

Diegogattaite, $\text{Na}_2\text{CaCu}_2\text{Si}_8\text{O}_{20}\cdot\text{H}_2\text{O}$: a new nanoporous copper sheet silicate from Wessels Mine, Kalahari Manganese Fields, Republic of South Africa

M. S. RUMSEY^{1,*}, M. D. WELCH¹, A. R. KAMPF² AND J. SPRATT³

¹ Mineral and Planetary Sciences Division, Department of Earth Sciences, Natural History Museum, Cromwell Road, London SW7 5BD, UK

² Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, USA

³ Image and Analysis Centre, Department of Facilities, Natural History Museum, Cromwell Road, London SW7 5BD, UK

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ABSTRACT

Diegogattaite (IMA2012-096), $\text{Na}_2\text{CaCu}_2\text{Si}_8\text{O}_{20}\cdot\text{H}_2\text{O}$, is a new mineral from the Wessels mine in the Kalahari manganese fields of South Africa. It occurs as a minor phase with other copper-bearing silicates, Cu-rich pectolite, sugilite, quartz, aegirine and undifferentiated Fe-Mn oxides. Diegogattaite is pale turquoise through teal blue. It is found as sub-mm sized grains in a main crystalline patch 3–4 mm in size, and is currently known from only one sample. The mineral is transparent with a vitreous lustre and may have a good cleavage on $\{001\}$. It is brittle, with an uneven fracture and a very pale-blue streak. It is non-fluorescent in short- and long-wave UV light and has an estimated Mohs hardness of ~5–6. Diegogattaite is biaxial (–), $\alpha = 1.598(2)$, $\beta = 1.627(2)$, $\gamma = 1.632(2)$; $2V_{\text{meas}} = 44.0(6)^\circ$, $2V_{\text{calc}} = 44.5^\circ$; dispersion: strong $r < v$, orientation: $X = b$, $Y \approx \perp(001)$, $Z \approx a$; pleochroism X colourless $\ll Y \approx Z$ blue green. The calculated density is 3.10 g/cm^3 . Electron-microprobe analysis gave: Na₂O 8.07, CaO 7.3, CuO 20.5, FeO 0.36, SiO₂ 62.4, H₂O_(calc) 2.34, total 100.97 wt.%. A charge-balanced formula on the basis of 21 oxygen a.p.f.u. is: $\text{Na}_{2.00}\text{Ca}_{1.00}\text{Cu}_{1.98}\text{Fe}_{0.04}\text{Si}_{7.99}\text{H}_2\text{O}_{21}$. Diegogattaite is monoclinic, space group $C2/m$, $a = 12.2439(6) \text{ \AA}$, $b = 15.7514(4) \text{ \AA}$, $c = 10.6008(3) \text{ \AA}$, $\beta = 125.623(2)^\circ$, $V = 1661.87(10) \text{ \AA}^3$ and $Z = 4$. The five strongest lines in the X-ray powder pattern are [d_{obs} in \AA ($I_{\text{obs}}(hkl)$): 4.25(75)(002, $\bar{2}22, 220$), 3.951(77)(040), 3.261(100)($\bar{1}31, \bar{1}13$), 2.898(89)(042, $\bar{4}03, 003$), 2.332(66)(331, $\bar{4}43, \bar{2}62, 260, 043$). The crystal structure of diegogattaite was determined by single-crystal X-ray diffraction to final agreement indices of $R_1 = 0.027$, $wR_2 = 0.071$ and $\text{GoF} = 1.090$. It represents a completely new silicate topology based upon a double-sheet of SiO₄ tetrahedra composed of connected $6^4 8^2$ cages. The structure of diegogattaite is related to those of synthetic nanoporous Na-Cu-Si-O-(OH)-H₂O (CuSH) compounds, which are of interest to the solid-state chemistry community as potential ion-exchangers, catalysts and molecular sieves. The structure of diegogattaite forms a bridge between these structures and those of the gillespite-group minerals, including wesselsite. The close spatial association of wesselsite and diegogattaite suggests a possible reaction between them that may point to a synthetic route for the production of novel alkaline-earth-based nanoporous copper silicates.

