




Article

Bosoite, a new silica clathrate mineral from Chiba Prefecture, Japan

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Abstract

Bosoite (IMA2014-023) is a new silica clathrate mineral containing hydrocarbon molecules in its crystal structure. Bosoite can be considered structurally as a silica analogue of the structure-H gas hydrate, where guest molecules are trapped in cage-like voids constructed of the host framework. The mineral occurs in the Miocene tuffaceous sedimentary rocks at Arakawa, Minami-boso City, Chiba Prefecture, Japan. Bosoite is hexagonal, and it crystallises as an epitaxial intergrowth on chibaite crystals, with the {0001} of bosoite parallel to octahedral {111} form of chibaite. Crystals are colourless and transparent with vitreous lustre. The calculated density is 2.04 g/cm³. The empirical formula (based on 2 O apfu and guest molecules assumed as CH₄) is Na_{0.01}(Si_{0.98}Al_{0.02})_{Σ1.00}O₂·0.50CH₄; the end-member formula is SiO₂·nC_xH_{2x+2}. Bosoite has the space group *P6/mmm*, with the unit-cell parameters *a* = 13.9020(3) Å, *c* = 11.2802(2) Å, *V* = 1887.99(6) Å³ and *Z* = 34. The crystal structure of bosoite was refined by single-crystal X-ray diffraction and converged to *R*₁ = 4.26% for the average model and *R*₁ = 2.96% for the model where all oxygen sites are split.

Keywords: bosoite, new mineral, silica clathrate, chibaite, hydrocarbon, Japan

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Introduction

Silica clathrates (or clathrasils) are zeolite-like materials constructed of pure silica framework structures with small cage-like voids. Melanophlogite, a rare silica mineral first reported from Sicily, Italy in the 19th century (von Lasaulx, 1876), is the first example of a silica clathrate. Melanophlogite's chemical composition was at first considered to be essentially SiO₂, and the >6 wt.% C, H and S detected by chemical analyses were thought to be impurities of organic matter trapped as inclusions (Skinner and Appleman, 1963). It turned out to have a crystal structure similar to the cubic structure-I gas hydrate that can incorporate organic molecules (Kamb, 1965). Gas molecules such as CH₄, CO₂, N₂ and H₂S have been reported in natural melanophlogite and noble gases as well as other small molecules can be incorporated into the cages (Gies *et al.*, 1982; Yagi *et al.*, 2007; Tribaudino *et al.*, 2008). Starting from the 1980s, a variety of silica clathrates such as melanophlogite, dodecasil-3C and dodecasil-1H, as well as pure silica zeolites (zeosils) have been synthesised successfully and studied (e.g. Gies *et al.*, 1982; Gies 1984, Gerke and Gies, 1984). For each unique

framework topology, the framework type code (FTC) consisting of three capital letters (in bold type) are assigned by the Structure Commission of the International Zeolite Association (IZA-SC) (Baerlocher *et al.*, 2007). The FTC of melanophlogite is **MEP**.

Chibaite from the Chiba Prefecture, Japan was the second silica clathrate found in Nature (Momma *et al.*, 2011). It has the **MTN**-type framework structure and it is isostructural with the cubic structure-II hydrate. Associated with chibaite, another silica clathrate mineral that is isostructural with the hexagonal structure-H gas hydrate (Lu *et al.*, 2007) was also found. This mineral has been fully characterised and named as bosoite (Momma *et al.*, 2014). Bosoite is the natural analogue of a synthetic silica clathrate compound with the **DOH**-type framework structure, known as dodecasil-1H (Gerke and Gies, 1984). The mineral and its name were approved by the International Mineralogical Association (IMA) Commission on New Minerals, Nomenclature and Classification (IMA2014-023). The mineral is named after the Boso Peninsula, the large peninsula just east of Tokyo across the Tokyo Bay. Type material has been deposited in the collections of the National Museum of Nature and Science, Japan, registered number NMS-M43775 and the Tohoku University Museum, Aoba, Sendai, Japan, mineral collection specimen A-153. A single-crystal X-ray diffraction study was done for both the holotype and cotype (NMS-M43763) samples, and data of the cotype are reported here.

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Occurrence

Bosoite occurs in association with chibaite, which was found from Arakawa, Minami-boso City, Chiba Prefecture, Japan (Momma *et al.*, 2011). The Boso Peninsula encompasses the entire Chiba Prefecture located in the middle of the Honshu Island, and Arakawa is located in the south of the Peninsula. Bosoite and chibaite occur in small quartz and calcite veins partly developed at fault planes in tuffaceous sandstone and mudstone of the Miocene Hota Group. They are considered to be a series of forearc sediments deposited near the plate margin by the Palaeo-Izu arc and accreted along the proto-Sagami trough by subduction of the Philippine Sea plate during the Early to Middle Miocene (Ogawa and Ishimaru, 1991; Takahashi *et al.*, 2016).

The sequence of mineral formation from rim to centre of the vein is generally as follows: a very thin layer of clinoptilolite-(Na) and/or opal-A, melanophlogite, chibaite, bosoite and calcite. Melanophlogite 'crystals' were always found as cubic forms of semi-translucent quartz pseudomorphs, with only one exception of an unaltered sample. Many of chibaite 'crystals' are also altered and occur as white quartz pseudomorphs. Some parts of the veins are composed of primary quartz grains or microcrystalline chalcedony. Other associated minerals are pyrite, dachiardite, sepiolite, gypsum and baryte. These minerals were identified by a Gandolfi XRD camera and scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS). The mineral was formed under low-temperature hydrothermal conditions during diagenesis.

