

Hydroxymcglasssonite-(K), $\text{KSr}_4\text{Si}_8\text{O}_{20}(\text{OH}) \cdot 8\text{H}_2\text{O}$, the first Sr-bearing member of the apophyllite group, from the Wessels mine, Kalahari Manganese Field, South Africa

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ABSTRACT

A new mineral species, hydroxymcglasssonite-(K), ideally $\text{KSr}_4\text{Si}_8\text{O}_{20}(\text{OH}) \cdot 8\text{H}_2\text{O}$, has been found in the Wessels mine, Kalahari Manganese Field, Northern Cape Province, South Africa. It is granular (<0.05 mm), associated with meieranite, sugilite, aegirine, pectolite, and yuzuxiangite. The mineral is colorless, transparent with a white streak and a vitreous luster. It is brittle and has a Mohs hardness of 4.5–5.0; cleavage is perfect on {001} and no parting or twinning was observed. The measured and calculated densities are 2.60(3) and 2.614 g/cm³, respectively. Optically, hydroxymcglasssonite-(K) is uniaxial (+), with $\omega = 1.555(5)$, $\epsilon = 1.567(5)$ (white light), and absorption $O > E$. Hydroxymcglasssonite-(K) is insoluble in water or hydrochloric acid. An electron microprobe analysis yielded an empirical formula (based on 13 non-H cations pfu) $\text{K}_{1.01}(\text{Sr}_{2.99}\text{Ca}_{1.03})_{\Sigma 4.02}\text{Si}_{7.99}\text{O}_{20}(\text{OH}) \cdot 8\text{H}_2\text{O}$, which can be simplified to $\text{K}(\text{Sr,Ca})_4\text{Si}_8\text{O}_{20}(\text{OH}) \cdot 8\text{H}_2\text{O}$.

Hydroxymcglasssonite-(K) is tetragonal with space group $P4/mnc$ and unit-cell parameters $a = 9.0792(2)$, $c = 16.1551(9)$ Å, $V = 1331.70(9)$ Å³, and $Z = 2$. It is isostructural with hydroxyapophyllite-(K), $\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{OH}) \cdot 8\text{H}_2\text{O}$, with Sr substituting for Ca. The crystal structure of hydroxymcglasssonite-(K) is characterized by SiO_4 tetrahedra sharing corners to form $(\text{Si}_8\text{O}_{20})^{8-}$ sheets parallel to (001), which are connected by the K and $B (= \text{Sr} + \text{Ca})$ cations, as well as hydrogen bonding. The K cation is coordinated by eight H_2O groups, and the average K–O distance of 2.941(3) Å is shorter than that of 2.950(3)–2.975(3) Å in hydroxyapophyllite-(K) or fluorapophyllite-(K). The B cation is sevenfold-coordinated ($4\text{O} + 2\text{H}_2\text{O} + \text{OH}$), and the average B–O distance of 2.522(3) Å is noticeably longer than that of 2.422–2.435 Å in hydroxyapophyllite-(K) or fluorapophyllite-(K). The Raman spectra of hydroxymcglasssonite-(K) and hydroxyapophyllite-(K) are very comparable, especially in the O–H stretching region. The discovery of hydroxymcglasssonite-(K), the first Sr-bearing mineral of the apophyllite group, implies that more Sr-bearing members of the group may be found in nature or synthesized in laboratories, but the possibility for an incomplete solid solution between hydroxyapophyllite-(K) and hydroxymcglasssonite-(K), due to the size difference between Sr^{2+} and Ca^{2+} , cannot be ruled out.

