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Article

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Calciolangbeinite-*O*, a natural orthorhombic modification of $K_2Ca_2(SO_4)_3$, and the langbeinite–calciolangbeinite solid-solution system

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Abstract

Calciolangbeinite, ideally $K_2Ca_2(SO_4)_3$, exists in two modifications, cubic and, first described in the present paper, orthorhombic. They are topologically-similar polymorphs which can be designated as calciolangbeinite-*C* and calciolangbeinite-*O*. Calciolangbeinite-*O* is the first natural orthorhombic langbeinite-like sulfate. It clearly differs from calciolangbeinite-*C* in the powder X-ray diffraction pattern, optical data and Raman spectrum. Calciolangbeinite-*O* is found in sublimates of the active Arsenatnaya fumarole at the Tolbachik volcano, Kamchatka, Far Eastern Region, Russia and in pyrometamorphic rocks of the Hatrurim Complex at Jabel Harmun, Judean Desert, Palestinian Autonomy and Har Parsa, Negev Desert, both in Israel. Calciolangbeinite-*C* is known only in fumarole sublimates at Tolbachik. Calciolangbeinite forms a continuous solid-solution system with langbeinite $K_2Mg_2(SO_4)_3$. The majority of the system is represented by cubic phases, and only members with compositions $K_2(Ca_{2.0-1.9}Mg_{0.0-0.1})(SO_4)_3$ have orthorhombic symmetry under room-temperature conditions. The crystal structure of calciolangbeinite-*O* was studied on a single crystal, chemically very close to $K_2Ca_2(SO_4)_3$, from Tolbachik ($R_1 = 2.75\%$). The unit-cell parameters are: $a = 10.3330(2)$, $b = 10.5027(2)$, $c = 10.1763(2)$ Å, $V = 1104.37(4)$ Å^3 and $Z = 4$; space group is $P2_12_12_1$. Calciolangbeinite-*O* is a low-temperature modification of $K_2Ca_2(SO_4)_3$ belonging to the $K_2Cd_2(SO_4)_3$ structure type whereas calciolangbeinite-*C* (space group $P2_13$), a high-temperature modification, has the langbeinite-type structure. The significant Mg admixture in calciolangbeinite-*C* from Tolbachik probably stabilises its cubic structure at room temperature. In both high-temperature fumaroles and pyrometamorphic rocks calciolangbeinite crystallises in the cubic modification, and during cooling its chemical variety close to the end-member $K_2Ca_2(SO_4)_3$ undergoes phase transition to calciolangbeinite-*O*, whereas the Mg-enriched varieties of the mineral remain calciolangbeinite-*C*.

Keywords: calciolangbeinite-*O*, calciolangbeinite-*C*, langbeinite group, fumarole sublimate, pyrometamorphic rock, Tolbachik volcano, Hatrurim Complex

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Introduction

The langbeinite group includes five isostructural cubic (space group $P2_13$) double sulfates: the widespread langbeinite $K_2Mg_2(SO_4)_3$ (Anthony *et al.*, 2003) and four rare mineral species, namely efremovite $(NH_4)_2Mg_2(SO_4)_3$ (Shcherbakova and Bazhenova, 1989; Shimobayashi *et al.*, 2011), ferroefremovite $(NH_4)_2Fe^{2+}_2(SO_4)_3$ (Kasatkin *et al.*, 2021), calciolangbeinite $K_2Ca_2(SO_4)_3$ (Pekov *et al.*, 2012), and an insufficiently studied manganolangbeinite $K_2Mn_2(SO_4)_3$ (Zambonini and Carobbi, 1924; Bellanca, 1947). All these minerals are known in exhalations of volcanic fumaroles and in their genetic counterparts related to natural or anthropogene coal fires (see references above); moreover, all members of the group, except langbeinite, a typical evaporite mineral, have only been described from fumaroles or so called 'pseudo-fumaroles'.

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In this paper we characterise an orthorhombic (space group $P2_12_12_1$) modification of $K_2Ca_2(SO_4)_3$, new for Nature and found in two regions, Kamchatka, Far-Eastern Region, Russia and Israel, in different geological environments. It is the first natural langbeinite-like sulfate with orthorhombic symmetry that differs clearly from cubic calciolangbeinite in the powder X-ray diffraction pattern, optical data and Raman spectrum. However, cubic and orthorhombic forms of $K_2Ca_2(SO_4)_3$ possess the same topology of crystal structure: the structure of the orthorhombic modification can be derived from the cubic one by distortion (see below). Such cases are regulated by the rules of the current mineral nomenclature: "*…if the crystal structures of the polymorphs have essentially the same topology, differing only in terms of a structural distortion or in the order–disorder relationship of some of the atoms comprising the structure, such polymorphs are not regarded as separate species, and the names of such topologically-similar polymorphs can be distinguished by the addition of crystallographic suffixes to the mineral name*" (Nickel and Grice, 1998). Thus, cubic and orthorhombic modifications of $K_2Ca_2(SO_4)_3$ are *topologically-similar polymorphs* and, from the nomenclature viewpoint, can be considered as structural varieties (or, maybe, the term 'sub-species' would be more correct) of the mineral species calciolangbeinite. Such varietal names should include the corresponding crystallographic suffixes, therefore, cubic calciolangbeinite described by Pekov *et al.* (2012) is now calciolangbeinite-*C* whereas its orthorhombic dimorph first described in the present paper is calciolangbeinite-*O*. Though no new mineral name has been introduced, and thus no official Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA) approval is necessary, we did discuss the naming of these varieties with the officers of the IMA and received approval.