Physical and optical properties

Bosoite occurs as an epitaxial intergrowth on chibaite, where the {0001} face of hexagonal bosoite is parallel to the octahedral {111} of chibaite (Figs 1 and 2). It exhibits platy shapes parallel to {0001}. The grain size of an individual crystal is ~0.01 mm to 0.05 mm thick and 0.05 mm to 0.3 mm in diameter. Crystals are transparent and colourless, have a white streak and a vitreous lustre. Crystals are brittle with an irregular fracture. The Mohs hardness is estimated to be 6½–7 by scratching a thin section sample by hard metal needles. It is non-fluorescent under shortwave or longwave ultraviolet radiation (254 and 365 nm). The density could not be measured because of the small grain size. The calculated density is 2.04 g/cm³ based on the empirical formula Na_{0.01}(Si_{0.98}Al_{0.02})_{Σ1.00}O₂·0.50CH₄. It is optically uniaxial (+). Due to the small amount of sample available the refractive indices could not be determined. Through observation of the Becke line at grain boundaries between bosoite and chibaite under a polarised light microscope equipped with universal stage, the refractive index (*n*_ω) of bosoite was found to be slightly higher than that of chibaite, which is optically isotropic and *n* = 1.470(1).

Raman spectroscopy

Raman spectra (Fig. 3) were measured using a JASCO NRS-5100 spectrometer. Spectra were obtained using a 532 nm laser with the 600 grooves/mm grating and a 100× objective lens. A list of Raman shift positions of the hydrocarbon molecules measured in bosoite are given in Table 1 along with those in the free gas state, in chibaite, and in melanophlogite for comparison. The presence of hydrocarbons is shown by bands in the range 2850 to 3050 cm⁻¹. In the C–H stretching bands, existence of CH₄, C₂H₆, and C₃H₈ or even larger molecules were detected.

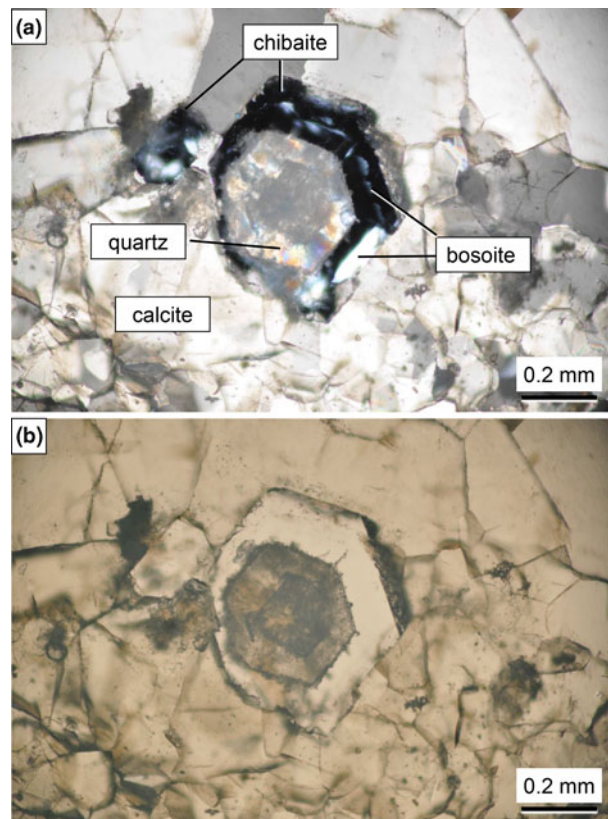


Fig. 1. Photomicrographs of bosoite sample (NSM-M43775) under crossed polarised light (a) and plane polarised light (b). The quartz domain inside chibaite is a pseudomorph of chibaite. The slightly darker area inside the quartz domain is also chibaite overlapped with quartz (see Fig. 2).

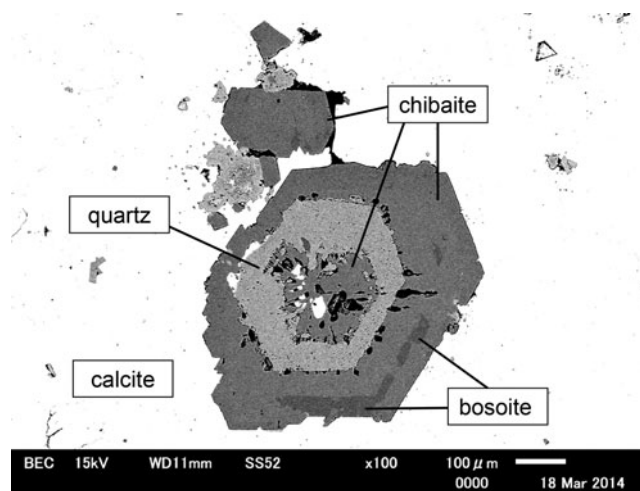


Fig. 2. Back-scattered electron image (BSE) of the sample (NSM-M43775). Bosoite is observed to be slightly darker than chibaite in BSE because the framework density of bosoite (18.0 tetrahedral atoms per 1000 Å³) is lower than that of chibaite (18.7 tetrahedral atoms per 1000 Å³).