KEYWORDS: Diegogattaite, $\text{Na}_2\text{CaCu}_2\text{Si}_8\text{O}_{20}\cdot\text{H}_2\text{O}$, new mineral, nanoporous sheet silicate, $6^4 8^2$ cage, synthetic CuSH phases, Wessels mine, South Africa.

Introduction

* E-mail: m.rumsey@nhm.ac.uk
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DIEGOGATTAITE was discovered during routine verification of rare species using both energy-

dispersive (EDX) and X-ray diffraction (XRD) analysis, which is standard curatorial protocol at the Natural History Museum (NHM) in London, UK. It was found on a specimen obtained as effenbergerite and was investigated because of its subtly different colouration from the dominant blue mass of this mineral. It is of note that the 'effenbergerite' was actually determined to be its Sr-analogue, wesselsite, $\text{SrCuSi}_4\text{O}_{10}$. The discovery of diegogattaite alongside the incorrectly identified effenbergerite highlights the importance of a well resourced museum, with a systematically maintained reference collection, as well as the investment of time in routine and speculative identification of mineral species.

Diegogattaite is named in honour of Giacomo Diego Gatta (*b.* 1974), Professor of Mineral Sciences in the Department of Earth Sciences, University of Milan, Italy. Professor Gatta has published extensively on the structures and crystal chemistry of zeolites and related silicates with cage structures, which are of wide mineralogical and technological interest. Both the new mineral and mineral name, have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2012-096). The holotype material is registered as BM 2012,2, housed at the NHM and consists of the original specimen and two fragments removed from it, one mounted for single-crystal study and the other embedded into a microprobe block (P18313) for chemical study. A few other tiny separated fragments exist for future destructive research.

Occurrence

The specimen used in this study was obtained during the Tucson mineral show in February of 2012. It was labelled originally as 'effenbergerite' from the Wessels mine and was part of a small suite of specimens that were brought to the US for the commercial mineral market at the Tucson show. Before its acquisition by the NHM, the specimen was part of a specimen about twice the size, which was split in two, the other half currently resides in a private collection in the US. It is likely that more specimens from the suite also contain diegogattaite. Specimens from this find have also yielded the new minerals scottyite, $\text{BaCu}_2\text{Si}_2\text{O}_7$, (Yang *et al.*, 2013) and lavinskyite, $\text{K}(\text{LiCu})\text{Cu}_6\text{Si}_8\text{O}_{22}(\text{OH})_4$, (Yang *et al.*, 2012). The suite of minerals originated from the central-eastern ore-body of the Wessels mine (27°12'S, 22°58'E) in the Kalahari Manganese

fields, Northern Cape Province, Republic of South Africa. The 'Wessels type' orebody that is mined here has been altered hydrothermally to produce a more diverse mineral assemblage compared with the other mines in the region (Gutzmer and Beukes, 1996). It is thought that the orebody formed in the temperature range 300–400°C and at a maximum lithological pressure of 0.05–0.1 GPa (Gutzmer and Beukes, 1996). More information on the geology of the Kalahari manganese fields can be found in Kleyenstuber (1984), and Gutzmer and Beukes (1996).

Diegogattaite is disseminated in areas of wesselsite and is found irregularly dispersed across specimen BM2012,2. Associated minerals include wesselsite, aegirine, Cu-rich pectolite, sugilite, quartz and undifferentiated Fe-Mn-oxides. Other minerals reportedly found in the same assemblage (Yang *et al.*, 2013) include scottyite, lavinskyite and richterite.

Physical and optical properties

Diegogattaite occurs sparingly in the bright blue wesselsite-rich areas of specimen BM2012,2 (Fig. 1). It is observed in a main patch with a massive habit ~3 mm in diameter and as a number of sub-millimetre aggregates nearby. Scanning electron microscopy (SEM) and optical imaging indicate that some of the blue colouration in hand specimen is due to bounding rims of barium-rich wesselsite surrounding diegogattaite rather than diegogattaite proper, which is a pale 'teal' blue colour. In probe-section, the diegogattaite is seen to enclose tiny grains of Cu-rich pectolite and is in close association with aegirine, as well as blue Ba-rich wesselsite. Due to the massive crystalline nature of the specimen, there are no cavities that contain well formed crystals of diegogattaite.



