Article

Instalment of the margarosanite group, and data on walstromite–margarosanite solid solutions from the Jakobsberg Mn–Fe deposit, Värmland, Sweden

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Abstract

The margarosanite group (now officially confirmed by IMA-CNMNC) consists of triclinic Ca-(Ba, Pb) cyclosilicates with three-membered \([\text{Si}_3\text{O}_9]^{6+}\) rings (3R), with the general formula \(A_2B\text{Si}_3\text{O}_9\), where \(A = \text{Pb}, \text{Ba}\) and \(B = \text{Ca}\). A closest-packed arrangement of O atoms parallel to (101) hosts Si and B cations in interstitial sites in alternating layers. The 3R layer has three independent Si sites in each ring. Divalent cations occupy three independent sites: Ca in B occupies two nonequivalent sites, \(\text{Ca}1\) (8-fold coordinated), and \(\text{Ca}2\) (6-fold coordinated). \(A = \text{Ca}3\) is occupied by \(\text{Pb}^{2+}\) (or \(\text{Ba}^{2+}\)) in 6+4 coordination, or 6+1 when occupied by Ca; this third site occurs within the 3R-layer in a peripheral position. Three minerals belong to this group: margarosanite (ideally \(\text{PbCa}_2\text{Si}_3\text{O}_9\)), walstromite (\(\text{BaCa}_2\text{Si}_3\text{O}_9\)) and breyite (\(\text{Ca}_2\text{Si}_3\text{O}_9\)). So far, no solid solutions involving the margarosanite binary, in the range \(\text{Ca}_0.50\text{–}0.70\) mol.% \(\text{Ba}_2\text{Ca}_2\text{Si}_3\text{O}_9\). The Pb-rich walstromite is associated closely with celsian, phlogopite, andradite, vesuvianite, diopside and nasonite. A crystal-structure refinement (\(R_I = 4.8\%\)) confirmed the structure type, and showed that the \(\text{Ca}3\) (Ba, Pb) site is split into two positions separated by 0.39 Å, with the Ba atoms found slightly more peripheral to the 3R-layers.

Keywords: margarosanite group, walstromite, breyite, cyclosilicate, mineral nomenclature, skarn, Jakobsberg

Introduction

Margarosanite, ideally \(\text{PbCa}_2\text{Si}_3\text{O}_9\), was first described and named by Ford and Bradley (1916), from the Parker Shaft in the Franklin Zn deposit, New Jersey, USA. Although it is an extremely rare mineral, Flink (1917) shortly thereafter reported its second occurrence, from the Långban Mn–Fe deposit, Värmland County, Sweden. Margarosanite was later also found at the nearby Harstigen and Jakobsberg mines. Anthropogenic margarosanite occurs on corroded lead bullets (Mera et al., 2015). Further studies on Franklin type specimens clarified the crystallography (Armstrong, 1963) and the crystal structure of the mineral (Freed and Peacor, 1969).

Walstromite, \(\text{BaCa}_2\text{Si}_3\text{O}_9\), was first described by Alfors et al. (1965) from the Big Creek-Rush Creek area, Fresno County, California, USA. It was later reported from several other deposits in Western North America (Dunning et al., 2018) and also from pyrometamorphic rocks (paravasalas) of the Hatrurim Formation, Israel (Kražtala et al., 2020). Dent Glasser and Glasser (1968) determined the crystal structure of synthetic walstromite, confirmed subsequently by Barkley et al. (2011) using material from the type locality.

The isostructurality of margarosanite and walstromite was first postulated by Glasser and Glasser (1964) and subsequently confirmed by several authors (Dent Glasser and Glasser, 1968; Freed and Peacor, 1969; Callegari and Boiocchi, 2016; Kražtala et al., 2020).

The Ca equivalent, \(\text{Ca}_2\text{Si}_3\text{O}_9\), has been synthesised under high pressure and characterised (Trojer, 1969). The presence of Ca-silicate phases with margarosanite–walstromite structure type as inclusions in diamonds (Joswig et al., 1999; Stachel et al., 2000; Nasdala et al., 2003; Brenker et al., 2005; Woodland et al., 2020) indicate a potentially Ca-rich lithology in the Earth’s deep mantle. The isostructural, high-pressure form of \(\text{Ca}_2\text{Si}_3\text{O}_9\), breyite (Brenker et al., 2021), was discovered as inclusions in a super-deep diamond from the Sáo Luiz placer deposits, Juina, Mato Grosso, Brazil.