However, the Raman bands of this region from C₃H₈ or larger molecules do not resolve very well. Signals of C–C stretching bands (~850–1000 cm⁻¹) could not be detected owing to the high background levels and low signal-to-noise ratios. Therefore, the existence of molecules larger than C₄H₁₀ could

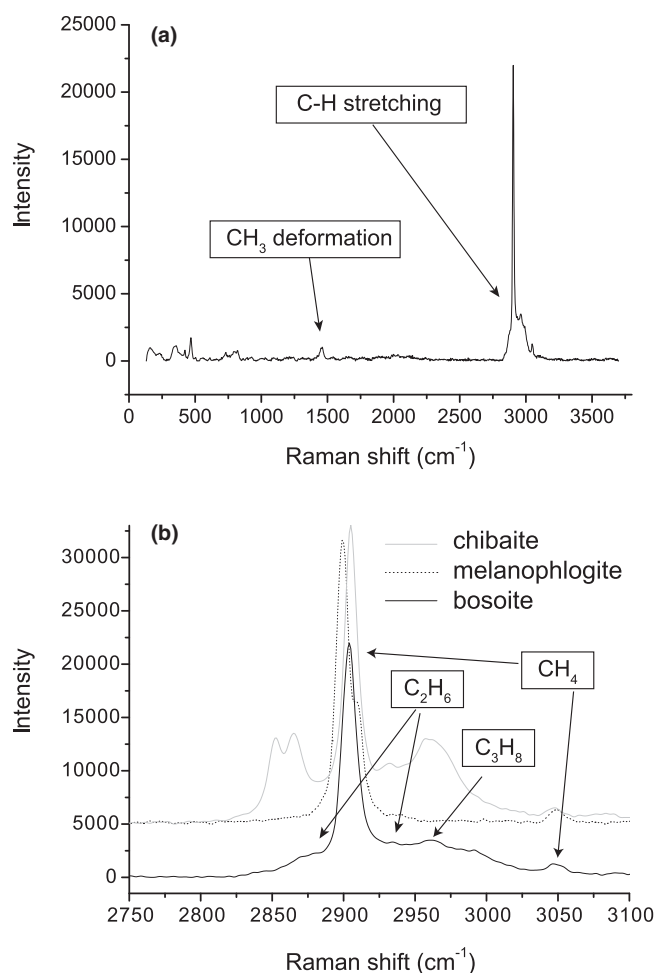


Fig. 3. The Raman spectrum of bosoite (NSM-M43775): (a) the whole measured range and (b) enlarged view of the C–H stretching region, overlaid with Raman spectra of chibaite and melanophlogite from the same locality for comparison. Background is subtracted from the data.

not be confirmed. A small peak observed at 1456 cm^{-1} corresponds to the CH_3 degenerate-deformation modes of alkanes with > 2 C atoms. Raman bands of other possible guest molecules, which have been reported in melanophlogite and chibaite, are as follows. N_2 : 2321 cm^{-1} ; CO_2 : 1277 and 1378 (Kolesov and Geiger, 2003) or 1380 cm^{-1} (Kanzaki, 2019); H_2S : 2594 and

Table 2. Chemical compositions of bosoite.

Constituent	Wt.%	Range	S.D.	Probe standard
SiO_2	86.38	85.10–87.36	0.94	Quartz
Al_2O_3	1.63	1.14–1.96	0.35	Corundum
Na_2O	0.34	0.32–0.37	0.02	Jadeite
$\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$	11.65*			
Total	100.00			

*Calculated based on the total. S.D. – standard deviation.

2604 cm^{-1} (Tribaudino *et al.*, 2008). Raman bands attributable to guest molecules other than hydrocarbons were not observed in bosoite.

Chemical composition

Three quantitative chemical analyses were carried out by means of an electron microprobe (JEOL JXA- 8800M, WDS mode, 15 kV, 5 nA and $1\text{ }\mu\text{m}$ beam diameter). Standard materials for quantitative analyses of the samples were: quartz for Si, corundum for Al and jadeite for Na. The acquired X-ray intensities were corrected by the ZAF method. The analytical results are given in Table 2. Hydrocarbon contents were not measured directly because of the small amounts of material available and thus their quantitative ratios remain undetermined. The total hydrocarbon is given based on the difference and is reported as $\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$. The empirical formula (based on 2 O atoms per formula unit with an assumption that all the hydrocarbon is CH_4), with rounding errors, is $\text{Na}_{0.01}(\text{Si}_{0.98}\text{Al}_{0.02})_{\Sigma 1.00}\text{O}_2 \cdot 0.50\text{CH}_4$.

A suitable simplified formula is not a straightforward choice since, as noted above, a number of guest molecules could be accommodated in the clathrate. Based on the results of the single-crystal refinement showing a large number of site-scattering factors in the largest cage, the broad Raman bands within the C–H stretching region, and previous studies reporting the necessity of large molecules for crystallisation of the DOH-type clathrasil (Gies and Marker, 1992; van Koningsveld and Gies, 2004), hydrocarbon molecules larger than C_4H_{10} are very likely to be included. Assuming just the presence of alkanes in the mineral, the simplified formula is $\text{SiO}_2 \cdot n\text{C}_x\text{H}_{2x+2}$, where x denotes average degree of polymerisation for alkanes and the limit of $(n \times x) \leq \sim 0.5$. More details about guest molecules are discussed in the Crystallography section below. The stoichiometry $\text{SiO}_2 \cdot 0.5\text{CH}_4$ requires SiO_2 88.22, CH_4 11.78, total 100.00 wt.%.

Table 1. Raman band positions of hydrocarbons in bosoite.

ν_{obs} (cm^{-1})	$\nu_{\text{gas/liquid/solid}}$ (cm^{-1})	$\nu_{\text{(Melanophlogite)}}$ (cm^{-1})	$\nu_{\text{(chibaite)}}$ (cm^{-1})	Assignment Molecule	Vibrational mode
1456	1468.1 ^e 1451 ^e 1460 ^e			Ethane Propane n-Butane	CH_3 degenerate deformation
2870	2900.4 ^c		2885 ^d	Ethane	C–H region Fermi resonance doublet bands ν_1 C–H symmetric stretching
2904	2917.6 ^b	2900 ^a 2909 ^a	2903 ^d 2911 ^d	Methane	
2935	2955.6 ^c		2939 ^d	Ethane	C–H ₃ degenerate stretching
2961	2968.7 ^e 2967 ^e 2965 ^e		2960 ^f	Ethane Propane n-Butane	
2992				unassigned	
3049		3047 ^a	3051 ^d	Methane	

^aKolesov and Geiger (2003), ^bSum *et al.* (1997), ^cSubramanian *et al.* (2000), ^dMomma *et al.* (2011), ^eShimanouchi (1972), ^fLikhacheva *et al.* (2016).

