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KAMPFITE, A NEW BARIUM SILICATE CARBONATE MINERAL SPECIES FROM FRESNO COUNTY, CALIFORNIA

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ABSTRACT

Kampfite, ideally $Ba_6[(Si,Al)O_2]_8(CO_3)_2Cl_2(Cl,H_2O)_2$, is a newly identified mineral species found in barium-silicate-rich deposits at Big Creek and Rush Creek, Fresno County, California. It forms irregular masses up to 10 mm in size enclosed in quartz-rich portions of the sanbornite-bearing rock. It is light blue-grey, with one perfect cleavage on {001}. Other physical properties are: brittle, translucent, nonfluorescent, vitreous luster, white streak, hardness 3, uneven fracture. Kampfite is uniaxial negative, ω 1.642(2), ε 1.594(2), nonpleochroic. It is hexagonal, with unit-cell parameters refined from powder data: a 5.244(2), c 29.83(1) Å, V 710.5(4) Å^3, and $Z = 1$. The strongest seven lines of the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are: 14.67(100)(002), 3.883(100)(104), 3.357(50)(106), 2.988(60)(0010), 2.887(50)(108), 2.616(70)(110), and 1.969(50)(1110). Precession photographs show that possible space-groups are $P6_3/mmc$, $P62c$, $P6_3mc$, $P\,3_1c$ and $P3_1c$. The empirical formula of kampfite (based on the average of three electron-microprobe analyses, normalized on 26 anions) is: $(Ba_{5.83}Na_{0.04}Ca_{0.02})_{\Sigma 5.89}[(Si_{5.18}Al_{2.36})_{\Sigma 7.54}O_{15.08}](CO_3)_2Cl_2[(H_2O)Cl_{0.45}]_{\Sigma 1.45}$. The calculated density is 3.51 g/cm^3. All crystals studied contain inclusions or are multiple. Thus, it was not possible to unambiguously determine the correct space-group or precise details of the structure. However, the preliminary results show that the structure is based on double layers of tetrahedra, $[T_4O_8]_\infty$, consisting of six-membered rings, with three layers of Ba polyhedra connecting the layers of tetrahedra. Kampfite is part of the monteregianite-(Y) – wickenburgite series (Strunz classification) and is structurally and chemically similar to cymrite. The mineral name honors Anthony R. Kampf, Los Angeles County Museum of Natural History, for his many significant contributions to the study of new and rare minerals.

Keywords: kampfite, new mineral species, barium chloride silicate carbonate hydrate, X-ray data, electron-microprobe data, Big Creek, Rush Creek, Fresno County, California.

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SOMMAIRE

La kampfite, dont la formule idéale serait $Ba_6[(Si,Al)O_2]_8(CO_3)_2Cl_2(Cl,H_2O)_2$, est une espèce minérale récemment identifiée dans les indices enrichis en silicates de barium à Big Creek et Rush Creek, dans le comté de Fresno, en Californie. Elle forme des masses irrégulières atteignant 10 mm que renferment les parties riches en quartz d'une roche à sanbornite. Elle est bleu–gris pâle, avec un clivage parfait sur {001}. De plus, elle est cassante, translucide, non fluorescente, à éclat vitreux, à rayure blanche, ayant une dureté de 3 et une fracture inégale. La kampfite est uniaxe négative, ω 1.642(2), ε 1.594(2), non pléochroïque. Elle est hexagonale, avec les paramètres réticulaires suivants affinés à partir d'un spectre de diffraction sur poudre: *a* 5.244(2), *c* 29.83(1) Å, *V* 710.5(4) $Å^3$, et *Z* = 1. Les sept raies les plus intenses de ce spectre [*d* en Å(*I*)(*hkl*)] sont: 14.67(100)(002), 3.883(100)(104), 3.357(50)(106), 2.988(60)(0010), 2.887(50)(108), 2.616(70)(110), et 1.969(50)(1110). Les clichés de précession montrent que les groupes spatiaux suivants sont possibles: $P6_3/mmc$, $P62c$, $P6_3mc$, $P3_1c$ et $P3_1c$. La formule empirique de la kampfite (moyenne des résultats de trois analyses à la microsonde électronique, normalisés sur une base de 26 anions) est: $(Ba_{5.83}Na_{0.04}Ca_{0.02})_{\Sigma 5.89}[(Si_{5.18}Al_{2.36})_{\Sigma 7.54}O_{15.08}](CO_3)_2Cl_2[(H_2O)Cl_{0.45}]_{\Sigma 1.45}$. La densité calculée est égale à 3.51 g/cm^3. Tous les cristaux étudiés contiennent des inclusions ou sont multiples. Ainsi, il ne nous a pas été possible d'établir le groupe spatial sans ambiguïté ou les détails précis de la structure. Toutefois, les résultats obtenus montrent que la structure est faite de couches doubles de tétraèdres, $[T_4O_8]_\infty$, contenant des anneaux à six membres, avec trois niveaux de polyèdres à barium assurant la connexion entre les couches de tétraèdres. La kampfite fait partie de la série montérégianite-(Y) – wickenburgite (classification de Strunz), et elle est semblable à la cymrite tant du point de vue structural que chimique. Le nom honore Anthony R. Kampf, du Los Angeles County Museum of Natural History, et reconnait ainsi ses contributions importantes à l'étude des minéraux rares et de nouvelles espèces.