The definition of the margarosanite group, presently including the three isostructural members margarosanite, walstromite and breyite, was approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA-CNMNC) in June 2021.
Mineralogical Association (IMA) in June 2020 (Memorandum 96–SM20, Miyawaki et al., 2020). The proposal to the IMA and the present contribution were instigated by a find of intermediate mineral compositions in the walstromite–margarosanite series, in samples from the Jakobsberg deposit.

**Description of walstromite-bearing skarn from the Jakobsberg deposit**

The ores of the Jakobsberg deposit (59.83°N, 14.11°E), 1 km southeast of Nordmark, Filipstad, Värmland, Sweden, form separate hausmannite and magnetite–hematite bodies along with characteristic commonly banded skarn masses (Magnusson, 1929). Modest amounts of Mn were mined from here 1864–1918, amounting to an equivalent of ∼200 tons of extracted metal (Tegengren, 1924). It is particularly known for exotic mineral assemblages of Pb silicates (Dunn et al., 1985; Charalampides and Lindqvist, 1988; Holtstam and Langhof, 1994) and ferrites (Holtstam, 1994; Holtstam et al., 1995). Jakobsberg belongs to the so-called Långban-type localities (Moore, 1970), carbonate-hosted Fe–Mn–(Ba–Pb–As–Sb) deposits in the Palaeoproterozoic Bergslagen ore region. They occur within supracrustal rock sequences dominated by ∼1.9 Ga felsic metavolcanics that altogether have been regionally metamorphosed under mid amphibolite-facies conditions (500–650°C and 200–400 MPa) and to some extent also affected by Svecokarelian intrusive events in the region (Björck, 1986). From a genetic point of view, the Långban-type ore deposits represent metamorphic analogues of shallow-marine, exhalative Mn–Fe deposits (Boström et al., 1979; Holtstam and Mansfeld, 2001).

The sample investigated (GEO-NRM catalogue #19940358) is a medium-grained silicate skarn, with subordinate baryte and native copper present. Carbonates and oxides are absent. The rock is exceedingly heterogeneous in terms of mineral composition, and irregularly banded, as clearly seen under short-wave ultraviolet light. Non-fluorescent parts mainly consist of ganomalite, phlogopite, vesuvianite and andradite. Bright orange-yellow fluorescent wollastonite crystals up to 5 mm occurs with mainly phlogopite and garnet. Minor amounts of ganomalite (low in MnO, ∼1 wt.%, thus forming a near-midpoint solid solution with wayneburnhamite, Pb₉Ca₆(Si₂O₇)₃(SiO₄)₃; Kampf et al., 2016) are also found here. A smaller portion of the rock (as 5–15 mm wide bands) is dominated by bluish-white (under ultraviolet) celsian, blue walstromite (i.e. the walstromite–margarosanite solid solution described here), phlogopite and Al-rich andradite. Walstromite forms subhedral, often lamellar crystals up to ca. 0.5 mm in longest dimension (Fig. 1), occasionally united in multigranular aggregates, sometimes showing a skeletal to poikiloblastic appearance, with inclusions of celsian. From the textural observations we conclude that phlogopite and celsian are the most primary constituents of the assemblage along with partially resorbed accessory andradite. Fluid-mediated remobilisation of Pb obtained from ganomalite or some other precursor Pb mineral might have led to formation of walstromite–margarosanite. Vesuvianite, Mn-rich diopside and sparse grossular also belong to this association. Nasonite occurs as grains up to 0.3 mm across, usually in direct contact with walstromite. On rims and along cracks and cleavage traces of walstromite, margarosanite with near-end member composition occurs as over- and intergrowths (Fig. 2), interpreted as a late pseudomorphic replacement. As can be seen in back-scatter electron (BSE) images with enhanced contrast, walstromite is sometimes heterogeneous, with a sector-like zonation linked to variations of Ba and Pb contents.

**Experimental**

Single-crystal X-ray diffraction data were collected with a Rigaku Oxford Diffraction XtaLAB Synergy diffractometer equipped with a PhotonJet (Mo) X-ray Source operating at 50 kV and 1 mA, and a Hybrid Pixel Array detector at 62 mm from the sample position. A large number of images (27,030) were taken at 0.2° rotation of
ω-rotations at 0.36 s per exposure in shutterless mode in order to cover a full sphere of the reciprocal space and to get accurate intensity data. The crystal structure was refined using SHELX-2018 (Sheldrick, 2015), starting from the atomic coordinates of Freed and Peacor (1969). Neutral scattering curves were employed and anisotropic displacement parameters were refined.