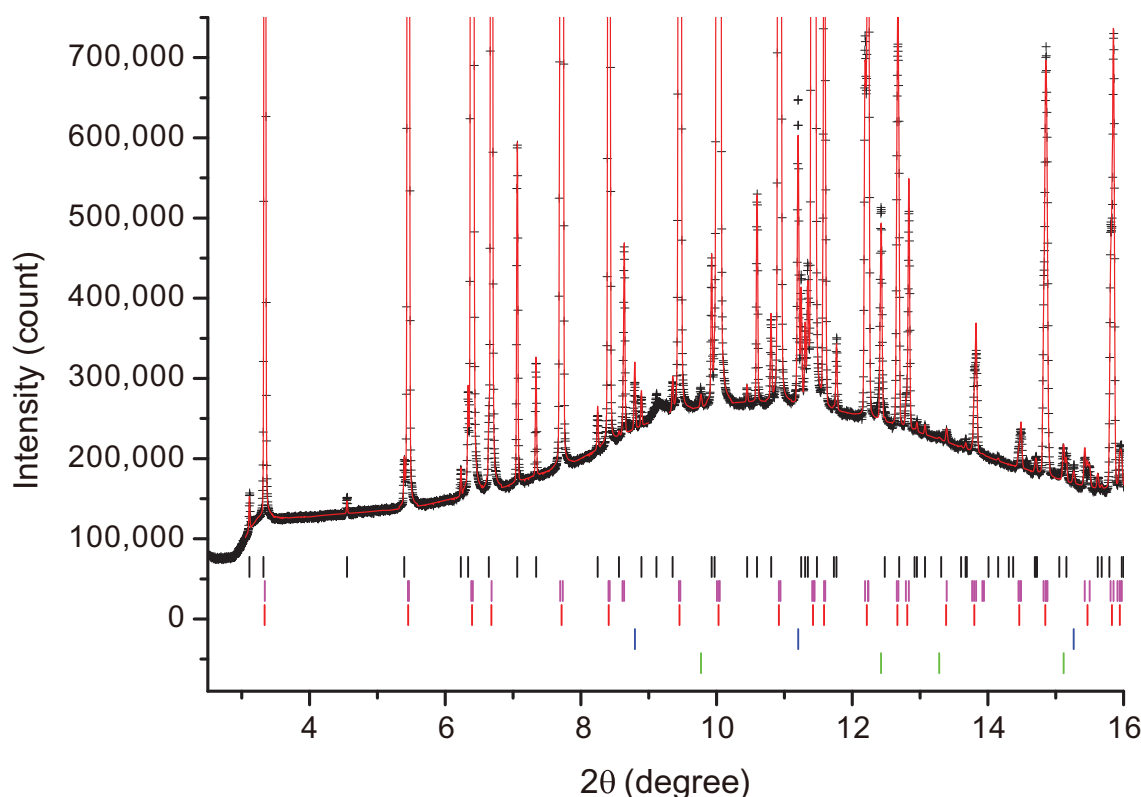


Fig. 4. Observed (black cross) and calculated (solid red line) powder diffraction pattern of sample (NSM-M43775). Tick marks below the pattern indicate diffraction position of bosoite (black), tetragonal phase of chibaite (magenta), cubic phase of chibaite (red), quartz (blue) and calcite (green). Data points from 9.0 to 9.3° were not used in the refinement because a broad halo from opal-A appearing at this range overlaps with a small bosoite peak. When this data range was used, the halo caused significant overestimate of I_0 of the overlapped bosoite peak, leading to drifts of various parameters of bosoite.

Crystallography

Powder X-ray diffraction (PXRD) data of the holotype sample were collected by the Debye-Scherrer method with synchrotron radiation using an imaging plate at BL15XU, SPring-8, Japan. As bosoite is always associated with chibaite, the chibaite crystals were separated carefully from the host rock and crushed in an alumina mortar. The obtained powder was sealed in a Lindemann glass capillary tube with inner diameter of 0.5 mm. Experimental conditions were as follows: $\lambda = 0.652973 \text{ \AA}$; exposure time = 6 s; and step interval = 0.003° . Data from 3.05° to 56° were used for refinement of unit cell parameters by Rietveld analysis using RIETAN-FP (Izumi and Momma, 2007). Atomic coordinates of bosoite were fixed at values reported by Gerke and Gies (1984) and only occupancies of guest sites and isotropic atomic displacement parameters were refined. For chibaite, both the cubic and tetragonal structural models were used because the symmetry of part of chibaite crystals is low (Momma *et al.*, 2011). Although fitting by two structural models for almost perfectly overlapping peaks might have caused overfitting of chibaite parameters, it was still preferable to retrieve better unit-cell parameters of bosoite. The refinement converged to $R_{\text{wp}} = 3.41\%$, $R_p = 2.31\%$, $\text{Gof} = 15.17$, $R_{\text{Bragg}}(\text{bosoite}) = 4.44\%$, $R_F(\text{bosoite}) = 2.09\%$. Note that the high Gof value is due to extremely high signal / background ratio of data. The refined unit-cell parameters of bosoite are $a = 13.8725(3)$, $c = 11.2694(3) \text{ \AA}$ and $V = 1878.18(8) \text{ \AA}^3$. The refined fraction of each phase is as follows: 2.7 wt.% bosoite; 19 wt.% cubic chibaite; 76 wt.% tetragonal chibaite; 0.9 wt.% quartz; and 1.4 wt.% calcite. Almost all PXRD data of chibaite samples showed the

existence of $\sim 2\text{--}3$ wt.% of bosoite. Diffraction data are shown in Fig. 4 and listed in Table 3.

