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 framework occurs in the Micocene tuffaceous sedimentary rocks at Arakawa, Minami-boso City, Chiba Prefecture, Japan. Bosoite is hexagonal, and it crystallises as an epistrial intergrowth with 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 Na₀.₀₁(Si₀.₉₈Al₀.₀₂)₂ₓ₋₂H₂O₂·₀.₅₀CH₄; the end-member formula is SiO₂·nC₂H₆. Bosoite has the space group P6/mmm, with the unit-cell parameters a = 13.₉₀₂₀(₃) Å, c = 11.₂₈₀₂(2) Å, V = 1₈₈₇.₉₉₉₆(₆) Å³ and Z = ₃₄. The crystal structure of bosoite was refined by single-crystal X-ray diffraction and converged to R₁ = 4.₂₆% for the average model and R₁ = 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 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 (zeolis) 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 isosstructural 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 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 specimens 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.
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, dichroicite, 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 \(6\frac{1}{2} – 7\) 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/cm\(^3\) based on the empirical formula \(\text{Na}_{0.01}\text{Si}_{4.98}\text{Al}_{0.02}\text{O}_{8}\cdot0.5\text{CH}_4\). 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 \((n_\omega)\) 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 CH\(_3\), C\(_2\)H\(_6\), and C\(_3\)H\(_8\) or even larger molecules were detected. However, the Raman bands of this region from C\(_3\)H\(_8\) or larger molecules do not resolve very well. Signals of C–C stretching bands (\(\sim\)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 C\(_4\)H\(_{10}\) could
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\(^{-1}\); C\(_2\)O: 1277 and 1378 (Kolesov and Geiger, 2003) or 1380 cm\(^{-1}\) (Kanzaki, 2019); H\(_2\)S: 2594 and 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 μm 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 CH\(_4\)/C\(_2\)H\(_6\)/C\(_3\)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 Na\(_{0.01}\)(Si\(_{0.98}\)Al\(_{0.02}\))\(\Sigma\)1.00O\(_2\)\(\cdot\)0.50CH\(_4\).

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\(_4\)H\(_{10}\) are very likely to be included. Assuming just the presence of alkanes in the mineral, the simplified formula is SiO\(_2\)\(\cdot\)nC\(_x\)H\(_{2x}\)\(_x\)+2, where \(x\) denotes average degree of polymerisation for alkanes and the limit of (\(n\times x\)) \(\leq\) ∼0.5. More details about guest molecules are discussed in the Crystallography section below. The stoichiometry SiO\(_2\)\(\cdot\)0.5CH\(_4\) requires SiO\(_2\) 88.22, CH\(_4\) 11.78, total 100.00 wt.\%.

### 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\(_2\)O\(_3\) | 1.63 | 1.14–1.96     | 0.35 | Corundum       |
| Na\(_2\)O    | 0.34 | 0.32–0.37     | 0.02 | Jadeite        |
| CH\(_4\)/C\(_2\)H\(_6\)/C\(_3\)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.

### Table 1. Raman band positions of hydrocarbons in bosoite.

| \(\nu_{\text{obs}}\) (cm\(^{-1}\)) | \(\nu_{\text{gas/liquid/solid}}\) (cm\(^{-1}\)) | \(\nu_{\text{Melanophlogite}}\) (cm\(^{-1}\)) | \(\nu_{\text{Chibaite}}\) (cm\(^{-1}\)) | Assignment                | Vibrational mode          |
|---------------------------------|---------------------------------|----------------------------------|----------------------------------|---------------------------|---------------------------|
| 1456                            | 1468.1\(^a\)                   |                                  |                                  | Ethane                    | CH\(_3\) degenerate deformation |
|                                 | 1451\(^a\)                     |                                  |                                  |                           |                           |
|                                 | 1460\(^a\)                     |                                  |                                  |                           |                           |
| 2870                            | 2900.4\(^d\)                   | 2900\(^a\)                       | 2885\(^d\)                       | Ethane                    | C–H region Fermi resonance doublet bands |
| 2904                            | 2917.6\(^b\)                   | 2909\(^a\)                       | 2903\(^d\)                       | n-Butane                  |                           |
|                                 |                                 |                                  | 2911\(^d\)                       | Methane                   | \(\nu_3\), C–H symmetric stretching |
| 2935                            | 2955.6\(^d\)                   | 2939\(^d\)                       |                                  | Ethane                    | C–H\(_2\) degenerate stretching |
| 2961                            | 2968.7\(^d\)                   | 2960\(^d\)                       |                                  | n-Butane                  |                           |
|                                 | 2967\(^d\)                     |                                  |                                  |                           |                           |
|                                 | 2965\(^d\)                     |                                  |                                  |                           |                           |
| 2992                            | 3049\(^d\)                     | 3051\(^d\)                       |                                  | Methane                   | 2\(\nu_2\) overtone        |
|                                 |                                 |                                  |                                  |                           |                           |