(Traduit par la Rédaction)

Mots-clés: kampfite, nouvelle espèce minérale, silicate carbonaté chloruré hydraté de barium, données de diffraction X, données de microsonde électronique, Big Creek, Rush Creek, comté de Fresno, Californie.

INTRODUCTION

Kampfite was discovered by one of us (REW) in 1964 at the Esquire #1 claim, Rush Creek, eastern Fresno County, California (NE¼ NW¼ Section 16, T11S, R25E, Mount Diablo Meridian, lat. 37° 05' N, long. 119° 16' 20" W). The mineral occurs as irregular masses up to 1 cm across enclosed in a steeply dipping quartz–sanbornite outcrop exposed for 3 m^2 along a steep hill overlooking Rush Creek. Associated minerals at the type locality include celsian, fresnoite, macdonaldite, pyrrhotite, titantaramellite, traskite, witherite, and two new minerals, UKBC–10, a Ba–Fe–Al–Cl silicate related to cerchiaraite (Basso *et al.* 2000) and UKRC–21, a hydrated form of SiO_2. Small inclusions of celsian, witherite and UKBC–10 have been identified within kampfite. Rare grains of kampfite have been identified at the Esquire #7 claim along Big Creek, Fresno County, California (SE¼ SE¼ Section 27, T11S, R25E, Mount Diablo Meridian, lat. 36° 56' 40" N, long. 119° 14' 28" W). The Big Creek site is the type locality for alforsite, bigcreekite and walstromite, and is known for a number of rare Ba-bearing minerals including anandite, bazirite, benitoite, celsian, gillespite, fresnoite, macdonaldite, muirite, pellyite, titantaramellite and verplanckite (Alfors *et al.* 1965, Alfors & Pabst 1984, Basciano *et al.* 2001). Additional minerals currently under study from the Big Creek locality include UKBC–10, UKBC–27, a Ba–Fe–Ca–Mn silicate–phosphate, and minerals UKBC–39a and 39b, the Fe–Cl analogues of ericssonite and orthoericssonite, respectively. Our eventual aim is to completely characterize the mineralogy of the Rush Creek and Big Creek occurrences and to draw conclusions regarding the paragenesis of Ba-bearing minerals.

The Big Creek and Rush Creek deposits consist of gneissic rocks composed of variable amounts of sanbornite and quartz with minor amounts of diopside, pyrrhotite and various Ba-bearing minerals. The rocks form conformable tabular bodies up to 13 m thick within foliated quartzite at or within 100 m of the contact with a granodiorite pluton (Alfors *et al.* 1965). They probably began as sediments of Paleozoic age that were metamorphosed prior to being uplifted to their present position. The mineral assemblages within the rocks are most likely related to the initial bulk chemical composition of the sediments prior to metamorphism. Hinthorne (1974) suggested that sanbornite was formed by the reaction of witherite with quartz, and that the sanbornite–quartz rocks formed at temperatures between 440 and 600°C. On the basis of textures observed in thin section, we believe that kampfite formed prior to both sanbornite and quartz, but the lack of Fe in the chemical formula suggests that it formed later than titantaramellite, traskite and UKBC–10.

Kampfite is named after Anthony Robert Kampf (b. 1948), Curator and Section Head of Minerals, Los Angeles County Museum of Natural History, for his many significant contributions to the crystallographic study of new and rare minerals. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA. Cotype material is housed in the M.Y. Williams Museum at the University of British Columbia, Vancouver, British Columbia, and in the Systematic Reference Series of the National Mineral Collection of Canada, Geological Survey of Canada, Ottawa, Ontario (NMCC 68090).