FIG. 1. A portion of the hand specimen from which the holotype crystal was taken. The circled area encloses the main diegogattaite aggregate, showing that its slight 'teal' colour is very difficult to distinguish from the cobalt blue wesselsite. The image width is 10 cm.

Consequently, forms are hard to assess, but tiny broken fragments appear platy and parallel fractures seen in section are interpreted as (001) cleavage. Individual crystal size is difficult to assess, but is probably <0.5 mm.

Diegogattaite is transparent, pale-blue with a vitreous lustre and a pale-blue streak. The hardness is estimated to be ~5–6 on the Mohs scale which was determined approximately using VHN methods. It is non-fluorescent in both short- and long-wave UV light. The new mineral is brittle with an uneven fracture and no obvious parting. The density could not be measured due to paucity of sample, but is calculated from the empirical formula and unit-cell volume determined by single-crystal XRD as 3.101 g/cm³.

Diegogattaite is optically biaxial (–) with refractive indices $\alpha = 1.598(2)$, $\beta = 1.627(2)$ and $\gamma = 1.632(2)$ measured in white light. The 2V angle determined from extinction data using *EXCALIBRW* (Gunter *et al.*, 2004) is 44.0(6)°; this compares closely with the calculated value of 44.5°. Strong $r < v$ dispersion was observed. The optical orientation is $X = b$, $Y \approx \perp(001)$, $Z \approx a$. The crystal is pleochroic: $X =$ colourless, Y and $Z =$ blue green; $Y \approx Z \gg X$. The Gladstone-Dale compatibility index (Mandarino, 1981) is -0.028 , in the range of excellent compatibility.

Chemical composition

A small fragment of specimen BM2012,2 measuring 0.4 mm × 0.3 mm × 0.3 mm was removed, mounted in epoxy and polished using aluminium oxide abrasive. The polished block was carbon-coated for analysis using a Cameca SX100 electron microprobe at the NHM. The analyses were conducted in wavelength-dispersive mode (WDS) with an accelerating potential

of 15 kV, probe current of 10 nA and a beam diameter of 10 µm. Greater currents and smaller spot sizes were tested, but resulted in the migration of lighter elements. The elements K, Ba, Sr, Ca, Cu, Si, Al and Fe were sought, but only Na, Ca, Cu, Si and Fe were above the detection limits. A PAP correction (Pouchou and Pichoir, 1988) was applied to the raw electron microprobe analysis (EMPA) data.

There is not enough material for the determination of H by CHN analysis; therefore, H₂O was calculated by stoichiometry based on the crystal-structure analysis. Analytical results obtained from 17 point analyses are given in Table 1. The empirical formula (based on 21 oxygen a.p.f.u. is Na_{2.00}Ca_{1.00}Cu_{1.98}Fe_{0.04}Si_{7.99}H₂O₂₁, corresponding very closely to the ideal formula Na₂CaCu₂Si₈O₂₀·H₂O.

Crystal structure

The crystal structure of diegogattaite is reported by Welch and Rumsey (2013), but its basic features are described here. Diegogattaite is monoclinic, space group *C2/m*, with unit-cell parameters determined by single-crystal XRD: $a = 12.2439(6)$ Å, $b = 15.7514(4)$ Å, $c = 10.6008(3)$ Å, $\beta = 125.623(2)^\circ$, $V = 1661.87(10)$ Å³ and $Z = 4$. Structure data acquired from a small single crystal (0.08 mm × 0.06 mm × 0.02 mm) provided a structure solution by direct methods and a refinement to final agreement indices of $R_1 = 0.027$, $wR_2 = 0.071$, $\text{GoF} = 1.090$ based upon 3418 independent reflections. The asymmetric unit contains three Na, one Ca, one Cu, four Si, twelve O and two H atoms. Refinement in *C2/m* gave by far the best resulting structure compared with space groups *Cm* or *C2* (see Welch and Rumsey, 2013). A CIF file and a

TABLE 1. Chemical data for diegogattaite obtained by EMPA analysis.