In addition to the characterisation of calciolangbeinite-*O*, in this paper we give new data on calciolangbeinite-*C*, discuss the relationship between cubic and orthorhombic modifications of $K_2Ca_2(SO_4)_3$ and describe a novel solid-solution system between langbeinite and calciolangbeinite.

Occurrence and general appearance

The Kamchatka samples of calciolangbeinite-*O* originate from the active Arsenatnaya fumarole located at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano (55°41'N, 160°14'E). The Arsenatnaya fumarole is one of the mineralogically interesting fumaroles at the Tolbachik volcano. It was described by Pekov *et al.* (2014, 2018) and Shchipalkina *et al.* (2020). Calciolangbeinite-*O* occurs in the intermediate, so-called polymineralic zone of the fumarole. Temperatures measured by us using a chromel–alumel thermocouple in areas with this sulfate at the time of its collecting in 2013, 2014 and 2015 were 300–380°C. Calciolangbeinite-*O* forms interrupted porous crusts up to 1 cm × 1.5 cm in area and up to 0.5 mm thick on basalt scoria altered by fumarole gas, or on incrustations consisting mainly of sublimate silicates (sanidine and/or fluorophlogopite) and oxides (hematite and tenorite) overgrowing basalt scoria (Figs 1 and 2). Other associated minerals are aphthitalite, metathénardite, belomarinaite, langbeinite, calciolangbeinite-*C*, anhydrite, arcanite, krasheninnikovite, wulffite, fluoborite, pseudobrookite, gahnite, corundum, johillerite, nickenichite, bradaczekite, svabite, tilasite, lammerite, lammerite-β, urusovite, ericlaxmanite, kozyrevskite and popovite. Irregularly shaped single-crystal individuals of calciolangbeinite-*O* in the crusts are up to 0.3 mm across.

In Israel, calciolangbeinite-*O* has been described from two localities, as 'calciolangbeinite', by Galuskina *et al.* (2014) and Galuskin *et al.* (2016). At Jabel Harmun, Judean Desert, West Bank, Palestinian Autonomy (31°46′N, 35°26′E) calciolangbeinite-*O* was identified in the specimen described as the holotype of harmunite (Galuskina *et al.*, 2014). This sample is a fragment of larnite pseudoconglomerate, a pyrometamorphic rock belonging to the well-known Hatrurim Complex (Gross, 1977; Novikov *et al.*, 2013). Calciolangbeinite-*O* together with aphthitalite and minor thénardite fill small fractures on the boundary between porous ferrite aggregate (consisting of magnesioferrite, srebrodolskite and harmunite) and a rock mainly composed of larnite, fluorellestadite, ye'elimite, gehlenite, ternesite and fluormayenite–fluorkyuygenite and brownmillerite–srebrodolskite series minerals. Here calciolangbeinite-*O* forms interrupted granular incrustations up to 0.15 mm thick and up to 1 mm^2 in area (Fig. 3a). The size of its single-crystal grains usually do not exceed 0.1 mm. The formation of görgeyite $K_2Ca_5(SO_4)_6{\cdot}H_2O$ in the areas of supergene alteration of calciolangbeinite-*O* was observed (Fig. 3b). At Har Parsa, Hatrurim Basin, Negev Desert calciolangbeinite-*O* was detected in a pyrometamorphic rock which mainly consists of larnite and contains ternesite. Calciolangbeinite-*O* fills channels ~0.1 mm in diameter hosting gas bubbles and also occurs in intergranular cavities on the front of growth of ternesite poikilitic crystals (Galuskin *et al.*, 2016).

In the present paper, calciolangbeinite-*O* from Tolbachik and Jabel Harmun is characterised.

Calciolangbeinite-*C* was described originally from the Yadovitaya (Poisonous) fumarole at the same Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, (as 'calciolangbeinite': Pekov *et al.*, 2012). Later, in 2013 we also found it in the Arsenatnaya fumarole, in the same mineral association as calciolangbeinite-*O*. In the majority of samples, these varieties of calciolangbeinite are visually indistinguishable from one another. A common specimen of calciolangbeinite-*C* from the Arsenatnaya fumarole is shown in Fig. 4. However, in some samples well-shaped crystals of

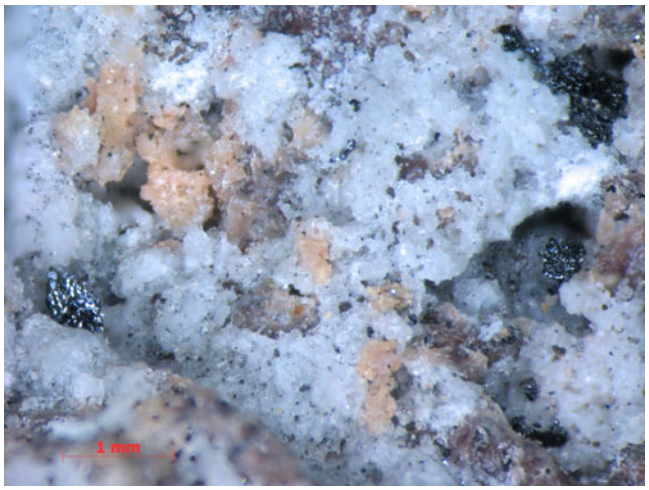


Fig. 1. Porous interrupted crust of colourless to white calciolangbeinite-*O* with iron-black tenorite overgrowing beige sanidine and reddish-brown basalt scoria altered by fumarole gas. Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. FOV width: 5.7 mm. Photo: I.V. Pekov & A.V. Kasatkin.