PHYSICAL AND OPTICAL PROPERTIES

Kampfite is light blue-grey and has a well-developed cleavage on {001} (Fig. 1). The cleavable masses are brittle, translucent, nonfluorescent and have a vitreous luster, uneven fracture and a white streak. Kampfite has an approximate Mohs hardness of 3 and a calculated density (on the basis of the empirical formula and cell dimensions derived from the X-ray powder-diffraction study) of 3.51 g/cm^3. The density of kampfite could not be measured directly owing to the presence of numerous inclusions of UKBC–10, celsian and witherite.

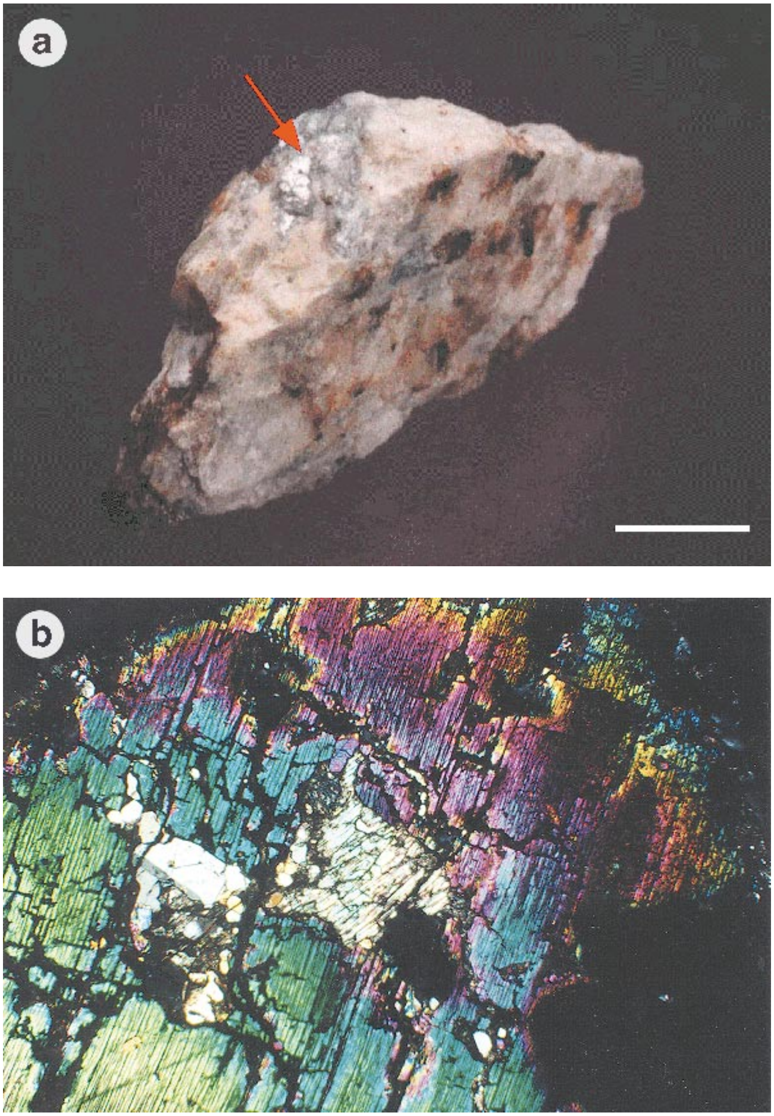

FIG. 1. (a) A mass of kampfite in quartz–sanbornite-bearing rock. The scale bar is 1 cm in length. (b) Photomicrograph of kampfite (center of field, third-order interference colors). The large surrounding grain with second-order interference colors is sanbornite; the grain to the left with first-order white–grey interference colors is celsian. Polarized light; the field of view is 5.1 mm.

Kampfite is uniaxial negative, with indices of refraction ω 1.642 ± 0.002 and ε 1.594 ± 0.002 (measured at 589 nm). The mineral is nonpleochroic, and extinction is parallel to the {001} cleavage. One grain is biaxial negative with $2V_{\mathrm{meas}}$ of 20(5)° and indices of refraction α 1.641 ± 0.001, β 1.642 ± 0.001, γ_{calc} 1.642, slight dispersion, $r < v$; at present we regard this as anomalous and not representative of the mineral. Application of the Gladstone–Dale relationship (Mandarino 1981) gives a compatibility index of –0.059, which is considered to be fair.