Keywords: Hydroxymcglasssonite-(K), apophyllite, new mineral, crystal structure, X-ray diffraction, Raman spectra

INTRODUCTION

A new mineral species, hydroxymcglasssonite-(K), ideally $\text{KSr}_4\text{Si}_8\text{O}_{20}(\text{OH}) \cdot 8\text{H}_2\text{O}$, has been found in the Wessels mine, Kalahari Manganese Fields, Northern Cape Province, Republic of South Africa. It is named in honor of James (Jim) A. McGlasson, who has been interested in collecting minerals since age 10 and started field collecting after graduation from college. Jim earned his B.S. degree in geology at the New Mexico Institute of Mining and Technology and M.S. degree in geology at the Colorado School of Mines. A successful 45-year career as an exploration geologist, mine manager, and consultant has allowed him to obtain geological and mineralogical knowledge at many diverse deposits worldwide. Jim has served as the president of the Tucson Gem and Mineral Society, and he has been on the board of directors of the Friends of Mineralogy. With a strong belief that getting children interested in science of any kind,

especially geology and mineralogy, is critical for our society and future, he has been actively and constantly involved in various educational programs for children and young students and has donated considerable amounts of mineral specimens for their interests/hobbies. Since his retirement in 2016, Jim has been a volunteer at the University of Arizona Mineral Museum and the mineralogy laboratory of the Department of Geosciences at the University of Arizona to continue his passion for minerals while contributing his knowledge and experience to help the society and other people. The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2020-066). The co-type samples have been deposited at the University of Arizona Mineral Museum (catalog no. 22691) and the RRUFF Project (deposition no. R200004).

Hydroxymcglasssonite-(K) is the first Sr-bearing mineral of the apophyllite group. This paper describes its physical and chemical properties and its crystal structure determined from single-crystal X-ray diffraction data.

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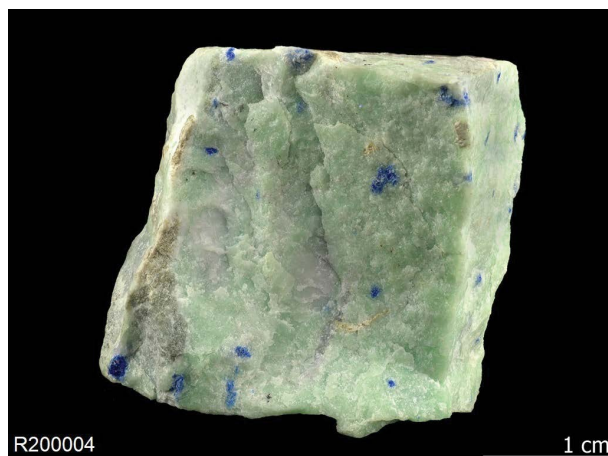


FIGURE 1. The specimen on which colorless hydroxymcglassonite-(K) crystals are found in intergrowth with isolated blue granular meieranite aggregates, which are embedded in a matrix consisting of mainly massive pale-green sugilite, along with minor prismatic gray aegirine, bladed white pectolite, and brownish fibrous yuzuxiangite. (Color online.)

SAMPLE DESCRIPTION AND EXPERIMENTAL METHODS

Occurrence, physical and chemical properties, and Raman spectra

Hydroxymcglassonite-(K) was found on a specimen (Fig. 1) collected from the Wessels mine, Kalahari Manganese Field, Northern Cape Province, Republic of South Africa (27°6'51.82"S, 22°51'18.31"E). This specimen is also the type sample for meieranite (Yang et al. 2019) and yuzuxiangite (Gu et al. 2021). Hydroxymcglassonite-(K) crystals are found intergrown with isolated blue granular meieranite aggregates, which are embedded in a matrix consisting of mainly massive pale-green sugilite, along with minor prismatic gray aegirine, bladed white pectolite, and fibrous brownish yuzuxiangite (Figs. 2, 3, and 4). The mineral assemblage probably formed as a result of a hydrothermal event. Conditions during metamorphism were in the range of 270–420 °C at 0.2–1.0 kbar (Kleyenstuber 1984; Gutzmer and Beukes 1996). Detailed reviews on the geology and mineralogy of the Kalahari Manganese Field have been presented by Kleyenstuber (1984), Von Bezing et al. (1991), and Gutzmer and Beukes (1996).