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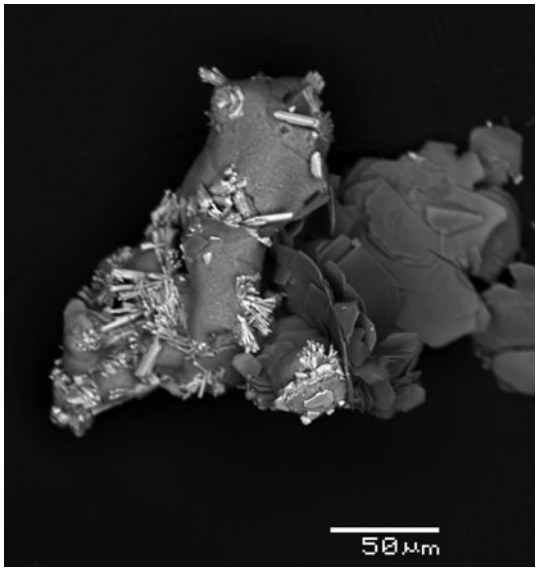


Fig. 2. Calciolangbeinite-*O* crust overgrowing aggregates of lamellar crystals of fluorophlogopite and long-prismatic crystals of johillerite (white). Arsenatnaya fumarole, Tolbachik volcano. SEM back-scattered electron image.

calciolangbeinite-*C* occur (Fig. 5), unlike calciolangbeinite-*O* which was observed only as irregularly shaped individuals (Figs 1 and 2). Langbeinite with different contents of admixed Ca is widespread in sublimates of both Arsenatnaya and Yadovitaya fumaroles. The most common variety of Tolbachik fumarolic langbeinite is Ca-poor (<1 wt.% CaO).

Physical properties and optical data of calciolangbeinite-*O*

Calciolangbeinite-*O* is transparent or, in aggregates, translucent, with vitreous lustre. It is colourless to white; some specimens from Tolbachik are orange-reddish to reddish-brown or greenish due to the presence of scattered micro-inclusions of hematite or copper arsenates, respectively. It is brittle, cleavage or parting was not observed. The fracture is uneven or conchoidal. The Mohs hardness is *ca.* 3. Density calculated for the sample from Tolbachik using the empirical formula and unit-cell volume determined from the single-crystal X-ray diffraction (XRD) data is 2.685 g cm^{-3}.

In plane polarised transmitted light, calciolangbeinite-*O* from Tolbachik is colourless and non-pleochroic. It is optically biaxial (+), $\alpha = 1.475(3)$, $\beta = 1.490(2)$, $\gamma = 1.508(3)$ (589 nm); $2V_{meas.} = 85(5)°$; and $2V_{calc.} = 86°$. Dispersion of optical axes was not observed.

Raman spectroscopy

The data on analytical technique and conditions are given as supplementary information.

The Raman spectra of calciolangbeinite-*O* from Jabel Harmun and from Tolbachik (Figs 6a–c) are similar to one another and clearly differ from the spectra of calciolangbeinite-*C* (Fig. 6d) and langbeinite (Fig. 6e).

The assignments of Raman bands for calciolangbeinite-*O* made in accordance with Prieto-Taboada *et al.* (2019) are given in Table 1. All bands with Raman shifts above 300 cm^{-1} correspond to vibrations in $(SO_4)^{2-}$: ν_3 is 1090–1180 cm^{-1}; ν_1 is 996, 1011 and 1021 cm^{-1}; ν_4 is 700–550 cm^{-1}; and ν_2 is 550–400 cm^{-1}. Very weak unresolved bands below 200 cm^{-1} (in the spectrum of calciolangbeinite-*O* from Jabel Harmun) correspond to external modes involving K···O and Ca···O stretching vibrations ('···' denotes weak non-covalent bonds) as well as libration and translational vibrations of SO_4^{2-} as a whole (Table 1). The very weak band at 3520 cm^{-1} in the Raman spectrum of calciolangbeinite-*O* from Jabel Harmun is probably caused by a minor impurity of görgeyite (see Fig. 6b).