Crystal and refinement data are given in Table 1. Atomic coordinates, equivalent displacement parameters, and site occupancies are reported in Table 2, whereas selected bond distances and angles obtained are found in Table 3. The crystallographic information file has been deposited with the Principal Editor of Mineralogical Magazine and is available as Supplementary material (see below).

Table 1. Data and experimental details for single-crystal X-ray diffraction study of Pb-rich walstromite from Jakobsberg.

| Crystal data | (Ba0.53Pb0.43)Ca2Si3O9 | 0.20 × 0.15 × 0.10 |
|--------------|-----------------------|-------------------|
| Ideal formula|                       | Triclinic, P1      |
| Crystal system, space group |         | Z 2            |
| Temperature (K) | 293(2)   | 6.73527(7), 9.57172(12), 6.68718(6) |
| a, b, c (Å) | 6.73527(7), 9.57172(12), 6.68718(6) | 110.1760(10), 102.6060(8), 83.2059(9) |
| V (Å³) | 394.466(7) | 394.466(7) |
| Calculated density (g·cm⁻³) | 4.006 | 4.006 |
| μ (mm⁻¹) | 28.048 | 28.048 |
| Data collection | Colourless block | Rigaku Oxford Diffraction XtaLAB Synergy, HyPix |
| Crystal description | Colourless block | MoKα, 0.71073 Å |
| Instrument | 27,030 | 2.27 to 45.08 |
| Radiation type, wavelength (Å) | Multi-scan (SCALE3 ABSPACK, Rigaku Oxford Diffraction *) | 0.028, 1 |
| Number of frames | 65908, 6531, 5677 | 65908, 6531, 5677 |
| θ range (°) | 2.27 to 45.08 | 0.057 |
| T_min, T_max | 0.028, 1 | 99.9 |
| Number of measured, independent and observed reflections | -13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -13 ≤ l ≤ 13 | -13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -13 ≤ l ≤ 13 |
| R_int | 0.048, 0.0547 | 0.048, 0.0547 |
| R1 | 1.25 | 1.25 |
| wR2 | 0.105, 0.107 | 0.105, 0.107 |
| Extinction coefficient | 0.0027(5) | 0.0027(5) |
| Δρ_max, Δρ_min (e·Å⁻³) | 3.16, -2.14 | 3.16, -2.14 |

Fig. 2. SEM-BSE image, detail of Fig 1. Arrow points to a phase with margarosanite end-member composition (GEO-NRM catalogue #19940358).
Table 2. Fractional atomic coordinates, thermal parameters and occupancies.

| Site  | Atom | x/a  | y/b  | z/c  | u eq |
|-------|------|------|------|------|------|
| Ca3a*| Ba   | 0.05053(16) | 0.15010(8) | 0.31843(17) | 0.01179(13) |
| Ca3b*| Pb   | 0.08539(15) | 0.16033(7) | 0.28603(14) | 0.01398(12) |
| Ca1  | Ca   | 0.27312(10) | 0.49225(7) | 0.76280(10) | 0.01143(10) |
| Ca2  | Ca   | 0.43927(9)  | 0.17017(7) | 0.93833(10) | 0.00998(10) |
| Si1  | Si   | 0.09646(13) | 0.77913(10) | 0.15456(14) | 0.00822(13) |
| Si2  | Si   | 0.23222(14) | 0.51723(10) | 0.28343(14) | 0.00817(13) |
| Si3  | Si   | 0.44019(14) | 0.80132(10) | 0.51420(14) | 0.00817(13) |
| O1   | O    | 0.2317(4)   | 0.7409(3)   | 0.9718(4)   | 0.0115(4)   |
| O2   | O    | 0.1029(4)   | 0.1240(3)   | 0.9021(4)   | 0.0126(4)   |
| O3   | O    | 0.228(4)    | 0.8750(3)   | 0.3927(4)   | 0.0126(4)   |
| O4   | O    | 0.0451(4)   | 0.6274(3)   | 0.1970(4)   | 0.0107(4)   |
| O5   | O    | 0.3734(4)   | 0.4423(3)   | 0.0106(4)   | 0.0107(3)   |
| O6   | O    | 0.1304(4)   | 0.4108(3)   | 0.3636(4)   | 0.0140(4)   |
| O7   | O    | 0.3600(4)   | 0.6405(3)   | 0.5074(4)   | 0.0115(4)   |
| O8   | O    | 0.4853(4)   | 0.0943(3)   | 0.2425(4)   | 0.0127(4)   |
| O9   | O    | 0.3856(4)   | 0.2369(3)   | 0.6289(4)   | 0.0111(3)   |