Hydroxymcglassonite-(K) crystals are granular (<0.05 mm). The mineral is colorless, transparent with a white streak and vitreous luster. It is brittle and has

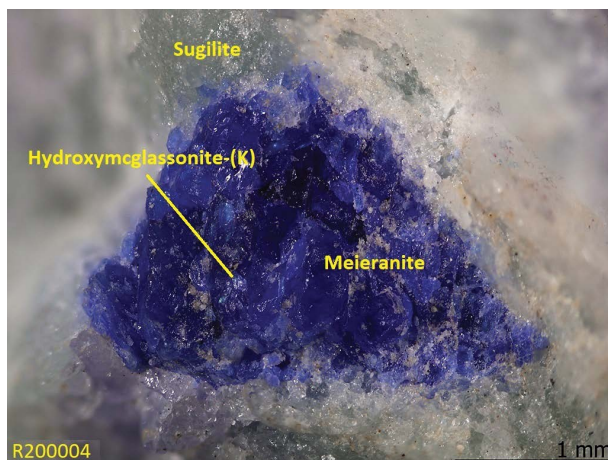


FIGURE 2. A microscopic view of colorless hydroxymcglassonite-(K) intergrown with blue granular meieranite. (Color online.)

a Mohs hardness of 4.5–5.0; cleavage is perfect on {010}, and no twinning was observed. The density measured by floatation in heavy liquids is 2.60(3) g/cm³, and the calculated density is 2.614 g/cm³. Optically, hydroxymcglassonite-(K) is uniaxial (+), with $\omega = 1.555(5)$, $\epsilon = 1.567(5)$ (white light), and absorption $O > E$. The compatibility index based on the empirical formula is 0.031 (excellent) (Mandarino 1981). Hydroxymcglassonite-(K) is insoluble in water or hydrochloric acid.

The chemical composition of hydroxymcglassonite-(K) was determined using a Shimadzu EPMA-1720 electron microprobe (WDS mode, 15 kV, 10 nA, and a beam diameter of 5 μ m). Because of the small size and vulnerability to the damage (dehydration) by the electron beam, only five analysis points were obtained from the single crystal used for the X-ray structure determination. As minerals in the apophyllite group commonly have the OH-F substitution, before the measurements, fluorine was particularly searched by the EDS method and then checked by the WDS scan for the $FK\alpha$ peak. No F was detected by either method with a detection limit of ~0.08 wt%. The standards used are listed in Table 1, along with the determined compositions. The resultant chemical formula, calculated on the basis of 13 non-H cations pfu, is $K_{1.01}(Sr_{2.99}Ca_{1.03})_{24.02}Si_{7.99}O_{20}(OH) \cdot 8H_2O$, which can be simplified to $K(Sr,Ca)_4Si_8O_{20}(OH) \cdot 8H_2O$. It should be pointed out that the Sr and Ca contents vary noticeably from point to point and are inversely correlated, resulting in large standard deviations in their measurements. The crystal analyzed has $Sr/(Sr+Ca) = 75\%$. We also found another crystal with $Sr/(Sr+Ca) > 80\%$, but its structure data are not as good as those reported here.

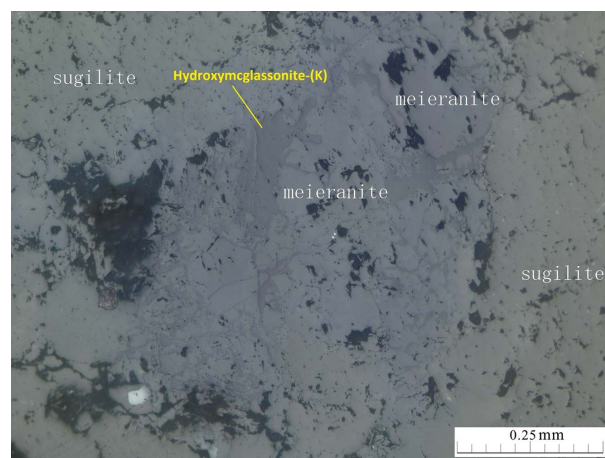


FIGURE 3. A photomicrograph showing the occurrence and association of hydroxymcglassonite-(K) (reflected light, parallel nicols). (Color online.)