In the Raman spectrum of Ca-free langbeinite from the Stebnik potassium salt deposit, Ukraine (Fig. 3e), the total number of bands is less than in the spectra of calciolangbeinite-*O* because the SO_4 tetrahedron occupies only one site in the structure of the former. This is confirmed by the presence of a single band at 1053 cm^{-1} corresponding to the nondegenerate symmetric S–O stretching mode. This band is shifted towards higher frequencies as compared to analogous

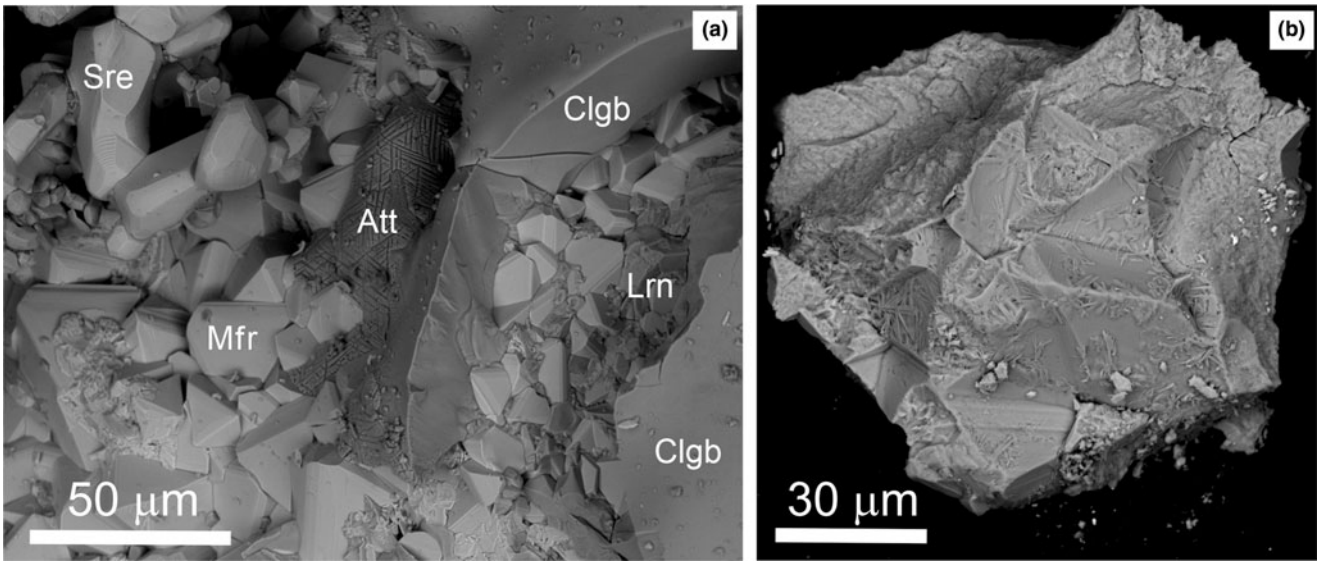


Fig. 3. (a) Crust of calciolangbeinite-*O* (Clgb) and aphthitalite (Att) on magnesioferrite (Mfr) aggregate with larnite (Lrn) and srebrodolskite (Sre) from Jabel Harmun, Palestine Autonomy, Israel. (b) Grain of calciolangbeinite-*O* extracted from the aggregate shown in Fig. 3a, which after a few days was partially covered by tiny acicular görgeyite crystals.

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Fig. 4. Numerous reddish-brown (impregnated with hematite micro-inclusions) aggregates of calciolangbeinite-*C* overgrowing a white sanidine crust. Arsenatnaya fumarole, Tolbachik volcano. FOV width: 3.2 mm. Photo: I.V. Pekov & A.V. Kasatkin.

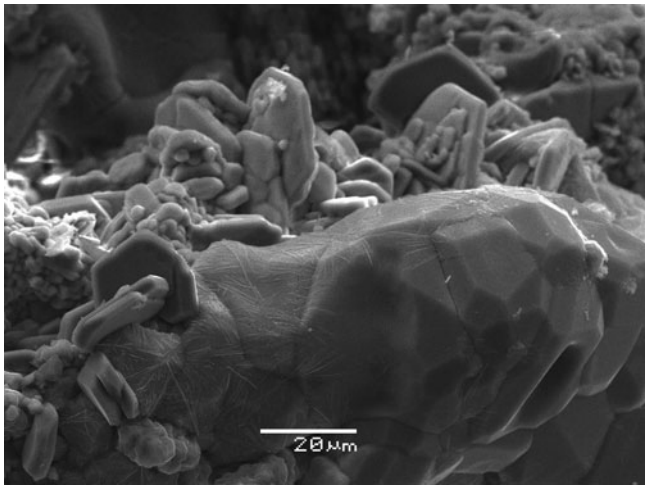


Fig. 5. Compact aggregate of well-shaped calciolangbeinite-*C* crystals with numerous hexagonal flattened corundum crystals. Arsenatnaya fumarole, Tolbachik volcano. SEM (SE) image.

bands of calciolangbeinite which confirms the involvement of Mg cations in S–O stretching vibrations. The shoulder at 1004 cm^{-1} and a poor resolution of Raman bands in the range 600–670 cm^{-1} in the spectrum of calciolangbeinite-*C* from the Arsenatnaya fumarole (Fig. 3d) may be due to a different local environment around the SO_4^{2-} anion (presumably, without Mg and including Mg).

Thus, Raman spectroscopy seems a good, express tool to distinguish calciolangbeinite-*C* and calciolangbeinite-*O*, especially in micro-samples.

Chemical composition

The chemical composition of the langbeinite-group minerals studied from the Arsenatnaya fumarole was determined in the Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University (MSU), using a Jeol JSM–6480LV scanning electron microscope (SEM) equipped with an INCA-Wave 500 wavelength-dispersive spectrometer. The conditions were: an acceleration voltage of 20 kV, a beam current of 20 nA and a 5 µm beam diameter. Calciolangbeinite-*O* from Jabel Harmun was studied using a Philips XL30 scanning electron microscope in EDS mode (Laboratory of Electron Microscopy, Faculty of Earth Sciences, University of Silesia (UoS), Sosnowiec) with an acceleration voltage of 15 kV, a beam current of 1 nA, and a ~5 µm beam diameter.