Occupancies: Ca3a = 0.570(4); Ca3b = 0.430(4)

Chemical data were obtained through an FEI Quanta 650 field-emission scanning electron microscope (SEM) fitted with an 80 mm² X-MaxN Oxford Instruments energy-dispersive spectroscopy (EDS) detector (accelerating voltage 20 kV, beam size 1 μm and working distance 10 mm). Beam current was calibrated on Co metal, with the instrument calibrated against reference materials for each element (quartz for Si; wollastonite for Ca, BaF2 for metal, with the instrument calibrated against reference materials.

Micro-Raman measurements were performed using a Horiba (Jobin Yvon) LabRam HR Evolution. Polished sample surfaces were excited with an air-cooled frequency doubled 532 nm Nd:YAG laser utilising an Olympus 100× objective (NA = 0.9). Spectra were generated in the range of 1800 to 200 cm⁻¹ utilising a 600 grooves/cm grating. The spectral resolution was in the order of 1 cm⁻¹ and the lateral resolution was ~1 μm. The wavenumber calibration was done using the 520.7 cm⁻¹ for each element (quartz for Si; wollastonite for Ca, BaF2 for metal, with the instrument calibrated against reference materials.

Selected interatomic distances (Å), angles (°), tetrahedral angle variances (TAV, °²) and quadratic elongations (TQE) according to Robinson et al. (1971) for walstromite-margarosanite.

| Si1–O1 | 1.599(4) | Si2–O4 | 1.684(3) |
|--------|----------|--------|----------|
| Si1–O2 | 1.591(3) | Si1–O3 | 1.683(4) |
| Si1–O4 | 1.600(4) | <Si1–O> | 1.629 |
| V (Å³) | 2.209 |
| TQE   | 1.0033 |
| TAV (²⁻) | 12.051 |
| Co1–O1 | 2.327(3) | Co2–O1 | 2.347(3) |
| Co1–O4 | 2.650(4) | Co2–O2 | 2.304(3) |
| Co1–O5 | 2.444(3) | Co2–O5 | 2.484(3) |
| Co1–O5 | 2.427(3) | Co2–O8 | 2.446(3) |
| Co1–O6 | 2.506(3) | Co2–O8 | 2.335(4) |
| Co1–O6 | 2.811(3) | Co2–O9 | 2.313(4) |
| Co1–O7 | 2.763(3) | <Co2–O> | 2.372 |
| Co1–O9 | 2.386(3) | V (Å³) | 17.384 |
| V (Å³) | 28.040 |
| Co2–O9 | 2.702(3) | Co3b–O9 | 2.655(3) |
| Co2–O8 | 2.304(3) | Co3b–O8 | 2.748(4) |
| Co3a–O6 | 3.035(3) | Co3b–O6 | 2.314(4) |
| Co3a–O2 | 2.805(3) | Co3b–O2 | 2.497(4) |
| Co3a–O3 | 2.926(3) | Co3b–O3 | 2.307(4) |
| Co3a–O4 | 3.362(4) | Co3b–O4 | 2.733(3) |
| Co3a–O3 | 2.790(3) | Co3b–O3 | 4.656(3) |
| Co3b–O2 | 2.891(3) | Co3b–O2 | 2.891(3) |
| Co3b–O3 | 2.795 |
| Co3b–O4 | 37.069 |

Raman spectra

The Raman spectrum of Pb-rich walstromite is affected by both a high fluorescence background (in particular above 800 cm⁻¹) and broadening of peaks (Fig. 3). As expected, there is significant resemblance between the spectra of walstromite and of pure margarosanite (obtained from GEO-NRM #g38818, a Jakobsberg sample). The considerable broadening of the walstromite peaks can be explained by positional disorder induced by randomly distributed Pb/Ba cations; see also Alia et al. (2000).