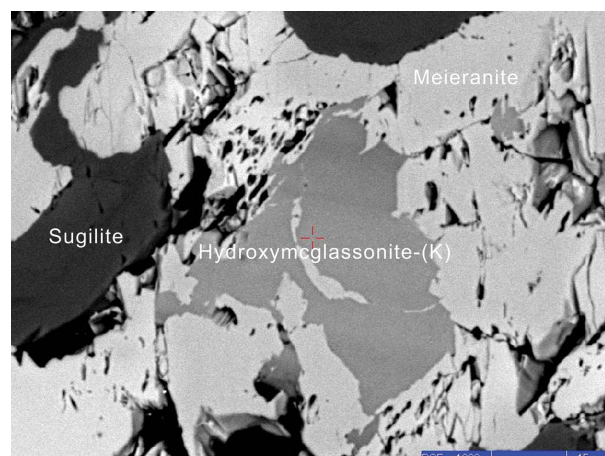


FIGURE 4. Backscattered electron image of hydroxymcglassonite-(K), associated with meieranite and sugilite. (Color online.)

TABLE 1. Electron microprobe analysis data (in wt%) for hydroxymcglassonite-(K)

Constituent	Mean	Range	St. dev.	Probe standard
SiO ₂	45.99	44.94–47.27	0.99	SiO ₂
K ₂ O	4.56	4.17–5.93	0.32	KAlSi ₃ O ₈
CaO	5.52	3.06–7.21	2.19	CaSiO ₃
SrO	29.66	26.36–33.67	3.11	SrSO ₄
H ₂ O ^a	14.67			
Total	100.40	100.05–100.78	0.28	

^a Calculated based on the structure.**TABLE 2.** Comparison of mineralogical data for hydroxyapophyllite-(K) and hydroxymcglassonite-(K)

	Hydroxyapophyllite-(K)	Hydroxymcglassonite-(K)
Ideal chemical formula	KCa ₄ Si ₈ O ₂₀ (OH,F)·8H ₂ O	KSr ₄ Si ₈ O ₂₀ (OH)·8H ₂ O
Crystal symmetry	Tetragonal	Tetragonal
Space group	<i>P4/mnc</i>	<i>P4/mnc</i>
<i>a</i> (Å)	8.979(4)	9.0792(2)
<i>c</i> (Å)	15.83(1)	16.1551(9)
<i>V</i> (Å ³)	1276.253	1331.70(10)
<i>Z</i>	2	2
$\rho_{\text{obs}}, \rho_{\text{cal}}$ (g/cm ³)	2.37, 2.36	2.59, 2.60
Optical properties	uniaxial (+)	uniaxial (+)
Ω	1.52	1.555
Σ	1.53	1.567
2 θ range for data collection	≤54.77	≤67.31
No. of reflections collected	1049	10474
No. of independent reflections	757	1262
No. of reflections with $I > 2\sigma(I)$	696	1046
No. of parameters refined		61
<i>R</i> _{int}		0.039
Final <i>R</i> ₁ , <i>wR</i> ₂ factors [$I > 2\sigma(I)$]	0.035, 0.038	0.040, 0.088
Goodness-of-fit		1.069
Reference	Rouse et al. (1978)	This study

TABLE 3. Selected bond distances (Å) for hydroxymcglassonite-(K) and hydroxyapophyllite-(K)

	Hydroxymcglassonite-(K)	Hydroxyapophyllite-(K)
K–O4 ×8	2.941(3)	2.954(3)
B–O3 ×2	2.487(2)	2.403(2)
B–O3 ×2	2.509(2)	2.416(2)
B–O5	2.5497(5)	2.435(1)
B–O4 ×2	2.555(3)	2.486(3)
Avg.	2.522	2.435
Si–O3	1.590(2)	1.584(3)
Si–O1	1.6185(11)	1.622(3)
Si–O2	1.629(2)	1.617(2)
Si–O2	1.636(2)	1.644(2)
Avg.	1.619	1.616

The Raman spectrum of hydroxymcglassonite-(K) (Fig. 5) was collected from a randomly oriented crystal on a Horiba Labram HR spectrometer in the State Key Laboratory of Powder Metallurgy, Central South University, China. The laser beam (488 nm, laser power 2 mW) was focused to 1 μm with a 100× objective on an Olympus microscope. The time of each scan in the range 100–4000 cm^{−1} was 20 min with a resolution of 2 cm^{−1}.