Single-crystal X-ray diffraction (SXRD) studies were carried out using a Rigaku R-Axis Rapid II microdiffractometer with $\text{CuK}\alpha$ radiation from the VariMax rotating-anode target combined with a confocal mirror. The epitaxial relation of bosoite and chibaite was confirmed from the holotype sample. However, due to overlap of diffraction peaks of chibaite and bosoite, even small volumes of chibaite associated with bosoite prevented us from doing the structure refinement of bosoite. As the two minerals cannot be distinguished under normal stereomicroscope, we had to make several thin sections to find and cut out a single-crystal of bosoite under polarised light. We decided not to consume the holotype for this purpose and used the cotype because the holotype is much better as a specimen but smaller than the cotype. The Rigaku RAPID AUTO software package (Rigaku, 1998) was used for processing the diffraction data, including the application of numerical absorption correction. The structure was solved by the charge flipping method using *Superflip* (Palatinus and Chapuis, 2007). From the electron-density distributions obtained by the charge flipping method, space group $P6/mmm$ reported by Gerke and Gies (1984) was confirmed. All the framework atoms and two guest sites in the small cages were found by the charge flipping method. The rest of the guest sites were found by difference-Fourier syntheses. For the refinement of crystal structure, *SHELXL-2018/1* software (Sheldrick, 2008, 2015) was used, with neutral atom-scattering factors. Details of the data

Table 3. Powder X-ray data (d in Å, I in %) with normalised intensity of bosoite.

I_{obs}	I_{calc}	d_{obs}	d_{calc}	hkl	I_{obs}	I_{calc}	d_{obs}	d_{calc}	hkl	I_{obs}	I_{calc}	d_{obs}	d_{calc}	hkl
11	8.9	12.002	12.014	100	21	22.9	3.184	3.185	203	3	2.8	1.964	1.964	305
*	2.2	11.198	11.270	001	*	1.3		3.004	400	*	9.8		1.943	423
5	3.4	8.215	8.219	101	4	3.3	2.894	2.894	213	5	7.0	1.887	1.887	602
14*	11.0	6.933	6.936	110	3	3.6	2.868	2.868	312	*	2.8		1.878	006
8	8.3	6.009	6.007	200	3	2.2	2.743	2.743	104	*	1.2		1.867	315
30	23.2	5.907	5.907	111	1.3	1.0	2.652	2.650	402	*	1.1		1.864	432
*	14.6	5.636	5.635	002		1.9		2.553	411	3	4.3	1.832	1.832	610
100	100.0	5.301	5.301	201	5	4.5	2.551	2.551	204	*	1.2		1.808	611
33	35.1	5.100	5.102	102	8	9.0	2.475	2.476	322	*	3.2		1.803	405
10	12.9	4.541	4.541	210	3	5.9	2.403	2.403	500	2	2.3	1.787	1.787	334
1.3	1.5	4.374	4.374	112	0.9	1.4	2.394	2.394	214	*	3.0		1.768	424
9	11.0	4.213	4.212	211	*	2.7, 1.5	2.350	2.350, 2.346	501, 403	*	4.2		1.748	433
4	5.7	4.108	4.110	202	4	4.8	2.311	2.312	330	*	2.0		1.745	325
9	10.4	4.006	4.005	300	9	7.2	2.304	2.304	304	3	3.7	1.736	1.736	216
44	44.2	3.773	3.774	301	*	3.7		2.222	323	*	1.0		1.714	441
*	7.5	3.757	3.757	003	1.7	1.5	2.210	2.210	502		2.3		1.701	306
4	5.6	3.586	3.585	103	1.4	0.6	2.186	2.187	224	*	7.4		1.697	701
62	68.4	3.535	3.536	212	1.7	1.1	2.143	2.144	115	*	1.2		1.648	621
24	27.8	3.467	3.468	220	1.0	0.5	2.106	2.106	422	*	2.1		1.644	505
38	37.4	3.331	3.332	310	1.2	0.9	2.055	2.055	404	*	1.9		1.632	604
22	23.6	3.315	3.315	221	*	2.3		1.975	430	*	2.2		1.614	335
42*	33.6	3.303	3.303	113	2	1.2, 1.3,	1.969	1.971, 1.970,	601, 324,					
	1.0		3.195	311		1.8		1.969	333					

Theoretical powder data are calculated on the basis of the structural model refined by Rietveld analysis using *RIETAN-FP*. For unobserved or overlapped peaks, only calculated lines with $I > 1$ are shown. The strongest lines are given in bold.

*These diffraction peaks were overlapped with peaks of other minerals in the powder sample, i.e. chibaite, quartz and calcite.

Table 4. Data collection and details of the single-crystal structural refinement.