Constituent	Wt.%	Range	SD	Standards
Na ₂ O	8.07	7.90–8.21	0.09	Jadeite
CaO	7.3	7.0–7.56	0.15	Wollastonite
CuO	20.5	20.2–20.9	0.19	Copper
FeO	0.36	0.00–0.79	0.20	Fayalite
SiO ₂	62.4	62.2–62.7	0.15	Wollastonite
H ₂ O _(Calc)	2.34			
Total	100.97			

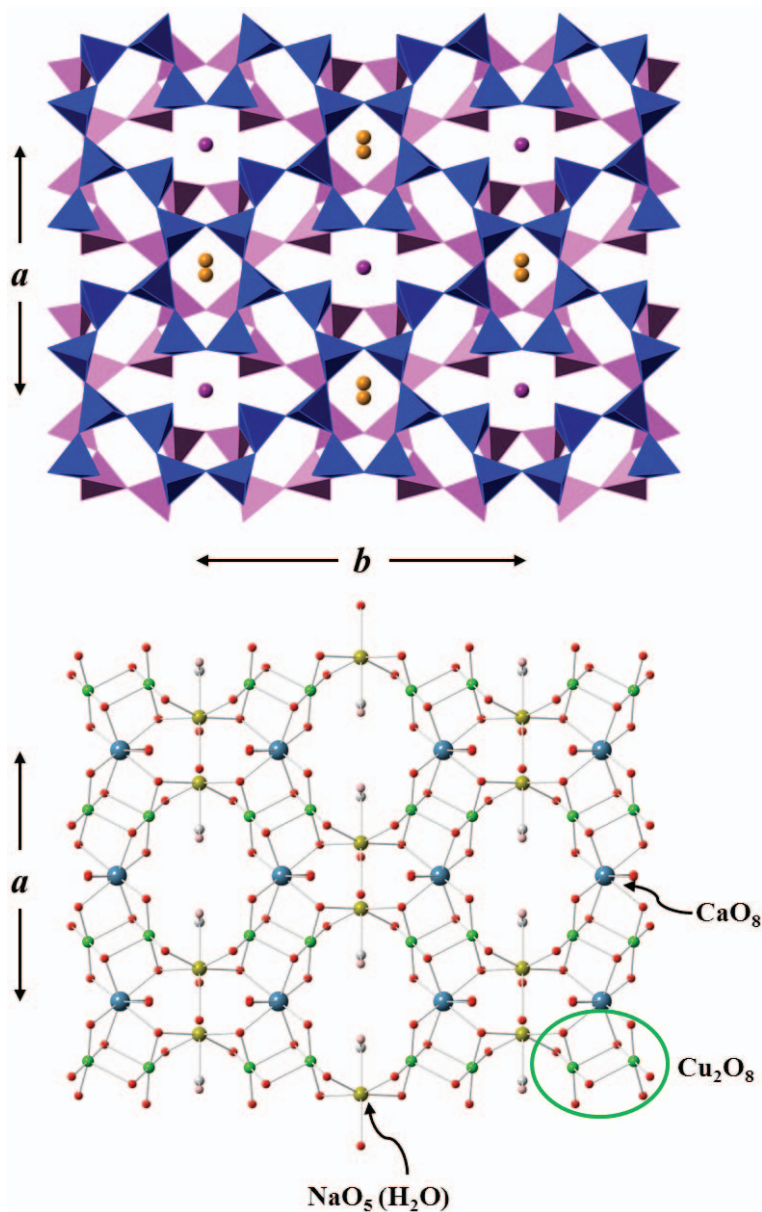


FIG. 2. *Upper diagram*: A view of the silicate double sheet of diegogattaite projected onto (001) and showing the two equivalent sub-sheets coloured differently to aid visualization of its construction and identification of the $6^4 8^2$ cages, of which four are shown here. The pairs of yellow atoms are the $\frac{1}{2}$ -occupied Na(1) sites, and the purple atom is Na(3). *Lower diagram*: A view of the non-silicate sheet of diegogattaite, projected onto (001), showing CaO₈, CuO₅ and NaO₅(H₂O) polyhedra. Ca = blue, Cu = green, Na(2) = yellow, oxygen = red. A pair of edge-sharing CuO₅ polyhedra forming a Cu₂O₈ dimer is circled at bottom-right. Four large cavities containing pairs of H₂O molecules bonded to Na(2) atoms are shown.

table of structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from: www.minersoc.org/pages/e_journals/dep_mat_mm.html.