The following standards were used (MSU / UoS): Na (albite / albite), K (microcline / orthoclase), Rb ($Rb_2Nb_4O_{11}$ / –), Mg (diopside / diopside), Ca ($CaSiO_3$ / anhydrite), and S ($SrSO_4$ / anhydrite). Contents of other elements with atomic numbers higher than carbon are below detection limits.

The chemical composition of the samples studied is given in Table 2. The empirical formulae were calculated on the basis of 12 O atoms per formula unit (apfu). The ratios of Ca and Mg, the major octahedrally coordinated cations *M* are shown in Fig. 7.

In general, the samples studied correspond well to the formula $A_2^+M_2^{2+}(SO_4)_3$ in which the major cations *M* = Mg or Ca with minor admixtures (≤ 0.08 apfu together) of Mn, Fe, Cu, Zn and/or Al, and *A* = K >> Na, Rb. Two samples (an. ## 6 and 7 in Table 2) contain less K (1.5–1.6 apfu) and larger amounts of bivalent cations: Ca + Mg = 2.2–2.3 apfu.

X-ray crystallography and crystal structure of calciolangbeinite-*O*

The data on analytical technique and conditions for both powder and single-crystal XRD studies are given in the Supplementary material (see below).

The powder XRD data of calciolangbeinite-*O* from Tolbachik are given in Table 3. Parameters of the orthorhombic unit cell calculated from the powder data are: *a* = 10.341(2), *b* = 10.509(3), *c* = 10.175(2) Å and *V* = 1105.8(8) $Å^3$.

The single-crystal XRD study of calciolangbeinite-*O* from Jabel Harmun gave the following parameters of the orthorhombic unit cell: *a* = 10.2828(2), *b* = 10.4675(2), *c* = 10.0996(3) Å and *V* = 1087.07(4) $Å^3$.

Single-crystal XRD studies of calciolangbeinite-*O* from Tolbachik were carried out using an Xcalibur S diffractometer equipped with a CCD detector. A full sphere of three-dimensional data was collected. Crystal data, data collection information and structure refinement details are given in Table 4. Data reduction was performed using *CrysAlisPro* Version 1.171.35.21 (Agilent Technologies, 2012). The XRD data were corrected for Lorentz factor and polarisation effects. The structure was solved by direct methods and refined with the use of *SHELX* software package (Sheldrick, 2008) on the basis of 4405 unique reflections with $I > 2\sigma(I)$ to the final *R* = 0.0275. Atom coordinates, their displacement parameters and bond-valence sums are given in Table 5 and selected interatomic distances in Table 6. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

As crystal structure data show, calciolangbeinite-*O* is a natural analogue of synthetic orthorhombic $K_2Ca_2(SO_4)_3$ (Speer and Salje, 1986), a representative of the structure type of $K_2Cd_2(SO_4)_3$ which is a distorted derivative of the cubic langbeinite-type structure (Abrahams and Bernstein, 1977). The crystal structure of calciolangbeinite-*O* (Fig. 8) is based upon the three-dimensional complex framework formed by $Ca(1)O_6$ and $Ca(2)O_6$ octahedra and SO_4 tetrahedra. Two crystallographically non-equivalent Ca sites centre *M* octahedra with mean Ca–O