Crystal data	
Structural formula	SiO ₂ ·0.50CH ₄
Space group	<i>P6/mmm</i> (#191)
Unit-cell dimensions	$a = 13.9020(3)$, $c = 11.2802(2)$
Volume (Å ³)	$V = 1887.99(6)$
Z	34
D_{calc} (g/cm ³)	2.04
$F(000)$	1190
μ (mm ⁻¹)	6.5
Crystal size (mm)	$0.060 \times 0.050 \times 0.040$
Data collection	
Temperature (K)	293(2)
Radiation	CuK α ($\lambda = 1.54187$ Å)
Voltage, current	40 kV, 30 mA
$2\theta_{\text{max}}$ (°)	136.4
No. of reflections measured	22,203
Independent reflections ($I > 2\sigma(I)$)	739 (705, $R_{\text{int}} = 0.031$)
Indices range of h, k, l	$-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-13 \leq l \leq 13$,
Absorption correction	Numerical (<i>NUMABS</i> ; Higashi, 1999)
Max. and min. transmission factors	0.710–0.771
Refinement	
No. of variables / restraints	Average model / Disordered model
Reflection/Parameter Ratio	73 / 0 / 138 / 15
R_1 , wR_2 ($I > 2\sigma(I)$)	10.1 / 5.36
R_1 , wR_2 (All reflections)	0.043, 0.120 / 0.030, 0.085
Goodness-of-fit:	0.044, 0.121 / 0.030, 0.086
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e ⁻ /Å ³)	1.17 / 1.09
	0.55 and -0.34 / 0.43 and -0.27

collection, refinement, and results of the refinement are summarised in Table 4.

An illustration of the average crystal structure is shown in Fig. 5. Refined atomic coordinates and equivalent isotropic displacement parameters are summarised in Table 5. Selected bond distances and bond angles are given in Table 6. From the difference-Fourier map, all of oxygen atom positions were

found to be split around their average positions. Subsequent refinements with all the O sites split around their average positions greatly reduced the residual electron densities and improved R_1 from 4.26% to 2.96% with a trade-off of poorer data / parameter ratio. The mean U_{eq} of O sites also changed from 0.076 Å² to 0.039 Å². To reduce the number of free parameters and their correlations, occupancy of each split O site was fixed at 1/3 and the position of each O site was restrained such that it is placed equidistant from neighbouring Si sites. Anisotropic displacement components of the split O atoms along the adjacent O–O direction were also restrained to be equal by using the *DELU* instruction. The crystallographic information files containing results of the refinements based on the average and split models have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

The unit cell of bosoite consists of three types of cages: two [4³5⁶6³] cages, three [5¹²] cages and one [5¹²6⁸] cage (here [4³5⁶6³] denotes a polyhedron having i quadrilateral, j pentagonal and k hexagonal faces). The former two types of cages are relatively small and mainly occupied by CH₄. C1 and C2 atoms are those of CH₄ molecules at the centre of [4³5⁶6³] and [5¹²] cages respectively, and their U_{eq} are relatively large owing to very weak van der Waals interaction with the host framework. Occupancies of these sites were fixed at 1 because they exceeded 1 when freely refined. Furthermore, the difference-Fourier map still showed small residuals around C1 and C2 atoms. Distances from C1 and C2 atoms to the residuals were ~ 1 Å and these residuals were interpreted as orientationally disordered hydrogen atoms of CH₄. When these H atoms were included in the refinement with their U_{iso} values constrained to the same and C–H distances fixed to 1.08 Å, R indices decreased $\sim 0.3\%$. In the final refinement of the average model, these H atoms are not included because they are less reliable, whereas they are included in the split model for reference. In the largest [5¹²6⁸] cage, large

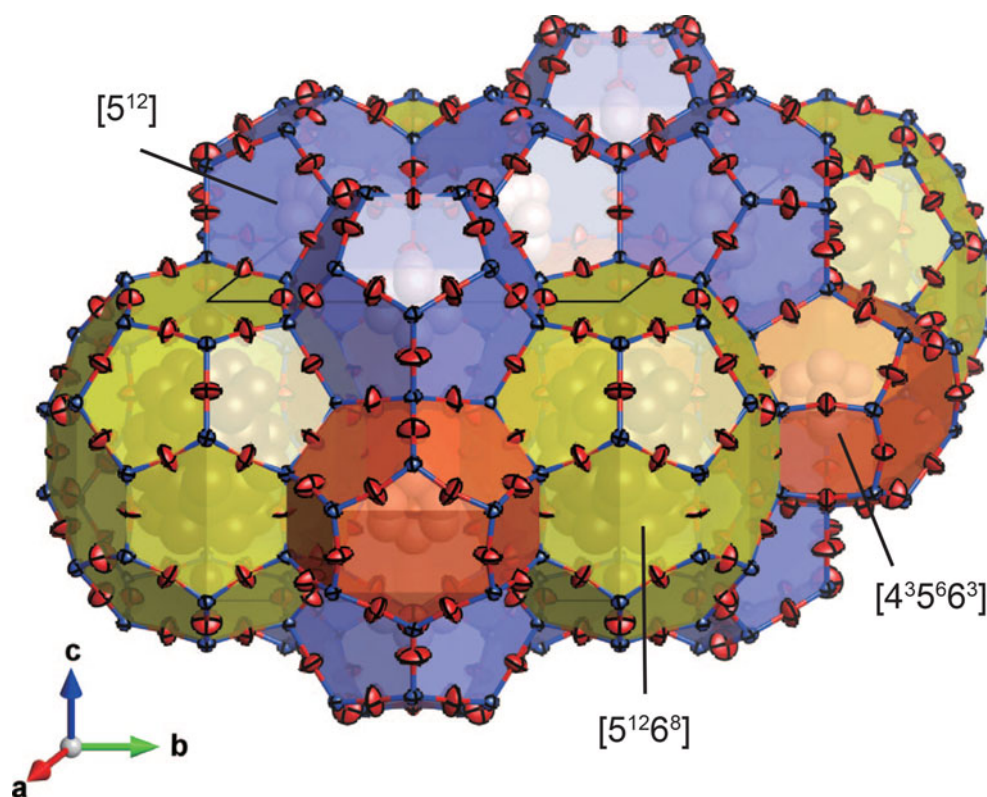


Fig. 5. The average framework structure of bososite refined without splitting of O sites.