The prominent Raman band at 654.5 cm⁻¹ obtained for end-member margarosanite is related to Si–O–Si symmetric stretching cycles with single counting times of 45 s in a close to back-scattered geometry, on regions previously analysed during SEM studies.

Mineral chemistry

The sample from the Jakobsberg deposit displays variable Ba–Pb compositions in the range from ca. 50 mol.% margarosanite–50 mol.% walstromite to ca. 30 mol.% margarosanite–70 mol.% walstromite (Fig. 4). The Mn content is low and constant, 0.01–0.02 apfu. No other elements were detected.

Electron probe microanalysis data in the literature show only minor compositional variations for these minerals. Margarosanite from Franklin includes 0.8 wt.% ZnO and 0.6 wt.% MnO (Dunn, 1985), whereas Längban samples could have up to 2.8 wt.% MnO and 0.2 wt.% BaO (Charalampides and Lindqvist, 1988). Walstromite from Fresno, California shows up to 0.4 wt.% SrO, 0.5% wt.% MnO (RRUFF no. R070634.2, Lafuente et al., 2015) and 0.3 wt.% Al₂O₃ (Basciano, 1999), whereas walstromite from Håturim contains up to 0.4 wt.% TiO₂ and 0.7 wt.% SrO (Krzažtala et al., 2020). Furthermore, there is no evidence for substitution between Ca²⁺ and the two larger cations Ba²⁺ and Pb²⁺ in walstromite or margarosanite, respectively. For breyite, no foreign cations are reported (Brenker et al., 2021). Intermediate compositions between margarosanite and walstromite, indicating an extensive solid-solution series, have never been shown to exist up to now.
vibrations in the 3-membered silicate rings, analogous to, e.g. the main band at $\sim 580 \text{ cm}^{-1}$ of benitoite and isostructural minerals (Takahashi et al., 2008) and the corresponding band at 666 nm in roebingite (Långban specimen, RRUFF ID: R140328, Lafuente et al., 2015). This particular band is shifted to 650–648 cm$^{-1}$, and the peak position is sensitive to composition of the analysed spot (shifted to lower frequency with higher BaO contents). The bands at ca. 980–960 are possibly related to Si–O stretching vibrations. Distinct bands at ca. 576 and 493 cm$^{-1}$ are common for all the spectra and due to bending vibrations in the silicate rings (Chukanov and Chervonnyi, 2016). The intense 1010 cm$^{-1}$ band of pure margarosanite has no defined counterpart in walstromite. End-member walstromite has a distinct band at 988 cm$^{-1}$ (measured with a 633-nm laser; Gaft et al., 2013), whereas the present analyses of the Jakobsberg sample shows only a broad feature at ca. 975 cm$^{-1}$.

**Single-crystal structural study**

The minerals of the margarosanite group are Ca-(Ba, Pb) cyclosilicates with three-membered [Si$_3$O$_9$]$^{6-}$ rings (3R) in layers with the apices of alternating rings pointing in opposite directions (Fig. 5a,b). The crystal structure can be described as a closest-packing of O atoms with compact layers parallel to (101), hosting Si and Ca (Ba, Pb) cations at interstitial sites. There are three unique Si sites in each ring, whereas Ca occupies two nonequivalent sites: Ca1 with 8-coordination to O; and Ca2 with 6-coordination. Ba$^{2+}$ and Pb$^{2+}$ reside in a unique 6+4 coordinated position (6+1 for Ca in breyite), within the 3R-layer in a peripheral position.

Trojer (1969) described the structure of 'wollastonite-II' as a high-pressure modification in a synthetic analogue. Later Joswig et al. (2003) described 'CaSiO$_3$-walstromite' and discussed the relationships with 'wollastonite-II'. These authors reported that the axial Si$_3$O$_9$-ring could be isomorphously replaced by the same ring with the 'inverse axiality'. A detailed study by Barkley et al. (2011) showed that the topology is identical (also to walstromite) and that both structures are equivalent after an opportune transformation of coordinates using the matrix

$$
\begin{pmatrix}
1 & 1 & 0 & \frac{1}{2} \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & \frac{1}{2}
\end{pmatrix}
$$

![Fig. 3. Raman spectra obtained with a 532-nm laser. Spectra are displaced 4000–6000 units on the Y axis for clarity.](image)