CHEMICAL COMPOSITION

Chemical analyses were performed on a JEOL 733 electron microprobe with Tracor Northern 5500 and 5600 automation, operated in the wavelength-dispersion mode with the following conditions: excitation voltage 15 kV, beam current 20 nA and beam diameter 30 μm. Data on standards were collected for 50 s or to 0.25% precision (4σ level), whichever was attained first; data on kampfite were collected for 25 s or to 0.5% precision, whichever was attained first. An element was considered to be observed only if it is significant at the 4σ (measured) level. The following standards were used: albite (Na*K*α), almandine (Al*K*α), sanbornite (Si*K*α, Ba*L*α), marialite (Cl*K*α), and diopside (Ca*K*α). F, Mg, Sc, Mn, Fe, and Sr were sought but not detected. Data reduction was performed with a PAP routine in XMAQNT (pers. commun., C. Davidson, CSIRO). The results of the electron-microprobe study are given in Table 1. On the basis of 26 anions (derived from the crystal-structure study), the empirical formula $(\mathrm{Ba}_{5.83}\mathrm{Na}_{0.04}\mathrm{Ca}_{0.02})_{\Sigma 5.89}[(\mathrm{Si}_{5.18}\mathrm{Al}_{2.36})_{\Sigma 7.54}\mathrm{O}_{15.08}](\mathrm{CO}_3)_2\mathrm{Cl}_2[(\mathrm{H_2O})\mathrm{Cl}_{0.45}]_{\Sigma 1.45}$ was calculated from an average of three analyses. The ideal formula for kampfite is $\mathrm{Ba}_6[(\mathrm{Si,Al})\mathrm{O}_2]_8(\mathrm{CO}_3)_2\mathrm{Cl}_2(\mathrm{Cl,H_2O})_2$.

The presence of H_2O and CO_2 was confirmed by micro-infrared-absorption spectroscopy. The infrared-absorption spectrum of kampfite, shown in Figure 2, was obtained using a Bomem Michelson MB–120 Fourier-transform spectrometer with a diamond-anvil cell microsampling device. The spectrum shows a small sharp peak at 1648 cm^{-1} due to H–O–H bending and a broad shallow peak centered at 3421 cm^{-1} due to O–H stretching, thus confirming the presence of H_2O molecules in the structure. In addition, the spectrum shows very large sharp peaks at 982 and 1436 cm^{-1} and a small sharp peak at 1758 cm^{-1}, confirming the presence of CO_3 groups in the structure.

TABLE 1. CHEMICAL COMPOSITION OF KAMPFITE

	Average	Ideal**		Average	Ideal**
SiO_2	20.14	20.47	Si^{4+}	5.18	5.33
Al_2O_3	7.76	8.70	Al^{3+}	2.36	2.67
CO_2*	5.69	5.63	C^{4+}	2.00	2.00
BaO	57.72	58.79	Ba^{2+}	5.83	6.00
CaO	0.06	0.00	Ca^{2+}	0.02	0.00
Na_2O	0.08	0.00	Na^+	0.04	0.00
Cl	5.60	6.80	Cl^-	2.45	3.00
H_2O*	1.16	1.15	H^+	2.00	2.00
O=Cl	-1.26	-1.53	O^{2-}	23.56	24.17
TOTAL	96.95	100.00			

Note: Average is of three analyses. Analyses are normalized on 26 anions assuming two C atoms per formula unit. *Determined by stoichiometry. **Calculated for Si:Al = 2:1, three Cl and one H_2O per formula unit, based on crystal-structure study.

X-RAY CRYSTALLOGRAPHY

Precession single-crystal photographs showed that kampfite is hexagonal, with approximate unit-cell dimensions *a* 5.25, *c* 29.8 Å. Possible space groups are $P6_3/mmc$, $P62c$, $P6_3mc$, $P3_1c$ and $P3_1c$. Unit-cell parameters refined using X-ray powder-diffraction data (Table 2) are *a* 5.244(2), *c* 29.83(1) Å, *V* 710.5(4) Å^3, *c*/*a* 5.6884. A significant amount of time was spent locating an inclusion-free crystal for structure determination. A full sphere of intensity data was collected using a Siemens *P*4/CCD diffractometer at the University of Manitoba. The structure was solved and refined in each of the space groups indicated by the precession single-crystal photographs. The best results were obtained for space group $P6_3mc$. However, the bond lengths in this case depart rather seriously from expected values and lack internal coherency. Careful inspection of the crystal under a polarizing microscope showed that it is likely