Table 5. Refined atomic position and equivalent isotropic displacement parameters (\AA^2) of the average model.

	Wyk.	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}	Occ.
Si1	12 <i>o</i>	0.41870(9)	0.20935(4)	0.22527(9)	0.0300(4)	1
Si2	12 <i>n</i>	0.38736(8)	0.38736(8)	0.36254(9)	0.0305(4)	1
Si3	6 <i>l</i>	0.26279(12)	0.13140(6)	0	0.0296(4)	1
Si4	4 <i>h</i>	$\frac{2}{3}$	$\frac{1}{3}$	0.13850(15)	0.0318(5)	1
O1	24 <i>r</i>	0.3946(3)	0.2885(2)	0.3036(3)	0.0786(10)	1
O2	12 <i>o</i>	0.5438(3)	0.27189(15)	0.1844(4)	0.0836(14)	1
O3	12 <i>o</i>	0.3394(3)	0.16968(17)	0.1142(3)	0.0724(12)	1
O4	6 <i>k</i>	0.3616(4)	0	$\frac{1}{2}$	0.0611(15)	1
O5	6 <i>j</i>	0.1850(4)	0	0	0.0651(15)	1
O6	6 <i>i</i>	$\frac{1}{2}$	0	0.3425(5)	0.0725(18)	1
O7	2 <i>c</i>	$\frac{2}{3}$	$\frac{1}{3}$	0	0.102(4)	1
C1	2 <i>d</i>	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	0.127(9)	1
C2	3 <i>f</i>	$\frac{1}{2}$	0	0	0.137(8)	1
C3A	2 <i>e</i>	0	0	0.265(9)	0.28(7)*	0.73(14)
C3B	12 <i>o</i>	-0.044(3)	0.044(3)	0.571(6)	0.28*	0.30(3)
C3C	12 <i>n</i>	0	0.112(6)	0.315(6)	0.28*	0.33(3)
C3D	2 <i>e</i>	0	0	0.06(2)	0.28*	0.21(6)
C3E	6 <i>m</i>	0.177(8)	0.088(4)	$\frac{1}{2}$	0.28*	0.50(6)

* U_{iso} were refined with their values constrained to the same.

molecules or multiple number of small molecules are included. The total site-scattering factor in the $[5^{12}6^8]$ cage, refined as occupancies of C, was $81 e^-$. The refined U_{iso} of C3A to C3E in the $[5^{12}6^8]$ cage are extremely large owing to the variety of guest species and their static/dynamic disorder. Therefore, guest species and their ratio in the $[5^{12}6^8]$ cage could not be interpreted. Depending on average degree of polymerisation for alkanes, $81 e^-$ corresponds to 8.1 CH_4 , 4.5 C_2H_6 , 3.12 C_3H_8 , or 2.38 C_4H_{10} molecules. When these four cases are considered, the total

Table 6. Selected bond distances and bond angles in bososite.

	Distance (\AA)		Angle($^\circ$)
Si1-O1 $\times 2$	1.573(2)	Si1-O1-Si2	167.7(2)
Si1-O2	1.575(4)	Si4-O2-Si1	177.7(4)
Si1-O3	1.575(3)	Si1-O3-Si3	178.3(3)
Si2-O1 $\times 2$	1.574(2)	Si2-O4-Si2	154.0(4)
Si2-O6	1.5821(13)	Si3-O5-Si3	167.8(4)
Si2-O4	1.5914(15)	Si2-O6-Si2	163.6(4)
Si3-O3 $\times 2$	1.584(3)	Si4-O7-Si4	180
Si3-O5 $\times 2$	1.5909(10)		
Si4-O7	1.5623(17)		
Si4-O2 $\times 3$	1.568(4)		
<Si-O>	1.578	<Si-O-Si>	170

number of guest C atoms in the unit cell is ~ 13.1 – 14.5 . Assuming that widely spread electrons of H atoms in the $[5^{12}6^8]$ cage were not fully reflected to the refined site-scattering factor, and the $[5^{12}6^8]$ cage is occupied mainly by large hydrocarbons, these numbers are within an acceptable range compared to the number estimated by the chemical analysis (17C per unit cell).

The electron-density distribution in bososite calculated by the maximum entropy method (MEM) is shown in Fig. 6. *Dysnomia* (Momma *et al.*, 2013) with the *L-BFGS* algorithm was used for calculation and *VESTA* (Momma and Izumi, 2011) was used for visualisation. To reduce correlation of residuals $|F_o - F_c| / \sigma(F_o)$ with *d* spacing of reflections, an exponential-type weighting scheme proportional to $m \times \exp(-A/d)$ was used, where *m* is multiplicity of reflections and *A* is a weighting parameter optimised as 12.7. The electron-density distribution also confirms that all cages are almost fully occupied.