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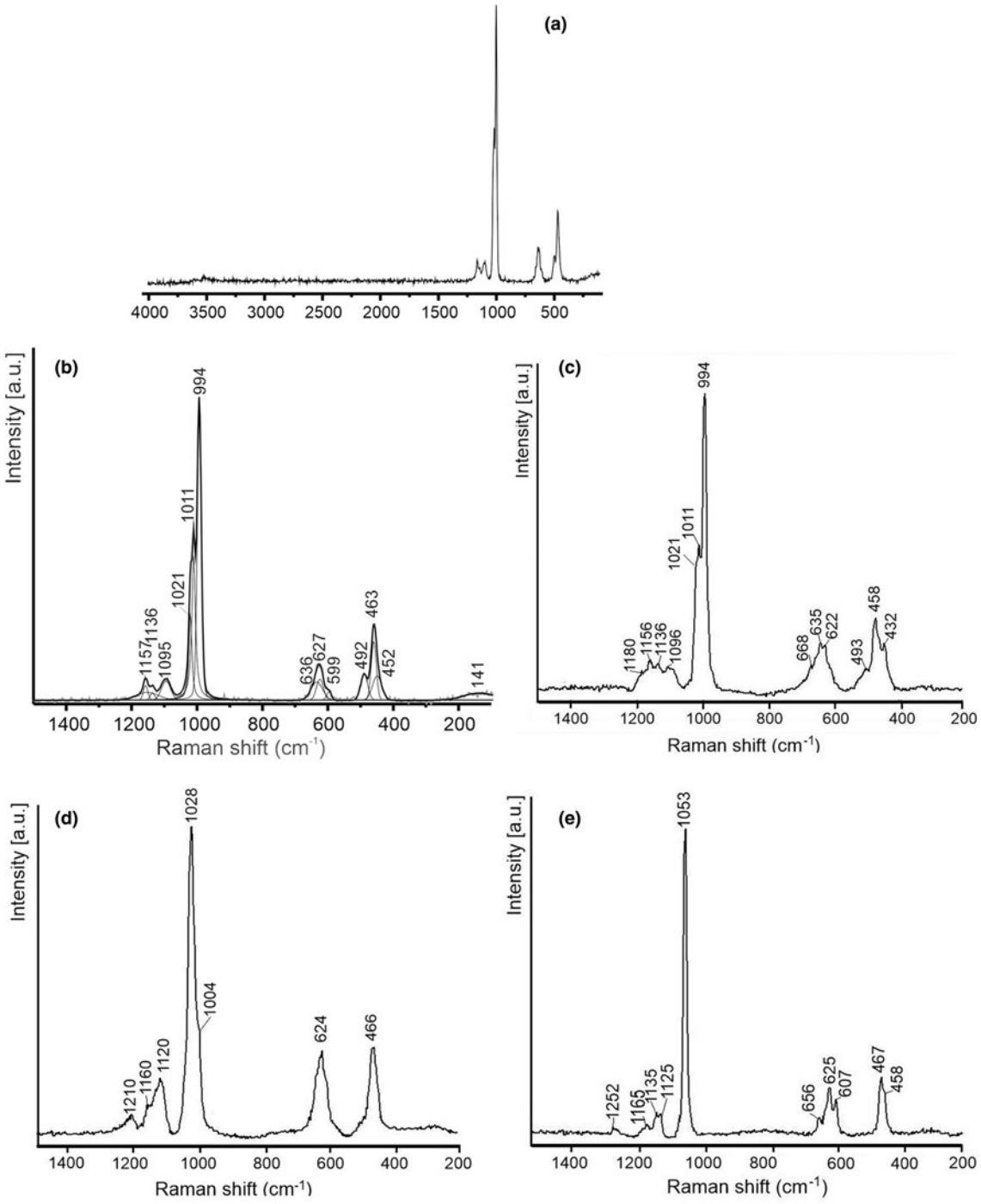


Fig. 6. The Raman spectra of (a, b) calciolangbeinite-*O* from Jabel Harmun, Israel (a – spectrum in the range 100–4000 cm^{-1}, b – in the range 100–1500 cm^{-1}); (c) calciolangbeinite-*O* from Arsenatnaya fumarole, Tolbachik, Kamchatka, Russia; (d) calciolangbeinite-*C* from Arsenatnaya fumarole; (e) langbeinite from Stebnik potassium salt deposit, Ukraine.

distances of 2.351 [Ca(1)] and 2.337 Å [Ca(2)]. There are three crystallographically non-equivalent S sites centring tetrahedra with mean S–O distances of 1.470 [S(1)], 1.467 [S(2)] and 1.466 Å [S(3)] (Table 6). Each CaO_6 octahedron shares all oxygen vertices with SO_4 tetrahedra and thus there is no linkage between CaO_6 polyhedra. Potassium atoms occupy two crystallographically non-equivalent sites in the voids of the framework: K(1) cations are located in ten-fold polyhedra while K(2) cations centre nine-fold polyhedra. The K–O distance limit was 3.3 Å.

Discussion

Solid-solution series between langbeinite and calciolangbeinite

As our data on Tolbachik samples show (Fig. 7; Table 2), a solid-solution system between langbeinite and calciolangbeinite exists, and the samples studied occupy the whole compositional range from $K_2Mg_2(SO_4)_3$ to $K_2Ca_2(SO_4)_3$. In the langbeinite part of the series, most analyses lie in the region $(Mg_{2.0–1.6}Ca_{0.0–0.4})$

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Table 1. Raman shifts (cm^{-1}) of bands in Raman spectra of calciolangbeinite-*O*, calciolangbeinite-*C* and langbeinite and their assignment, in accordance with Nakamoto (2008).

Assignment	Calciolangbeinite-*O* Tolbachik, Kamchatka, Russia	Calciolangbeinite-*O* Jabel Harmun, Israel	Calciolangbeinite-*C* Tolbachik, Kamchatka, Russia	Langbeinite Stebnik, Ukraine
Lattice modes (K···O and Ca···O stretching and/or SO_4^{2-} libration and translation)	-	141 vw, br	-	-
ν_2 (E) bending mode of SO_4^{2-}	432	452 sh	466	458 sh
	458	463		467
	493 sh	492		
ν_4 (F_2) bending mode of SO_4^{2-}	622	599 sh	624	607
	635	627		625
	668	636 sh		656 w
ν_1 (A_1) symmetric stretching mode of SO_4^{2-}	994 s	994 s	1004 sh	1053 s
	1011	1011	1028 s	
	1021 sh	1021 sh		
ν_3 (F_2) stretching mode of SO_4^{2-}	1096	1095	1120	1125
	1136	1136 w	1160 sh	1135
	1156	1157	1210 w	1165 w
	1180 sh			1252 w

Characteristics of spectral bands: s – strong, w – weak, vw – very weak, sh – shoulder, br – broad.