The diegogattaite structure represents a new silicate topology (Figs 2 and 3) based on a double sheet of SiO_4 tetrahedra, parallel to (001), composed of connected 6^48^2 cages. A single cage is shown in Fig. 3a. Three non-equivalent Na atoms occupy very different coordination polyhedra. Na(1) and Na(3) atoms occupy cavities within the silicate double sheet. Na(1) is slightly displaced from the centre of the 6^48^2 cage in two half-occupied sites 0.77 Å apart. Na(3) lies at the centre of a large cavity between four nearby 6^48^2

cages and is coordinated by eight oxygen atoms in a slightly sheared cuboidal configuration, very much like that in sodium heptasilicate (Fleet, 1998). Na(2) forms a $\text{NaO}_5(\text{H}_2\text{O})$ octahedron located outside the double sheet. The Ca atom is eight-coordinated to oxygen in a distorted square-antiprism. Cu is five-coordinated by oxygen in a nearly perfect square-pyramidal geometry. Pairs of CuO_5 pyramids share an edge to form a Cu_2O_8 dimer. Single sheets of Cu, Ca and Na(2) polyhedra (Fig. 2) lie between the silicate double-sheets.

In addition to the 6^48^2 cage sites, diegogattaite has a large cavity occupied by two H_2O molecules, each bonded to a Na(2) atom, as

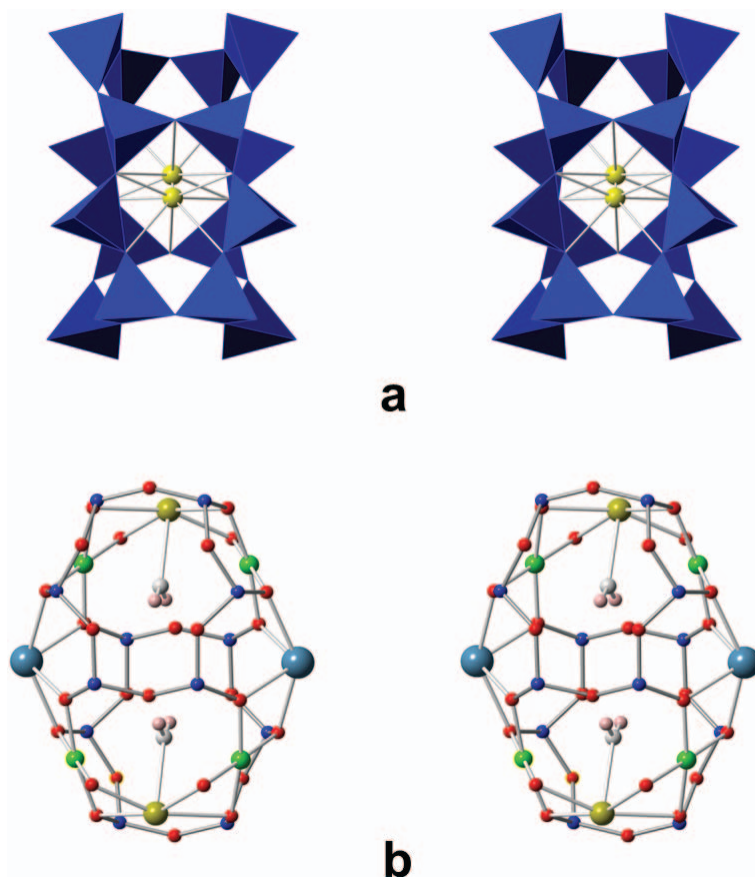


FIG. 3. (a) Stereo-pair of the 6^48^2 cage of diegogattaite projected onto (001). The two $\frac{1}{2}$ -occupied Na(1) sites 0.77 Å apart are shown in yellow. (b) Stereo-pair of the large H_2O -containing cavity of diegogattaite: O = red, Si = dark blue, Ca = blue-grey, Cu = green, Na(2) = yellow. Oxygen atoms lying outside the cavity are omitted for clarity. The cavity is bisected by a mirror plane $\parallel(010)$ in which the Na(2), O(12), H(1) and H(2) atoms lie. The view is slightly oblique, with the a axis being vertical, the b axis is almost in the plane of the paper and the c axis is rotated 5° to the left of the normal to the plane of the paper.