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR KAMPFITE

I_{est}	d_{meas}	d_{calc}	*hkl*	I_{est}	d_{meas}	d_{calc}	*hkl*
100	14.67	14.917	002	*10	1.864	1.865	$00\underline{16}$
20	7.468	7.459	004	5	1.806	1.807	$20\underline{10}$
20	4.535	4.541	100	5	1.725	1.725	$10\underline{16}$
		4.490	101	3	1.713	1.716	210
30	4.343	4.345	102			1.714	211
15	4.123	4.131	103	*20	1.672	1.673	214
*100	3.883	3.879	104	1	1.653	1.650	215
5	3.731	3.729	008	*10	1.621	1.622	216
*15	3.619	3.614	105	1	1.593	1.592	217
*50	3.357	3.353	106			1.559	218
*15	3.113	3.108	107	40	1.557	1.557	$10\underline{18}$
*60	2.988	2.983	$00\underline{10}$			1.554	$20\underline{14}$
*50	2.887	2.882	108	*15	1.516	1.514	300
5	2.675	2.677	109	10	1.489	1.492	$00\underline{20}$
*70	2.616	2.622	110			1.489	$21\underline{10}$
5	2.582	2.582	112	1	1.444	1.450	$21\underline{11}$
40	2.495	2.494	$10\underline{10}$			1.441	$20\underline{16}$
		2.486	$00\underline{12}$	3	1.415	1.417	$10\underline{20}$
5	2.330	2.329	$10\underline{11}$	15	1.402	1.413	$21\underline{12}$
*20	2.272	2.271	200			1.403	308
1	2.242	2.245	202			1.401	$11\underline{18}$
1	2.216	2.214	203	1	1.372	1.374	$21\underline{13}$
*40	2.176	2.172	204	*10	1.350	1.350	$30\underline{10}$
*30	2.144	2.145	118	15	1.337	1.339	$20\underline{18}$
*20	2.063	2.065	206			1.337	$21\underline{14}$
1	2.005	2.004	207	*10	1.311	1.311	220
*50	1.969	1.969	$11\underline{10}$	*15	1.296	1.297	$11\underline{20}$
*30	1.930	1.929	$10\underline{14}$				

Note: Data collected using a 114.6 mm Debye-Scherrer powder camera, Cu radiation, Ni filter (λ Cu*K*α = 1.54178 Å), visually estimated intensities; not corrected for shrinkage and no internal standard; indexed with *a* 5.244, *c* 29.83 Å. *Reflections used for unit-cell refinement.