\(^a\)Kolesov and Geiger (2003), \(^b\)Sum et al. (1997), \(^c\)Subramanian et al. (2000), \(^d\)Momma et al. (2011), \(^e\)Shimanouchi (1972), \(^f\)Likhacheva et al. (2016).
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 0.5mm. Experimental conditions were as follows: \( \lambda = 0.652973 \text{ Å} \); 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 \( R_{wp} = 3.41\% \), \( R_p = 2.31\% \), \( Gof = 15.17 \), \( R_{	ext{merge}} \text{(bosoite)} = 4.44\% \), \( R_f \text{(bosoite)} = 2.09\% \). Note that the high Gof value is due to extremely high signal / background ratio of data. The refined unit-cell parameters of bosoite are \( a = 13.8725(3) \text{ Å} \), \( c = 11.2694(3) \text{ Å} \) and \( V = 1878.18(8) \text{ Å}^3 \). 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 \( \sim 2-3 \text{ wt.\% } \) 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 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. 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.

| I₀bs | Icalc | d₀bs | dcalc | hkl | I₀bs | Icalc | d₀bs | dcalc | hkl |
|------|-------|------|-------|-----|------|-------|------|-------|-----|
| 11   | 8.9   | 12.002 | 12.014 | 100 | 21  | 22.9  | 3.184 | 3.185 | 203 |
| *    | 2.2   | 11.198 | 11.270 | 001 | 1   | 1.3   | 3.004 | 3.004 | 400  |
| 5    | 3.4   | 8.215  | 8.219  | 101 | 4   | 3.3   | 2.894 | 2.894 | 213  |
| 14   | 11.0  | 6.933  | 6.936  | 110 | 3   | 3.6   | 2.868 | 2.868 | 312  |
| 8    | 8.3   | 6.009  | 6.007  | 200 | 3   | 2.2   | 2.743 | 2.743 | 104  |
| 30   | 23.2  | 5.907  | 5.907  | 111 | 1.3 | 1.0   | 2.652 | 2.650 | 402  |
| *    | 14.6  | 5.636  | 5.635  | 002 | 1.9 | 1.0   | 2.553 | 2.553 | 411  |
| 100  | 100.0 | 5.301  | 5.301  | 201 | 5   | 4.5   | 2.551 | 2.551 | 204  |
| 35   | 35.1  | 5.100  | 5.102  | 102 | 8   | 9.0   | 2.475 | 2.476 | 322  |
| 10   | 12.9  | 4.541  | 4.541  | 210 | 3   | 5.9   | 2.403 | 2.403 | 500  |
| 1.3  | 1.5   | 4.374  | 4.374  | 112 | 0.9 | 1.4   | 2.394 | 2.394 | 314  |
| 9    | 11.0  | 4.213  | 4.212  | 211 | 1   | 2.7   | 2.350 | 2.350 | 501  |
| 4    | 5.7   | 4.108  | 4.110  | 202 | 4   | 4.8   | 2.311 | 2.312 | 330  |
| 9    | 10.4  | 4.006  | 4.005  | 300 | 9   | 7.2   | 2.304 | 2.304 | 304  |
| 44   | 44.2  | 3.773  | 3.774  | 301 | *   | 3.7   | 2.222 | 2.222 | 332  |
| *    | 7.5   | 3.757  | 3.757  | 003 | 1   | 1.5   | 2.210 | 2.210 | 502  |
| 4    | 5.6   | 3.586  | 3.585  | 103 | 1   | 1.4   | 2.186 | 2.186 | 224  |
| 62   | 68.4  | 3.525  | 3.526  | 212 | 1   | 1.1   | 2.143 | 2.143 | 115  |
| 24   | 27.8  | 3.467  | 3.468  | 220 | 1.0 | 0.5   | 2.106 | 2.106 | 422  |
| 38   | 37.4  | 3.331  | 3.332  | 310 | 1.2 | 0.9   | 2.055 | 2.055 | 404  |
| 22   | 23.6  | 3.315  | 3.315  | 221 | *   | 2.3   | 1.975 | 1.975 | 430  |
| 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 | 3.195  | 3.111  | 311 | 1.8 | 1.3   | 1.969 | 1.969 | 333  |