TABLE 2. X-ray powder diffraction data for diegogattaitite obtained by the Gandolfi method using the same crystal as that used in the structure determination.

I_{obs}	d_{obs}	d_{calc}	I_{calc}	$h k l$	I_{obs}	d_{obs}	d_{calc}	I_{calc}	$h k l$	I_{obs}	d_{obs}	d_{calc}	I_{calc}	$h k l$		
39	8.63	8.6170	76	0 0 1				2.3482	31	3 3 1				1.6208	7	1 5 4
		8.4138	13	1 1 0				2.3298	3	$\bar{4}$ 4 3				1.6120	5	$\bar{4}$ 4 6
15	7.87	7.8757	33	0 2 0	66	2.332		2.3248	30	$\bar{2}$ 6 2	12	1.6082		1.6012	3	$\bar{3}$ 9 1
31	6.16	6.1218	29	$\bar{2}$ 0 1				2.3219	3	2 6 0				1.5967	3	$\bar{7}$ 3 5
21	5.84	5.8134	33	0 2 1				2.3206	9	0 4 3				1.5823	8	$\bar{6}$ 6 2
		5.0050	20	$\bar{2}$ 0 2				2.2907	16	$\bar{3}$ 5 3	8	1.5840		1.5788	5	0 4 5
57	5.01	4.9763	14	2 0 0				2.2828	5	1 5 2				1.5684	3	2 8 2
		4.9281	7	1 1 1	10	2.237		2.2348	16	$\bar{5}$ 1 4				1.5560	5	$\bar{7}$ 1 6
		4.8334	4	$\bar{2}$ 1 1				2.2026	5	$\bar{5}$ 3 3	12	1.5511		1.5495	4	0·10·1
		4.3085	11	0 0 2				2.1948	8	1 7 0				1.5475	13	1 9 2
75	4.25	4.2242	31	$\bar{2}$ 2 2	27	2.187		2.1909	16	1 3 3				1.5407	5	$\bar{3}$ 7 5
		4.2069	21	2 2 0				2.1664	17	2 4 2				1.5305	3	$\bar{8}$ 0 4
77	3.951	3.9379	100	0 4 0				2.1543	3	0 0 4				1.5239	4	$\bar{7}$ 5 4
		3.8558	7	$\bar{3}$ 1 2				2.1073	4	$\bar{2}$ 6 3				1.5225	3	$\bar{7}$ 5 3
		3.7799	14	0 2 2				2.1030	19	2 6 1				1.5115	3	$\bar{6}$ 6 5
		3.6993	7	$\bar{1}$ 3 2				2.0882	13	4 0 1				1.5067	12	$\bar{6}$ 6 1
33	3.524	3.5133	58	2 0 1	64	2.079		2.0779	4	0 2 4				1.5060	4	$\bar{5}$ 1 7
		3.3118	9	$\bar{2}$ 4 1				2.0740	15	$\bar{5}$ 3 4				1.5053	6	$\bar{8}$ 0 3
100	3.261	3.2643	33	$\bar{3}$ 1 3				2.0659	24	$\bar{1}$ 7 2	59	1.5024		1.5025	6	$\bar{2}$ ·10·2
		3.2516	23	$\bar{1}$ 1 3				2.0406	4	$\bar{6}$ 0 3				1.4978	5	4 0 3
		3.2463	3	3 1 0				2.0282	7	2 0 3				1.4972	3	5 1 2
		3.2417	13	1 1 2				1.9754	7	$\bar{6}$ 2 3				1.4957	9	$\bar{5}$ 7 5
		3.2239	37	$\bar{2}$ 2 3				1.9712	3	$\bar{2}$ 2 5				1.4891	6	1 3 5
		3.1646	16	$\bar{3}$ 3 1	26	1.9731		1.9689	11	0 8 0				1.4860	3	$\bar{6}$ 0 7
		3.0948	15	$\bar{2}$ 4 2				1.9609	7	$\bar{3}$ 3 5				1.4797	13	$\bar{7}$ 5 5
54	3.098	3.0880	61	2 4 0				1.9518	4	3 3 2				1.4758	3	$\bar{7}$ 5 2
		3.0034	3	1 5 0				1.8706	12	$\bar{5}$ 3 5				1.4563	7	3 9 1
		2.9067	31	0 4 2				1.8632	4	$\bar{1}$ 7 3				1.4535	9	3 1 4
89	2.898	2.8899	62	$\bar{4}$ 0 3	22	1.8678		1.8622	3	3 7 0				1.4459	7	5 3 2