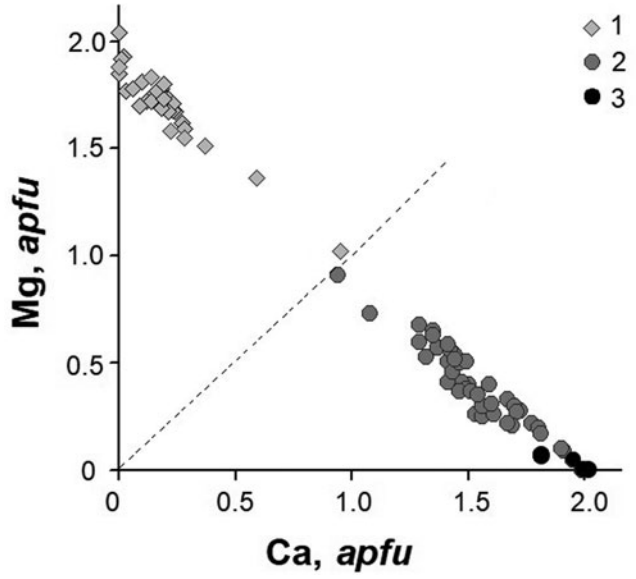


Fig. 7. Ratios of the major *M* cations: Mg and Ca in minerals of the langbeinite–calciolangbeinite solid-solution series from fumaroles of the Tolbachik volcano, Kamchatka, Russia: 1 – langbeinite; 2 – calciolangbeinite-*C*; 3 – calciolangbeinite-*O*.

and in the calciolangbeinite part – in the region ($Ca_{1.2–2.0}Mg_{0.8–0.0}$), whereas in the middle part, with ($Mg_{1.6–0.8}Ca_{0.4–1.2}$), only a few samples were found (Fig. 7). We suggest that it could be caused by the significant difference in ionic radii of Mg^{2+} and Ca^{2+} which hampers their occurrence in comparable amounts in the same *M* sites in the structure. For samples which contain fewer univalent cations (first of all, K) and more bivalent cations (Ca + Mg) in comparison with the idealised general formula $A_2^+M_2^{2+}(SO_4)_3$ (see, e.g. an. ## 6 and 7 in Table 2), we suggest partial substitution of K by Ca.

Scanning electron microscopic, XRD and Raman spectroscopic data confirm that the samples studied represent a homogeneous solid solution and not micro-intergrowths of Mg- and Ca-rich phases formed as a result of its exsolution. The Raman spectroscopy turned out to be both a reliable and express tool for checking the homogeneity of the langbeinite-type minerals and the identification of the calciolangbeinite form as cubic or orthorhombic (Fig. 6). The Raman spectra obtained for samples studied by electron microprobe showed that the border between calciolangbeinite-*C* and calciolangbeinite-*O* under room-temperature conditions lies near the following ratio of *M* cations: $Ca_{1.9}Mg_{0.1}$: the Mg-poorest samples belong to calciolangbeinite-*O* while the samples with Mg > 0.1 apfu correspond to calciolangbeinite-*C* (Fig. 7).

It is noteworthy that the continuous solid-solution series between synthetic $K_2Mg_2(SO_4)_3$ and $K_2Ca_2(SO_4)_3$ has been known since 1935. It was synthesised and studied using powder XRD by Ramsdell (1935) who reported that the calcium end-member of the series demonstrates a poor-quality (with diffuse reflections) langbeinite-type diffraction pattern and is optically birefringent, unlike $K_2Mg_2(SO_4)_3$ which is a full analogue of langbeinite. The synthetic solid solution $K_2Mg_2(SO_4)_3$–$K_2Ca_2(SO_4)_3$ was later studied in more detail and it was found that members of the series with >73.5 wt.% $K_2Ca_2(SO_4)_3$ are optically biaxial at room temperature whereas at 200°C all members of the series are isometric (Morey *et al.*, 1964). However, the structural study of $K_2Ca_2(SO_4)_3$ was carried out only in the 1980s (Speer and Salje, 1986).

Relationship between calciolangbeinite-O, calciolangbeinite-C and synthetic langbeinite-like sulfates with the general formula $K_2M_2+2(SO_4)_3$ in which M = Ca, Cd, Zn, Co, Ni or Mg

Orthorhombic [space group $P2_12_12_1$, structure type of $K_2Cd_2(SO_4)_3$] and cubic [space group $P2_13$, structure type of langbeinite] structural varieties ('sub-species') of calciolangbeinite, a mineral with the idealised, end-member formula $K_2Ca_2(SO_4)_3$, are dimorphous. The structural difference between cubic and orthorhombic modifications of this sulfate is in significant tilting of SO_4 tetrahedra, shifting of Ca and K sites and thus the distortion of the heteropolyhedral, octahedral–tetrahedral framework in calciolangbeinite-*O* in comparison with calciolangbeinite-*C*.

Dimorphism of synthetic $K_2Ca_2(SO_4)_3$ (Table 7) was studied by Speer and Salje (1986) who solved crystal structures of both modifications of this sulfate and found that the temperature of

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Table 2. Chemical composition (wt.%) and empirical formulae of minerals of the langbeinite–calciolangbeinite solid-solution system.