X-ray crystallography

The powder X-ray diffraction data for hydroxymcglassonite-(K) were collected on a Rigaku XtaLAB Synergy single-crystal diffractometer (MoK α radiation) in powder mode at 50 kV and 1 mA (Online Materials¹ Table S2). The unit-cell parameters obtained from the powder X-ray diffraction data using the program by Holland and Redfern (1997) are *a* = 9.0928 (6), *c* = 16.203 (2) Å, and *V* = 1339.65(4) Å³.

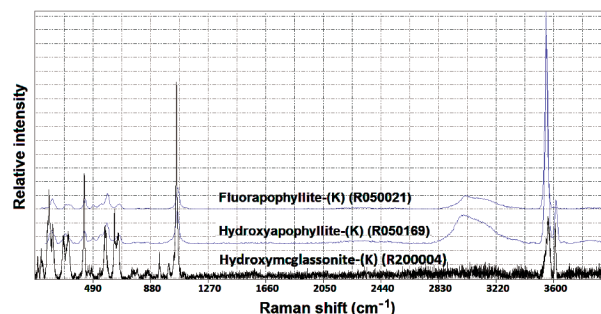
Single-crystal X-ray diffraction data for hydroxymcglassonite-(K) were collected from a 0.010 × 0.002 × 0.002 mm crystal on a Rigaku XtaLAB Synerg D/S 4-circle diffractometer equipped with MoK α radiation. All reflections were indexed on the basis of a tetragonal unit cell (Table 2). The systematic absences of reflections are compatible with space groups *P4nc* (#104) and *P4/mnc* (#128). The crystal structure was solved and refined using SHELX-2018 (Sheldrick 2015a, 2015b) based on space group *P4/mnc* because it produced the better refinement statistics in terms of bond lengths and angles, atomic displacement parameters, and *R* factors. Difference Fourier syntheses only revealed the two H atoms (H1 and H2) associated with the H₂O group (O4) but failed to locate the H atom in the OH group (O5). This is not surprising, considering

that there are only two equivalent H atoms from the OH group per unit cell, but 16 equivalent ones for each H1 and H2. During the refinements, the structure chemistry was constrained to the empirical formula determined from the electron microprobe analysis, i.e., K_{1.00}(Sr_{2.98}Ca_{1.02})_{24.00}Si₈O₂₀(OH)·8H₂O. All non-H atoms were refined anisotropically, whereas the two H atoms (H1 and H2) were refined isotropically. Final atomic coordinates and displacement parameters for hydroxymcglassonite-(K) are given in Online Materials¹ Tables S2 and S3, respectively. Selected bond distances are presented in Table 3.

CRYSTAL STRUCTURE DESCRIPTION AND DISCUSSION

Hydroxymcglassonite-(K), ideally KSr₄Si₈O₂₀(OH)·8H₂O, is isostructural with hydroxyapophyllite-(K), KCa₄Si₈O₂₀(OH)·8H₂O (Rouse et al. 1978) (Table 2), with Sr substituting for Ca. Its structure is characterized by SiO₄ tetrahedra sharing corners to form (Si₈O₂₀)^{8−} sheets parallel to (001) (Fig. 6), which are connected by the interstitial K⁺ and B²⁺ (= Sr + Ca) cations and by hydrogen bonding. In the sheet, SiO₄ tetrahedra form 4- and 8-membered rings (Fig. 6). The geometry of hydrogen bonding is in accord with that in hydroxyapophyllite-(K) (Rouse et al. 1978). The bond-valence sums calculated using the parameters from Brese and O'Keeffe (1991) (Table 4) indicate that O4 is H₂O and O5 is OH.