		2.8723	20	0 0 3				1.8614	15	1 7 2	27	1.4457		1.4407	4	0 6 5
		2.8530	5	$\bar{4}$ 2 2				1.8536	4	$\bar{4}$ 4 5				1.4394	9	$\bar{8}$ 0 2
		2.8161	15	$\bar{3}$ 3 3	13	1.8483		1.8449	11	4 4 1				1.4387	4	$\bar{2}$ ·10·3
		2.8080	7	$\bar{1}$ 3 3				1.8322	4	$\bar{2}$ 8 2				1.4373	3	$\bar{2}$ ·10·1
51	2.814	2.8046	15	3 3 0	21	1.8135		1.8118	16	$\bar{6}$ 4 3				1.4175	4	$\bar{1}$ 9 4
		2.8016	48	1 3 2				1.7750	4	$\bar{6}$ 4 4				1.4163	6	1 9 3
		2.7130	21	$\bar{4}$ 2 3	11	1.7737		1.7711	5	$\bar{6}$ 4 2				1.4064	14	3 3 4
		2.7039	24	$\bar{4}$ 2 1				1.7553	8	$\bar{3}$ 5 5	24	1.4040		1.4006	10	$\bar{4}$ ·10·2
51	2.714	2.6985	9	0 2 3				1.7307	5	$\bar{7}$ 1 4				1.4000	5	4 4 3
		2.6962	9	$\bar{1}$ 5 2	11	1.7264		1.7234	7	0 0 5				1.3903	5	$\bar{6}$ 4 7
		2.6252	11	0 6 0				1.7085	7	3 7 1				1.3818	14	$\bar{4}$ ·10·1
28	2.623	2.6216	25	2 4 1				1.6897	3	$\bar{5}$ 5 5				1.3809	7	$\bar{5}$ 9 1
		2.6049	6	$\bar{3}$ 1 4				1.6734	9	$\bar{6}$ 4 5				1.3798	4	$\bar{7}$ 3 7
		2.5943	7	2 0 2	9	1.6711		1.6683	5	$\bar{6}$ 0 6	24	1.3809		1.3771	7	$\bar{7}$ 7 4
		2.5113	13	0 6 1				1.6653	3	0 6 4				1.3753	8	$\bar{3}$ 7 6
		2.5025	7	$\bar{4}$ 0 4				1.6616	9	$\bar{2}$ 0 6				1.3724	3	7 3 0
45	2.482	2.4882	5	4 0 0				1.6591	7	$\bar{1}$ 9 2				1.3519	3	$\bar{8}$ 4 2
		2.4694	17	$\bar{3}$ 5 2				1.6527	12	$\bar{7}$ 3 4	8	1.3499		1.3481	9	$\bar{3}$ 9 5
		2.4668	18	$\bar{3}$ 5 1				1.6496	4	$\bar{3}$ 3 6				1.3442	5	$\bar{7}$ 7 5
14	2.414	2.4127	32	$\bar{2}$ 6 1	44	1.6539		1.6468	3	$\bar{1}$ 7 4				1.3289	3	$\bar{3}$ 5 7
		2.3982	7	$\bar{5}$ 1 3				1.6450	6	1 7 3				1.3280	3	$\bar{8}$ 2 1
		2.3886	5	$\bar{1}$ 1 4				1.6439	3	5 3 1	19	1.3203		1.3209	5	$\bar{9}$ 1 6
		2.3595	7	$\bar{3}$ 3 4				1.6427	13	3 3 3				1.3177	6	$\bar{5}$ 9 5
								1.6403	5	$\bar{4}$ 6 5				1.3126	10	0·12·0

Only calculated lines with relative intensities of 3 or greater are listed.

shown in Fig. 3b. The bounding environment of the cavity is composed of two opposed six-membered rings of SiO₄ tetrahedra, two CaO₈ polyhedra and four CuO₅ groups. A centre of symmetry lies at the cavity centre. The bounding polyhedra define a prolate-ellipsoidal volume having a major axis of 9.2 Å, an intermediate axis of 8.0 Å and a minor axis of 5.2 Å. O atoms of the two H₂O molecules occupying the cavity are 4.6 Å apart.