![Fig. 4. Chemical variation Ba vs. Pb in walstromite–margarosanite based on EDS analyses. The linear regression line ($R^2 = 0.99$) verifies the binary solid solution.](image)
The corresponding unit-cell parameters for wollastonite-II after the transformation are 
\[ a = 6.695, \quad b = 9.429, \quad c = 6.666 \, \text{Å}, \quad \alpha = 83.671, \quad \beta = 76.133 \text{ and } \gamma = 67.639°. \] 
This CaSiO\textsubscript{3} phase was subsequently thus named breyite (Brenker et al., 2021), also corresponding to the ‘walstromite-structured CaSiO\textsubscript{3}’ (e.g. Joswig et al., 1999; Brenker et al., 2007) or ‘CaSiO\textsubscript{3}-walstromite’ (Barkley et al., 2011; Anzolini et al., 2016).

The unit-cell parameters of all the members of the group, including our new data, are given in Table 4. Whereas those are all isotypic, each mineral has unfortunately been described with a different crystallographic setting. The Niggli cell for margarosanite is:
\[ a = 6.696, \quad b = 6.739, \quad c = 9.529 \, \text{Å}, \quad \alpha = 83.04, \quad \beta = 69.81, \quad \gamma = 76.95° \text{ and } V = 392.75 \, \text{Å}^3. \]

The setting used by Freed and Peacor (1969) can be obtained from the Niggli cell using the matrix
\[
\begin{pmatrix}
0 & 1 & 0 \\
0 & 0 & 1 \\
1 & 0 & 0
\end{pmatrix}
\]

The setting used for walstromite by Dent Glasser and Glasser (1968) can be obtained from the Niggli cell using the matrix
\[
\begin{pmatrix}
0 & 1 & 0 \\
0 & 0 & 1 \\
1 & 0 & 0
\end{pmatrix}
\]

The setting used for breyite by Brenker et al. (2021) can be obtained from the Niggli cell using the matrix
\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 0 & 1 \\
0 & 1 & 0
\end{pmatrix}
\]

The 3R-topology of the rings of SiO\textsubscript{4} tetrahedra is almost unique among minerals. Three-membered rings occur in ‘benitoite-group’ minerals (benitoite, bazirite and pabstite; informally grouped by Hawthorne, 1987) as well as in wadeite, calcio-cataleite and cataleite. However, only in the rare complex Pb oxysalt roeblingite, Pb\textsubscript{2}Ca\textsubscript{4}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{4}[Mn(Si\textsubscript{3}O\textsubscript{9})\textsubscript{2}], do the SiO\textsubscript{4} tetrahedra have exactly the same configuration as in margarosanite (Moore and Shen, 1984). In margarosanite and roeblingite the tetrahedra in the 3R units point all up or all down (u\textsubscript{3} or d\textsubscript{3}, following the Hawthorne et al., 2019 coding for nets) alternating in the same plane containing the 3R-units, whereas in the remaining above mentioned 3R-unit silicates the tetrahedra point neither up nor down (o\textsubscript{3}).

The crystal-structure analysis of the Jakobsberg specimen with composition ca. (Ba\textsubscript{0.57}Pb\textsubscript{0.43})Ca\textsubscript{2}Si\textsubscript{3}O\textsubscript{9} confirmed the structure type. In addition, it can be noted that the Ca\textsubscript{3} (Ba, Pb) site is split into two positions separated by 0.392(2) Å, with the position occupied by Ba found slightly more peripheral to the 3R-layers (Fig. 6). Moore et al. (1993) compared the crystal structures of end-member margarosanite and walstromite and found a difference of 0.43 Å, ascribed to the stereochemically active 6\textsuperscript{2} lone

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**Table 4.** Chemical formulae and crystallographic data for margarosanite-group members (natural samples). Triclinic symmetry, space group \( \overline{P\overline{T}} \) and \( Z = 2 \).