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

| Crystal data | Structural formula | SiO₂·0.5CH₄ | Ph³/mnm (#191) |
|--------------|--------------------|-------------|----------------|
| Space group  | 2                  | 11.2802(2)  | 2               |
| Unit-cell dimensions | a = 13.902(3), c = 11.2802(2) | 1.54187 Å | 1.54187 Å |
| Volume (Å³)  | 1887.99(6)         | 11.2802(2)  | 1.54187 Å |
| Z  | 34 | 34 | 34 |
| Dcalc (g/cm³)  | 2.04 | 2.04 | 2.04 |
| /F000  | 1190 | 1190 | 1190 |
| µ (mm⁻¹)  | 6.5 | 6.5 | 6.5 |
| Crystal size (mm) | 0.060 ± 0.050 | 0.060 ± 0.050 | 0.060 ± 0.050 |
| Data collection | Temperature (K) | 973(2) | CuKα (λ = 1.54187 Å) |
| Radiation | Voltage, current | 40 kV, 30 mA | 1.54187 Å |
| 2θmax (°) | 136.4 | 136.4 | 136.4 |
| No. of reflections measured | 22,203 | 22,203 | 22,203 |
| Independent reflections (I > 2σ(I)) | 739 (705, Rω = 0.031) | 739 (705, Rω = 0.031) | 739 (705, Rω = 0.031) |
| Indices range of h, k, l | −16 ≤ h ≤ 16, −16 ≤ k ≤ 16, −13 ≤ l ≤ 13 | −16 ≤ h ≤ 16, −16 ≤ k ≤ 16, −13 ≤ l ≤ 13 | −16 ≤ h ≤ 16, −16 ≤ k ≤ 16, −13 ≤ l ≤ 13 |
| Absorption correction | Numerical (NUMABS; Higashi, 1999) | Numerical (NUMABS; Higashi, 1999) | Numerical (NUMABS; Higashi, 1999) |
| Max. and min. transmission factors | 0.710–0.771 | 0.710–0.771 | 0.710–0.771 |
| Refinement | No. of variables / restraints | 138 / 15 | 138 / 15 |
| | Reflection/Parameter Ratio | 10.1 | 10.1 |
| | R₁, wR₂ (I > 2σ(I)) | 0.043, 0.120 | 0.030, 0.085 |
| | R₁, wR₂ (All reflections) | 0.044, 0.121 | 0.030, 0.086 |
| Goodness-of-fit: | Df/n = 1.70, Df/n = 1.09 | Df/n = 1.70, Df/n = 1.09 | Df/n = 1.70, Df/n = 1.09 |
| | | | | |
molecules or multiple number of small molecules are included. The total site-scattering factor in the [51268] cage, refined as occupancies of C, was 81 e\(^{-}\). The refined \(U_{iso}\) of C3A to C3E in the [51268] cage are extremely large owing to the variety of guest species and their static/dynamic disorder. Therefore, guest species and their ratio in the [51268] cage could not be interpreted.

Depending on average degree of polymerisation for alkanes, 81 e\(^{-}\) corresponds to 8.1 CH\(_4\), 4.5 C\(_2\)H\(_6\), 3.12 C\(_3\)H\(_8\), or 2.38 C\(_4\)H\(_{10}\) molecules. When these four cases are considered, the total number of guest C atoms in the unit cell is \(\sim\)13.1–14.5. Assuming that widely spread electrons of H atoms in the [51268] cage were not fully reflected to the refined site-scattering factor, and the [51268] 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 bosoite 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.