Thus, the diegogattaite structure is composed of two large cavities, one composed of sixteen SiO₄ tetrahedra (the 6⁴8² cage) and the other a large lacuna occupied by H₂O molecules bonded to Na. These two types of cavity share two bounding faces defined by six-membered rings of SiO₄ tetrahedra.

X-ray powder diffraction

Insufficient material was available (three small crystals) for routine powder diffraction. However, the crystal used in the structure determination was used to obtain a quasi-random powder dataset. It was mounted on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer and a dataset collected using MoK α radiation. A Gandolfi-type randomized crystal movement was achieved by rotations on the ϕ and ω axes. Unit-cell parameters refined from this experiment are: $a = 12.247(7)$, $b = 15.766(8)$, $c = 10.620(7)$ Å, $\beta = 125.71(2)^\circ$ and $V = 1665(2)$ Å³ ($Z = 4$). Observed d spacings and intensities were obtained by profile-fitting using *JADE 2010* software and are listed in Table 2.

Discussion

The structure of diegogattaite is closely related to those of a number of synthetic nanoporous copper silicates including Na₂Cu₂Si₄O₁₁·2H₂O (“CuSH-2Na”), Na₂Cu₂Si₄O₁₁, Na₂CuSi₃O₈ (“CuSH-3Na”), Cs₂Na₄Cu₂Si₁₂O₂₇[(OH)₂]₂ (“CuSH-4NaCs”), Na₂Cu₂Si₅O₁₃·3H₂O (“CuSH-6Na”), (Wang *et al.*, 2003, 2005; Cunha-Silva *et al.*, 2008). The structure of diegogattaite contains components present in these phases, such as a nanoporous silicate skeleton, CuO₅ and NaO₅(H₂O) groups. Among minerals, it shares some similarities with litidionite, KNaCuSi₄O₁₀ (Pozas *et al.*, 1975), which also has Cu₂O₈ dimers connecting silicate double sheets. The diegogattaite structure differs from the other structures in that it has the unique structural 6⁴8² cage, as

well as being the only example of this group of materials to contain essential Ca. Thus, it is easily distinguished, both crystallographically and compositionally, from related and associated copper silicates.

The juxtaposition of diegogattaite and Ba-rich wesselsite in specimen BM2012,2 is of interest because there is no Sr or Ba in diegogattaite and there is no Ca in wesselsite. Considering their structural similarities, this may seem surprising, but Yang *et al.* (2013) noted that scottyite (BaCu₂Si₂O₇) adjacent to wesselsite had almost no Sr and wesselsite had only a small amount of Ba, even though a complete solid solution between wesselite and effenbergerite BaCuSi₄O₁₀ is known to exist (Knight *et al.*, 2010). Yang *et al.* (2013) inferred that it might not be possible to substitute Sr²⁺ for Ba²⁺ in scottyite, and so perhaps the same is true for diegogattaite. However, the possibility of Sr- and Ba-analogues of diegogattaite cannot be ruled out until the distribution of the alkaline-earth elements within a number of related copper silicates is further studied. For example, it is surprising that no cuprorivaite CaCuSi₄O₁₀ component is observed in the wesselsite of BM2012,2.

The synthesis potential of diegogattaite and any other chemical analogues is unexplored. In the host rock diegogattaite is in direct contact with wesselsite at all crystal rims observed, which may reflect a reaction relationship between gillespite-type structures and alkaline-earth CuSH-type phases, thereby suggesting a possible synthesis route. Diegogattaite and gillespite-type minerals have sheet structures with interlayer Ca, Sr and Cu – a shared feature that could facilitate transformations between them. As such, diegogattaite may be a bridge between CuSH phases and alkaline-earth copper silicates, thereby opening up a new direction for synthetic studies of this family of nanoporous silicates.

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