydrogen atoms and are arranged parallel to the [101] direction (Fig. 4).

### Interatomic distances

As (OH)<sup>-</sup> has larger ionic radius than F<sup>-</sup> for the coordination numbers of four (1.35 Å for (OH)<sup>-</sup> and 1.31 Å for F<sup>-</sup>) and six (1.37 Å for (OH)<sup>-</sup> and 1.33 Å for F<sup>-</sup>) (Shannon, 1976), it can be considered that the interatomic distances of (OH)<sup>-</sup> and cations are longer than those of F<sup>-</sup> and cations. As shown in Table 4, the interatomic distances of Ca-OH (Ca-O1H1) and Al2-OH (Al2-O1H1 and Al2-O2H2) are longer than those of Ca-F and Al2-F in Ca dodecahedra and Al2 octahedra, respectively, and the size difference between the F sites and (OH) sites is apparent. However, such features of Al-F and Al-O distances are not observed in Al1 octahedral sites. The value of 1.8752(8) Å for Al1-F1 is larger than the expected



**Figure 4.** Crystal structure of prosopite as a perspective view from the direction close to [-101]. The crystal structure was drawn using VESTA (Momma and Izumi, 2011). The tunnels in which hydrogen atoms were located continuously are observed in parallel to [101]. Color version is available online from <https://doi.org/10.2465/jmps.170418>.

**Table 5.** Bond valence sum calculations for prosopite

	Al1	Al2	Ca	$\Sigma(\text{Al,Ca})v$	H1	H2	$\Sigma(\text{Al,Ca,H})v$
F1	0.410		0.221	0.860			0.860
F1			0.229				
F2		0.516	0.304	0.820		0.110	0.930
O1	0.511	0.490	0.193	1.195	0.904		2.099
O2	0.579	0.513		1.092	0.115	0.907	2.114
$\Sigma_{av}$	3.002	3.039	1.893		1.019	1.017	

**Table 6.** Selected interatomic distances (Å) and angles (°) including hydrogen bonding

X-H...A	Distance(X-H) (Å)	Distance(X-A) (Å)	Distance (H...A) (Å)	Angle (°)
O1-H1...O2	0.875	2.878	2.059	155.8
O2-H2...F2	0.876	2.784	1.977	152.7

value by Shannon's ionic radii and the Al1–O2 distance is 1.8535(9) Å in the Al1 octahedral site. The tendency of these interatomic distances in this study is similar to that reported by Pudovkina et al. (1973).

#### Bond valence sum calculation and hydrogen bonding

Pudovkina et al. (1973) reported that prosopite structure is characterized by two weak hydrogen bonds O1–H1...O2 and O2–H2...F2 with O1–O2 distance of 2.89 Å and O2–F2 distance of 2.80 Å, respectively. They did not determine the hydrogen positions, but proposed hydrogen bonds from the donor–acceptor anion distances. In order to investigate the electrostatic compensation in prosopite, we also carried out bond valence sum calculations using the method of calculations and parameters given by Brown and Altermatt (1985). Table 5 shows the bond valence sum calculations considering the hydrogen bonding. The O2 and F2 sites act as acceptors in the hydrogen bonds O1–H1...O2 and O2–H2...F2, respectively. The H1...O2 distance is 2.059 Å and the O1–H1...O2 angle is 155.8° (Table 6). The H2...F2 distance is 1.977 Å and the O2–H2...F2 angle is 152.7° (Table 6). We confirmed the same two hydrogen bonds reported by Pudovkina et al. (1973). They also performed the calculation of the valence balance in the prosopite structure and reported that the valence sum is similar to the formal valence of each atom. As shown in Table 5, the estimated crystal structure is appropriate, because the bond valence sum is similar to the ionic valence of each atom. The calculated bond valence sum of 0.860 for F1 is less than the expected value of 1.0. This is due to the long Al1–F1 distance. Similar phenomena were observed in legrandite (Jinnouchi et al., 2016). This phenomenon is caused by the failure to satisfy the local requirement in order to maintain three-dimensional periodicity.

#### ACKNOWLEDGMENTS

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#### SUPPLEMENTARY MATERIAL

Color version of Figure 4 is available online from <https://doi.org/10.2465/jmps.170418>.

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