The K⁺ cation in hydroxymcglassonite-(K) is coordinated by eight H₂O groups. The average K–O distance of 2.941(3) Å (Table 3) is shorter than that of 2.950(3)–2.975(3) Å in hydroxyapophyllite-(K) (Rouse et al. 1978) or fluorapophyllite-(K) (Chao 1971; Colville et al. 1971; Prince 1971; Pechar 1987; Ståhl et al. 1987). The B (= 0.74Sr + 0.26Ca) cation is 7-coordinated (4O + 2H₂O + OH). The average B–O distance of 2.522 (3) Å in hydroxymcglassonite-(K) (Table 3) is noticeably longer than that of 2.422–2.435 Å in hydroxyapophyllite-(K) (Rouse et al. 1978) or fluorapophyllite-(K) (Chao 1971; Colville et al. 1971; Prince 1971; Pechar 1987; Ståhl et al. 1987). This is understandable, as the B site is predominantly occupied by Ca²⁺ in both hydroxyapophyllite-(K) and fluorapophyllite-(K), which is significantly smaller than Sr²⁺ in ionic radius (1.06 vs. 1.21 Å) (Shannon 1976).

**FIGURE 5.** Raman spectra of hydroxymcglassonite-(K), hydroxyapophyllite-(K), and fluorapophyllite-(K). (Color online.)**TABLE 4.** Bond-valence sums for hydroxymcglassonite-(K)

	K	B	Si	Sum
O1			1.015 ×2→	2.029
O2			0.984	1.953
			0.969	
O3		0.337 ×2↓	1.100	1.754
		0.317 ×2↓		
O4	0.112 ×8↓	0.280 ×2↓		0.392
O5		0.237 ×4→		0.948
Sum	0.896	2.105	4.068	

Note: The bond valence sum for B was calculated based on (0.74Sr²⁺ + 0.26Ca²⁺).

In the ruizite-strontioruizite solid solution $(\text{Ca,Sr})_2\text{Mn}_3^{3+}\text{Si}_4\text{O}_{11}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, the B cation ($B = \text{Ca} + \text{Sr}$) is also sevenfold-coordinated (Hawthorne 1984; Fendrich et al. 2016; Yang et al. 2021) and the average $B\text{-O}$ bond distance increases linearly with increasing $X = \text{Sr}/(\text{Sr} + \text{Ca})$, following the equation $\langle B\text{-O} \rangle = 0.1468X + 2.4475$ (Å) ($R^2 = 0.98$) (Yang et al. 2021). With $\text{Sr} = 0.74$ for hydroxymcglassonite-(K), we obtain $\langle B\text{-O} \rangle = 2.556$ Å, which is slightly longer than our measured value of 2.522 Å.

The Raman spectrum of hydroxymcglassonite-(K) is plotted in Figure 5. Based on previous Raman spectroscopic studies on both hydroxyapophyllite-(K) and fluorapophyllite-(K) (Adams et al. 1981; Sidorov 2000; Frost and Xi 2012; Goryainov et al. 2012; Ogorodova et al. 2019), we made tentative assignments of major Raman bands for hydroxymcglassonite-(K) (Table 5). For comparison, the Raman spectra of hydroxyapophyllite-(K) (<http://rruff.info/R050169>) and fluorapophyllite-(K) (<http://rruff.info/R050021>) from the RRUFF Project were also plotted in Figure 5. The similarities among the three spectra are evident. The difference in peak intensities among the spectra principally results from the different crystal orientations when the data were collected.

According to Frost and Xi (2012), Goryainov et al. (2012), and Ogorodova et al. (2019), the key difference between the Raman spectra of hydroxyapophyllite-(K) and fluorapophyllite-(K) is the observation of two Raman bands in the O-H stretching region at ~ 3565 (due to the O-H stretching vibrations in H_2O) and 3625 cm^{-1} (due to the O-H stretching vibrations in OH) for the former and only one band at $\sim 3565\text{ cm}^{-1}$ for the latter. The observation of the Raman peak at $\sim 3625\text{ cm}^{-1}$ is regarded as a distinctive diagnostic feature indicating the presence of the OH group in the apophyllite-type structures (Ogorodova et al. 2019). The Raman spectrum of hydroxymcglassonite-(K) exhibits two major bands in the O-H stretching vibration region, consistent with that of