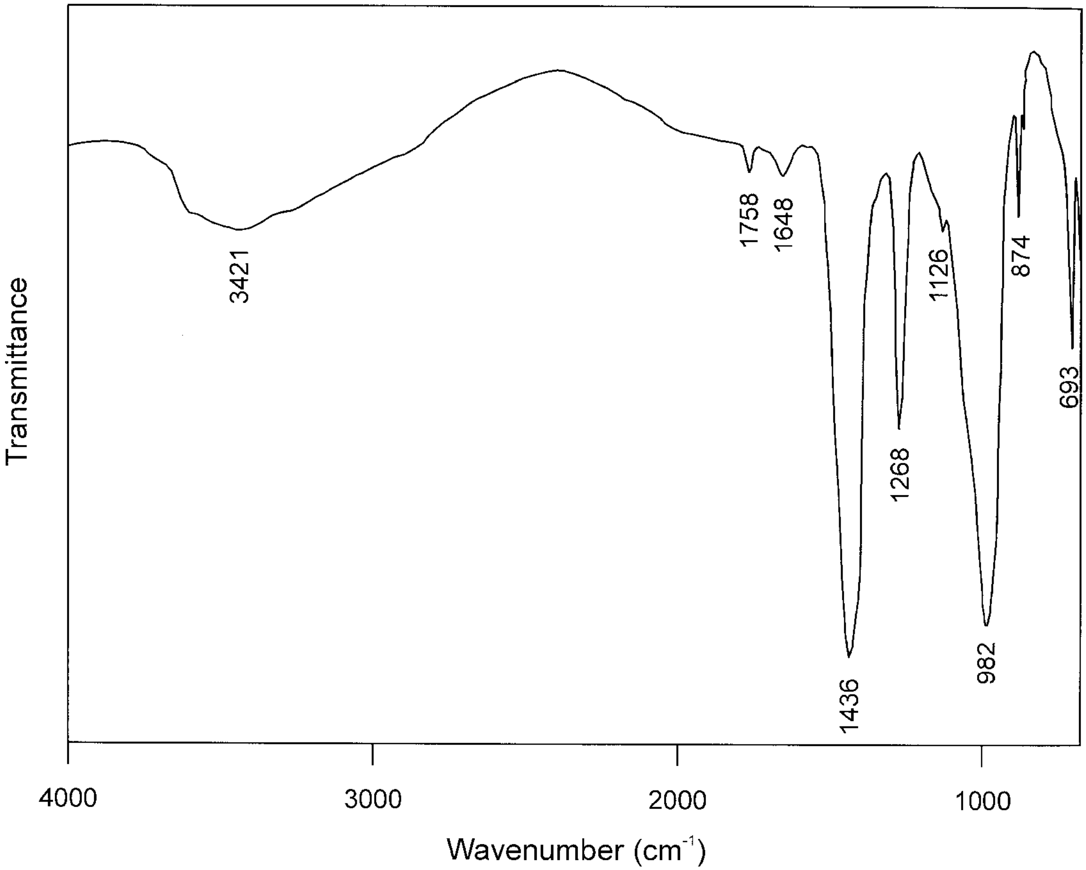

FIG. 2. Infrared-absorption spectrum of kampfite.

composed of two non-twinned individuals, and this is the most probable reason for the poor quality of the data. Although it was not possible to determine the correct space-group or precise details of the crystal structure, the results of the crystal-structure study show that kampfite is a sheet silicate. The main structural feature is the unbranched single layer $\{\boldsymbol{uB}, 1^2{}_\infty\}[T_2O_5]$ (Liebau 1985) of six-membered rings, which is typical for the mica group of minerals. In kampfite, however, pairs of polar sheets are joined *via* apical O atoms to form unbranched *zweier* double layers $\{\boldsymbol{uB}, 2^2{}_\infty\}[T_4O_8]$ (Liebau 1985) oriented parallel to (001).The layers of SiO_4 tetrahedra are connected by three layers of Ba polyhedra. Edge-sharing Ba(2) polyhedra form sheets that are bonded by O(2) atoms to the tetrahedra pointing along [001]. Edge-sharing Ba(3) polyhedra form sheets that are bonded by O(1) atoms to the tetrahedra pointing along [001], and Ba(1) polyhedra are located between the sheets of Ba(2) and Ba(3) polyhedra. Sheets of Ba(2) and Ba(3) polyhedra are bonded by Cl(1) atoms along [001] with Ba(1) atoms occupying the spaces between them. The H_2O molecules are located in spaces between Ba(2) polyhedra and Ba(3) polyhedra. The layering of SiO_4 tetrahedra and Ba polyhedra is responsible for the perfect {001} cleavage of kampfite.

DISCUSSION

The only other known barium silicate carbonate mineral is fencooperite, $Ba_6Fe^{3+}{}_3Si_8O_{23}(CO_3)_2Cl_3{\bullet}H_2O$ (Roberts *et al.* 2001). The crystal structure of fencooperite also contains layers of SiO_4 tetrahedra, but these do not form continuous double sheets as in kampfite; instead, they form Si_8O_{22} islands of double open-branched triple-branched tetrahedra (Grice 2001).

Kampfite belongs to Dana class 78.1 (unclassified silicates) and is part of VIII/H.38, the monteregianite-(Y) – wickenburgite series [phyllosilicates (layered) mica minerals with double layers of tetrahedra and related structures] in the Strunz system of classification.

The unbranched *zweier* double layers in kampfite have also been described for high-temperature phases of feldspar composition: Ca$[AlSiO_4]_2$ (hT) (Takéuchi & Donnay 1959), Sr$[AlSiO_4]_2$ (hT) and Pb$[AlSiO_4]_2$ (hT) (Pentinghaus 1975), Ba$[AlSiO_4]_2$ (hT) (Takéuchi 1958) and Rb$[AlSi_3O_8]$ (hT) (Sorrel & Negas 1963). They have also been described for the minerals cymrite, Ba$[AlSiO_4]_2$•H_2O (Drits *et al.* 1975, Bolotina *et al.* 1991), vertumnite, $Ca_8Al_4(Al_4Si_5)O_{12}(OH)_{36}$•$10H_2O$ (Galli & Passaglia 1978) and strätlingite, $Ca_8Al_4(Al_4Si_4)O_8(OH)_{40}$•$10H_2O$ (Rinaldi *et al.* 1990).

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