| Chemical formulae | Margarosanite\textsuperscript{1} | Walstromite\textsuperscript{2} | Breyite\textsuperscript{3} | Walstromite\textsuperscript{4} |
|------------------|-------------------------------|-----------------------------|---------------------|-----------------------------|
| Unit-cell parameters | PbCa\textsubscript{2}Si\textsubscript{3}O\textsubscript{9} | BaCa\textsubscript{2}Si\textsubscript{3}O\textsubscript{9} | CaCa\textsubscript{2}Si\textsubscript{3}O\textsubscript{9} | (Ba\textsubscript{0.4}Pb\textsubscript{0.6})Ca\textsubscript{2}Si\textsubscript{3}O\textsubscript{9} |
| \( a (\text{Å}) \) | 6.7370(3) | 6.7335(2) | 6.6970(4) | 6.73527(7) |
| \( b (\text{Å}) \) | 9.5295(4) | 9.6142(3) | 9.2986(7) | 9.57172(12) |
| \( c (\text{Å}) \) | 6.6961(3) | 6.6859(2) | 6.638(2) | 6.68718(6) |
| \( \alpha (°) \) | 110.185(2) | 69.638(2) | 83.458(6) | 110.1760(10) |
| \( \beta (°) \) | 103.048(2) | 102.281(2) | 76.226(6) | 102.6060(8) |
| \( \gamma (°) \) | 83.037(2) | 96.855(2) | 69.581(7) | 83.2059(9) |
| \( V (\text{Å}^3) \) | 392.63(3) | 396.01(2) | 376.72(4) | 394.466(7) |

\textsuperscript{1}Callegari et al. (2016); \textsuperscript{2}Barkley et al. (2011); \textsuperscript{3}Brenker et al. (2021); \textsuperscript{4}this work

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Fig. 5. The ‘layer’ of 3-membered rings of SiO\textsubscript{4} tetrahedra in margarosanite (a) and the relative position of sites occupied by Ca (Ca\textsubscript{1} and Ca\textsubscript{2}) and by Pb(Ba) (Ca\textsubscript{3}) (b). Figures obtained with Vesta 3.0 (Momma and Izumi, 2011).
electron pair of the Pb$^{2+}$ ion. An analogous splitting of $\sim$0.5 Å was found in the structure of hyalotekite (Ba,Pb,K)$_2$(Ca,Y)$_2$
(B,Ba)$_2$(Si,B)$_2$Si$_6$O$_{19}$F. Christy et al., 1998), a mineral described for the first time at Långban (Nordenskiöld, 1877).

**Supplementary material.** To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2021.15

**Acknowledgements.** Lennart Ohman (†) and Andreas Borsos called our attention to the blue-fluorescent mineral from Jakobsberg. F.C. acknowledges financial support by the grant "Ricerca Locale 2018–2022". Comments from two anonymous journal reviewers helped to improve the text.

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Comment on Ba–Pb isomorphism

Ba-for-Pb replacement is very rare among silicate minerals, found only in the hyalotekite group (Hawthorne et al., 2018). Members of the feldspar group could potentially host large amounts of Pb, such as in the Pb-rich orthoclase from Broken Hill, NSW, Australia (e.g. Plimer, 1976). Celsian in the present sample has no Pb (at the EDS detection limit, $\geq$ 0.2 wt.% PbO). Celsian from Jakobsberg is shown to be dominantly Al–Si ordered, has the monoclinc I$\overline{2}$/c structure (Griffin and Ribbe, 1976), and is essentially isostructural with ordered synthetic PbAl$_2$Si$_2$O$_8$ (Benna et al., 1996). There is no obvious reason why intermediate (Pb,Ba)Al$_2$Si$_2$O$_8$ compositions should not exist in Nature, in the same fashion as for margarosanite-walstromite, provided that the appropriate bulk composition can be achieved. The most Ba–Pb-rich feldspar known is a hyalophane from the Långban deposit (Christy and Gatedal, 2005). The effect of the Pb$^{2+}$ lone pair in feldspar is displacive for the Pb atoms, and it changes the anion coordination from nominally 7-fold to an irregular 6-fold configuration (Benna et al., 1996). Such phenomena could have an effect on the solid solubility, but are largely still unexplored. Margarosanite is stable to $\sim$800°C at ambient pressure (Jak et al., 1998), whereas walstromite has an extended stability to at least 1200°C (Shukla et al., 2018). No data are available for intermediate compositions of the series. If a solvus exists in it, the corresponding immiscibility gap must lie below the maximum temperature of regional metamorphism, not greatly exceeding 650°C in the area.

**Fig. 6.** The Ca$^3_b$ coordination polyhedron with shifted Pb atoms at the Ca$^3_b$ site due to the lone pair effect of Pb$^{2+}$. Figures obtained with Vesto 3.0 (Momma and Izumi, 2011).
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