TABLE 5. Tentative assignments of major raman bands for hydroxymcglassonite-(K)

Bands (cm^{-1})	Assignment
3621	O-H stretching vibration in OH groups
3572	O-H stretching vibration in H_2O groups
940–1060	Si-O stretching vibrations in SiO_4 units
772, 861	H_2O libration
662, 635	Si-O-Si bending vibrations
430, 574	O-Si-O bending vibrations
160–321	Lattice modes and $B\text{-O}$ interaction vibrations

Note: $B = \text{Sr}^{2+} + \text{Ca}^{2+}$.

hydroxyapophyllite-(K), indicating the presence of both H_2O and OH groups in its structure.

IMPLICATIONS

Apophyllite-type minerals are of great industrial and technological interest because they are examples of naturally occurring single-sheet silicates and their reactions with chlorosilanes yield apophyllite-based organosilicate polymers on both sides of silicate sheets, which possess a unique combination of hydrophobic and hydrophilic properties that are highly tunable (Chao et al. 2001; Chen et al. 2007; Specht et al. 2010). According to the IMA-CNMNC guidelines for mineral nomenclature (Hatert et al. 2013), minerals of the apophyllite group are named based on the chemical formula $A^+ \text{Ca}_4\text{Si}_8\text{O}_{20}X^- \cdot 8\text{H}_2\text{O}$, where A^+ ($= \text{K}, \text{Na}, \text{Cs}, \text{or } \text{NH}_4$) and X^- ($= \text{F}$ or OH) are used as suffixes and prefixes (fluor for F and hydroxy for OH), respectively, in the naming. To date, there are five members in the apophyllite group: fluorapophyllite-(K), fluorapophyllite-(Na), fluorapophyllite-(NH_4), fluorapophyllite-(Cs), and hydroxyapophyllite-(K). The discovery of hydroxymcglassonite-(K), the first Sr-bearing member of the apophyllite group, suggests that more Sr-dominant members of the group may be found in nature or synthesized in laboratories. For naturally occurring Sr-dominant members, the same naming guidelines with A and X as suffixes and prefixes, respectively, should be employed.

The $\text{Sr}^{2+}\text{-Ca}^{2+}$ substitution in various minerals and materials has been a subject of numerous investigations because of its effects on the properties of luminescent materials (e.g., Yu et al. 2012; Misevicius et al. 2019; Wang et al. 2020), bioactive glasses (e.g., Martin et al. 2012; Pedone et al. 2021), and solid solutions (e.g., Gottschalk et al. 1998; Ellemann-Olesen and Malcherek 2005). In some cases, the $\text{Sr}^{2+}\text{-Ca}^{2+}$ substitution may result in incomplete solid solutions due to the difference in the Ca^{2+} and Sr^{2+} ionic radii ($r = 1.06$ Å for sevenfold-coordinated Ca^{2+} and 1.21 Å for Sr^{2+}) (Shannon 1976). There are two kinds of incomplete solid solutions. One of them is that the two end-members assume different structure symmetries, such as CaCO_3 ($R\bar{3}c$ calcite) vs. SrCO_3 ($Pmcn$ strontianite) or CaSO_4 ($Bmmb$ anhydrite) vs. SrSO_4 ($Pnma$ celestine). The other kind is that the two end-members possess the same symmetry, but it is different from that for the intermediate phases, as a consequence of the Ca^{2+} and Sr^{2+} ordering into different crystallographic sites. For example, in the system of $\text{Ca}_2\text{Mn}_3^{3+}\text{Si}_4\text{O}_{11}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ – $\text{Sr}_2\text{Mn}_3^{3+}\text{Si}_4\text{O}_{11}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (ruizite-strontioruizite), the two end-members have the same $C2$ symmetry, but the intermediate phase with the $\text{Ca}:\text{Sr} \approx 1:1$, ideally $\text{SrCaMn}_3^{3+}\text{Si}_4\text{O}_{11}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (taniajacoite), exhibits the $C1$ symmetry due to the preferential occupation of Sr^{2+} and Ca^{2+} over two distinct, sevenfold-coordinated sites (Yang et al. 2021). Since both hydroxyapophyllite-(K), $\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{OH}) \cdot 8\text{H}_2\text{O}$, and hydroxymcglassonite-(K), $\text{KSr}_4\text{Si}_8\text{O}_{20}(\text{OH}) \cdot 8\text{H}_2\text{O}$, have the same symmetry