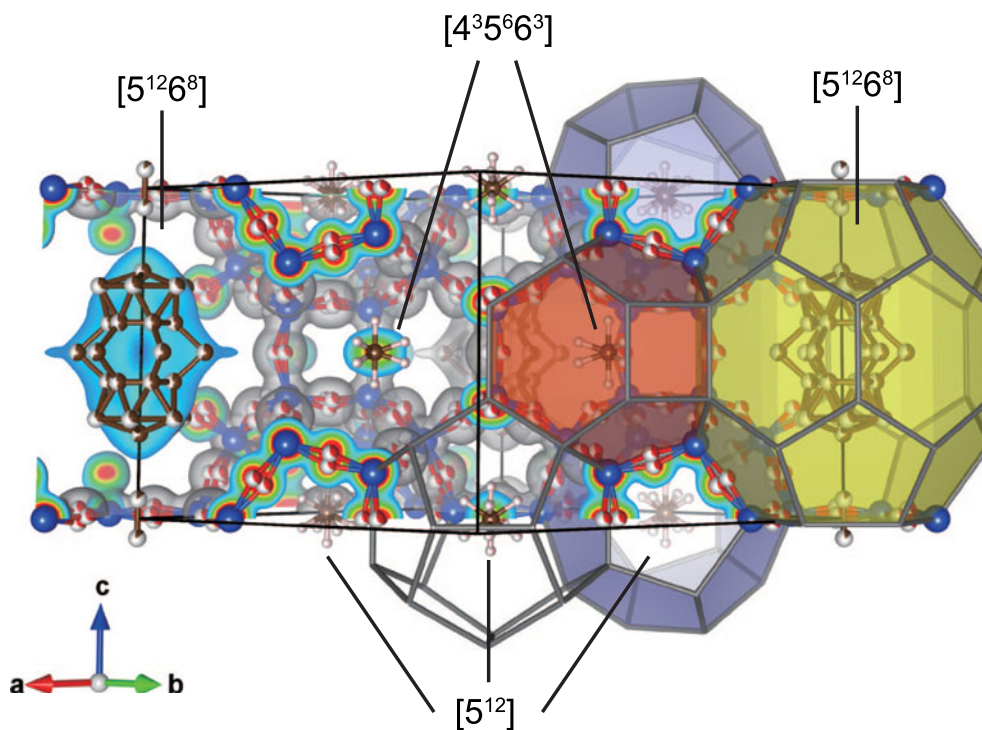


Fig. 6. Electron-density distribution in bosoiite determined by MEM analysis overlapped with the split atom model. Isosurface level is $0.5 \text{ e}^-/\text{\AA}^3$.

Discussion

The order of crystallisation of melanophlogite, chibaite and bosoiite observed in the present study indicates a decisive role of guest molecules on their crystallisation. The $[5^{12}]$ cage is common to all three minerals. Other types of cages making-up these minerals are: the $[5^{12}_6^2]$ cage in melanophlogite, the $[5^{12}_6^4]$ cage in chibaite as well as the $[4^3_5^6_6^3]$ and the $[5^{12}_6^8]$ cages in bosoiite. The $[5^{12}_6^8]$ cage is the largest and the $[5^{12}]$ cage is the smallest among them, whereas the $[4^3_5^6_6^3]$ cage is comparable in size to the smallest $[5^{12}]$ cage. From the previous studies on syntheses of these clathrasils, the presence of large molecules matching in size to the largest cage in the crystal structure is considered as a necessary condition for their crystallisation (e.g. van Koningsveld and Gies, 2004). This model can explain why bosoiite was always found associated with chibaite crystals and why it is so minor in volume compared to the other two. The $[5^{12}_6^2]$ cage in melanophlogite can incorporate small gas molecules such as CH_4 , CO_2 , N_2 and H_2S , which are abundant gases in Nature. As a result, among these clathrasils, melanophlogite is the most abundant and the first phase to crystallise in Nature. While C_2H_6 is also capable of fitting into the $[5^{12}_6^2]$ cage (Ohno *et al.*, 2009), C_3H_8 or larger hydrocarbons are too large for melanophlogite. As a result, the concentration of these large molecules in hydrothermal solutions increases as melanophlogite crystallises, and eventually crystallisation of chibaite is initiated. Similarly, the increase of the concentration of even larger molecules that cannot fit into the chibaite structure would initiate crystallisation of bosoiite. As bosoiite grows, large molecules would be consumed easily and overgrowth of chibaite on bosoiite also occurs. Larger hydrocarbons have higher molecular refraction. Therefore, the above model of crystallisation is also consistent with the fact that the refractive index of bosoiite is higher than that of chibaite regardless that the framework density of bosoiite is lower than that of chibaite.

Our observation that melanophlogite was almost always found to be replaced by quartz indicates that melanophlogite is less stable than both chibaite and bosoiite.

SiO_4 tetrahedra in framework silicates are known to be very stiff, to a first approximation they behave more like rigid units which rotate and translate without distortion of the tetrahedra (Hammonds *et al.*, 1996). On the other hand, the apparently short Si–O distances are often reported for clathrasils as a consequence of local tilting of the SiO_4 tetrahedra with the rigid-unit mode, where Si–O distances are almost constant but actual O atoms are distributed around the refined positions (Momma, 2014). This is why in the refinement of bosoiite without splitting of O sites, the mean value of Si–O distance (1.578 \AA) apparently looks shorter than the predicted value, 1.609 \AA , for tetrahedrally coordinated pure silica frameworks (Brown *et al.*, 1969; Wragg *et al.*, 2008). Si–O–Si angles range from $154.0(4)^\circ$ to 180° with a mean value of 170° , which is also larger than the average value of $154^\circ \pm 9$ for pure silica zeolite frameworks (Wragg *et al.*, 2008). With the splitting of O sites, mean values of Si–O distances and Si–O–Si angles changed to 1.604 \AA and 156° respectively. The splitting of O sites due to local disorder has also been reported for synthetic MTN- and DOH-type clathrasils (Könnecke *et al.*, 1992; Mieke *et al.*, 1993). In the case of melanophlogite and chibaite, the tilting of the framework SiO_4 tetrahedra at ambient or low temperature causes lowering of their space group symmetries (e.g. Nakagawa *et al.*, 2001; Scheidl *et al.*, 2018). On the other hand, as was reported for the synthetic DOH-type clathrasil (Mieke *et al.*, 1993), we could see no sign of symmetry lowering of bosoiite even though all of the O sites were found to be split.

Supplementary material. To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2020.91>

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