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

| Wyk. | \(x\) | \(y\) | \(z\) | \(U_{eq}\) | \(U_{iso}\) | Occ. |
|------|------|------|------|----------|-----------|------|
| Si1  | 12o  | 0.41870(9) | 0.20935(4) | 0.22527(9) | 0.0300(4) | 1    |
| Si2  | 12n  | 0.38736(8) | 0.38736(8) | 0.36254(9) | 0.0305(4) | 1    |
| Si3  | 6f   | 0.26279(12) | 0.13140(6) | 0          | 0.0296(4) | 1    |
| Si4  | 4h   | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) | 0.13850(15) | 0.0318(5) | 1    |
| O1   | 24r  | 0.3946(3) | 0.2885(2) | 0.3036(3) | 0.0786(10) | 1    |
| O2   | 12o  | 0.5438(3) | 0.27189(15) | 0.1844(4) | 0.0836(14) | 1    |
| O3   | 12o  | 0.3394(3) | 0.16968(17) | 0.1142(3) | 0.0724(12) | 1    |
| O4   | 6k   | 0.3616(4) | 0 | \(\frac{1}{2}\) | 0.0611(15) | 1    |
| O5   | 6j   | 0.1850(4) | 0 | 0 | 0.0651(15) | 1    |
| O6   | 6i   | \(\frac{1}{2}\) | 0 | 0.3425(5) | 0.0725(18) | 1    |
| O7   | 2c   | \(\frac{1}{2}\) | \(\frac{1}{2}\) | 0 | 0.102(4) | 1    |
| C1   | 2d   | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) | 0.127(9) | 1    |
| C2   | 3f   | \(\frac{1}{2}\) | 0 | 0 | 0.137(8) | 1    |
| C3A  | 2e   | 0 | 0 | 0.265(9) | 0.28(7)* | 0.73(14) |
| C3B  | 12o  | -0.044(3) | 0.044(3) | 0.571(6) | 0.28* | 0.30(3) |
| C3C  | 12n  | 0 | 0.112(6) | 0.315(6) | 0.28* | 0.33(3) |
| C3D  | 2e   | 0 | 0 | 0.00(2) | 0.28* | 0.21(6) |
| C3E  | 6m   | 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.

### Table 6. Selected bond distances and bond angles in bosoite.

| Distance (Å) | Angle(°) |
|-------------|----------|
| Si1–O1 ×2   | 1.573(3) |
| Si1–O2     | 1.575(4) |
| Si1–O3     | 1.575(3) |
| Si2–O4     | 1.5821(13) |
| Si2–O6     | 1.5914(15) |
| Si3–O5 ×2  | 1.584(3) |
| Si3–O7     | 1.5909(10) |
| Si4–O7     | 1.5623(17) |
| Si4–O2 ×3  | 1.568(4) |
| <Si–O>     | 1.578    |
| <Si–O–Si>  | 170      |
Discussion

The order of crystallisation of melanophlogite, chibaite and bosoite 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 \([4^{5}6^{6}]\) cage in melanophlogite, the \([5^{12}]\) cage in chibaite as well as the \([4^{5}6^{6}]\) and \([5^{12}]\) cages in bosoite. The \([5^{12}]\) cage is the largest and the \([5^{12}]\) cage is the smallest among them, whereas the \([4^{5}6^{6}]\) 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 bosoite was always found associated with chibaite crystals and why it is so minor in volume compared to the other two. The \([5^{12}]\) cage in melanophlogite can incorporate small gas molecules such as \(\text{CH}_4\), \(\text{CO}_2\), \(\text{N}_2\) and \(\text{H}_2\text{S}\), 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 \(\text{C}_2\text{H}_6\) is also capable of fitting into the \([5^{12}]\) cage (Ohno et al., 2009), \(\text{C}_2\text{H}_4\) 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 bosoite. As bosoite grows, large molecules would be consumed easily and overgrowth of chibaite on bosoite 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 bosoite 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 bosoite.

\(\text{SiO}_4\) 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 \(\text{SiO}_4\) 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 bosoite without splitting of O sites, the mean value of Si–O distance (1.578 Å) apparently looks shorter than the predicted value, 1.609 Å, for tetrahedrally coordinated pure silica frameworks (Brown et al., 1969; Wragg et al., 2008). Si–O–Si angles range from 154.0(4)° to 180° with a mean value of 170°, which is also larger than the average value of 154° ± 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 Å and 156° respectively. The splitting of O sites due to local disorder has also been reported for synthetic \(\text{MTN-}\) and \(\text{DOH-}\)type clathrasils (Könnecke et al., 1992; Miehe et al., 1993). In the case of melanophlogite and chibaite, the tilting of the framework \(\text{SiO}_4\) 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 \(\text{DOH-}\)type clathrasil (Miehe et al., 1993), we could see no sign of symmetry lowering of bosoite 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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