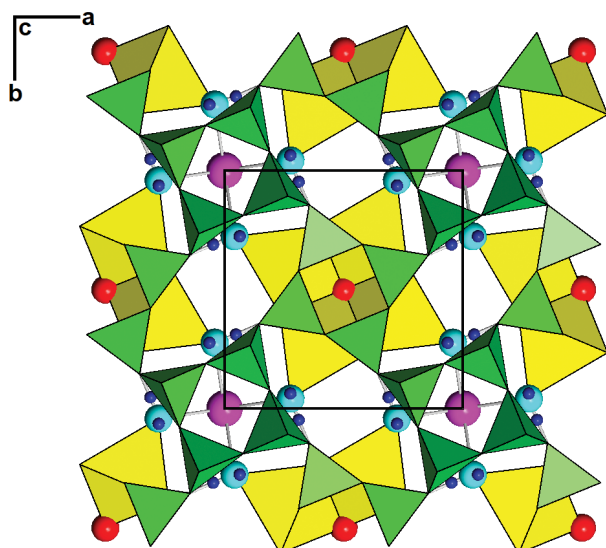


FIGURE 6. Crystal structure of hydroxymcglassonite-(K). SiO_4 tetrahedra and Sr-dominant polyhedra are green and yellow, respectively. The K, O4 (H_2O), O5 (OH), and H atoms are shown as large purple, medium aqua, medium red, and small blue spheres, respectively. Thin black lines show the unit cell. (Color online.)

P4/mnc, it then begs the question whether the intermediate phase, $K(Sr_2Ca_2)Si_8O_{20}(OH) \cdot 8H_2O$, possesses the same symmetry as the two end-members. In other words, could Sr^{2+} and Ca^{2+} in the intermediate phase be ordered into two distinct sites, as in taniajacoite, thus resulting in a reduction in the structure symmetry? Interestingly, Matsueda et al. (1981) reported that fluorapophyllite-(Na), $NaCa_4Si_8O_{20}F \cdot 8H_2O$, exhibits the orthorhombic symmetry *Pnmm*, rather than the tetragonal symmetry *P4/mnc* as for fluorapophyllite-(K). They ascribed this symmetry reduction to the silicate-sheet distortion caused by the substitution of small Na^+ for large K^+ . As a consequence, the eightfold position (*8h* with the site symmetry *m*) occupied by Ca^{2+} in the *P4/mnc* structure splits into two fourfold positions (*4g* with the site symmetry *m*), Ca1 and Ca2, in the *Pnmm* structure. An examination of the fluorapophyllite-(Na) structure (Matsueda et al. 1981) reveals that, although both Ca1 and Ca2 sites are still sevenfold-coordinated, as in fluorapophyllite-(K), the Ca1 site is significantly larger than the Ca2 site, with $\langle Ca1-(O,F) \rangle = 2.426 \text{ \AA}$ vs. $\langle Ca2-(O,F) \rangle = 2.367 \text{ \AA}$. This observation suggests that the apophyllite-type structure is intrinsically capable of assuming an ordered orthorhombic *Pnmm* structure with the Ca1 and Ca2 sites occupied by two different B^{2+} cations. Thus, we cannot rule out the possibility that the intermediate phase between hydroxyapophyllite-(K) and hydroxymcglossonite-(K) could possess an ordered structure with large Sr^{2+} and small Ca^{2+} occupying two distinct sites, such as the Ca1 and Ca2 sites in fluorapophyllite-(Na) (Matsueda et al. 1981).

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