No.	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]	[16]
Wt.%																
Na_2O		0.51	0.48	0.34	0.94	0.41	1.37	0.38	0.40	0.56	0.30	0.60	0.35	0.13		
K_2O	22.70	21.44	21.37	21.66	22.11	16.79	17.78	21.85	20.97	20.66	21.03	19.64	21.12	20.46	21.02	21.10
Rb_2O		0.42		0.29	0.22	0.23			0.33	0.29		0.59	0.48	0.56		
MgO	19.42	19.22	17.71	15.94	14.36	12.38	9.53	6.52	6.17	5.39	4.78	0.74				
CaO		0.13	2.87	3.44	5.04	13.77	15.13	16.00	16.29	16.26	19.45	23.98	24.37	24.59	25.57	25.12
MnO		0.29	0.41	0.38	0.24	0.26	0.27			0.21	0.32					
FeO			0.05				0.13	0.08		0.20	0.15					
CuO				0.79	0.44	0.10				0.87						
ZnO				0.40		0.53										
Al_2O_3			0.07				0.05	0.09			0.06					
SO_3	57.88	57.30	57.52	56.72	57.48	57.97	55.10	55.14	54.19	53.92	54.52	53.77	54.31	53.69	53.41	53.78
Total	100	99.02	100.36	99.99	100.83	100.42	99.35	100.63	98.56	98.36	100.51	99.32	100.63	99.43	100.00*	100
Empirical formula calculated based on 12 O atoms per formula unit																
Na		0.07	0.06	0.05	0.13	0.06	0.19	0.05	0.06	0.08	0.04	0.09	0.05	0.02		
K	2	1.91	1.89	1.94	1.97	1.50	1.62	2.01	1.98	1.96	1.95	1.87	1.99	1.95	2.00	2
Rb		0.02		0.01	0.01	0.01			0.02	0.01		0.03	0.02	0.03		
Mg	2	2.00	1.83	1.67	1.49	1.29	1.02	0.70	0.68	0.60	0.52	0.08				
Ca		0.01	0.21	0.26	0.38	1.03	1.16	1.24	1.29	1.29	1.52	1.91	1.93	1.97	2.04	2
Mn			0.02	0.02	0.01	0.01	0.02	0.02		0.01	0.02					
Fe			-				0.01	-		0.01	0.01					
Cu				0.04	0.02	0.01				0.05						
Zn				0.02		0.03										
Al			0.01				-	0.01			0.01					
S	3	3.00	2.99	2.99	3.01	2.95	2.96	3.00	3.00	3.00	2.98	3.00	3.01	3.01	2.99	3
$\sum Me$	4	4.01	4.02	4.01	4.01	3.94	4.02	4.03	4.03	4.01	4.07	3.98	3.99	3.97	4.04	4

[1] – $K_2Mg_2(SO_4)_3$; [2–6] – langbeinite; [7–11] – calciolangbeinite-*C*; [12–15] – calciolangbeinite-*O*; [16] – $K_2Ca_2(SO_4)_3$; [2–14] – Tolbachik volcano, Kamchatka, Russia [3, 7, 8 and 11] – Yadovitaya fumarole, others – Arsenatnaya fumarole); [15] – Jabel Harmun, Israel; [3, 7, 8 and 11] – after Pekov *et al.* (2012), others – this work. Analyses [8] and [14] represent the composition of samples on which the crystal structures of calciolangbeinite-*C* and calciolangbeinite-*O*, respectively, were solved. *Analytical total was normalized for 100 wt.%. Σ*Me* is the sum of all metal cations. Empty cell means that the content of a constituent is below detection limit and dash means 0.00 apfu (for minor admixtures).

the phase transition from high-temperature cubic langbeinite-type modification ($P2_13$, the structure was studied at 260°C) to the orthorhombic low-temperature modification ($P2_12_12_1$, the structure was studied at room temperature) is 184°C. Orthorhombic $K_2Ca_2(SO_4)_3$ belongs to the structure type of $K_2Cd_2(SO_4)_3$ attracting research attention due to ferroelastic properties (Abrahams and Bernstein, 1977). $K_2Cd_2(SO_4)_3$ demonstrates the same dimorphism as $K_2Ca_2(SO_4)_3$ with the temperature of transition from high-temperature cubic modification to low-temperature (room-temperature) orthorhombic form equal to 159°C. Unlike these two compounds, sulfates $K_2M_2^{2+}(SO_4)_3$ with M = Mg, Ni, Co and Zn belong to the langbeinite structure type (cubic, $P2_13$) at room temperature. In general, the temperature of transition from a cubic, langbeinite-type modification to the orthorhombic, $K_2Cd_2(SO_4)_3$-type modification for sulfates $K_2M_2^{2+}(SO_4)_3$ clearly depends on the ionic radius of M^{2+} [radius of M^{2+} for octahedral oxygen coordination, after Shannon (1976), is given below in square brackets]: 184°C for $K_2Ca_2(SO_4)_3$ [Ca: 1.00 Å], 159°C for $K_2Cd_2(SO_4)_3$ [Cd: 0.95 Å], –135°C for $K_2Zn_2(SO_4)_3$ [Zn: 0.74 Å] and –148°C for $K_2Co_2(SO_4)_3$ [Co: 0.745 Å]. Orthorhombic modifications are unknown for $K_2Mg_2(SO_4)_3$ [Mg: 0.72 Å] and $K_2Ni_2(SO_4)_3$ [Ni: 0.69 Å] (Speer and Salje, 1986).

Note also that both cubic and orthorhombic modifications of langbeinite-type $K_2Mn_2(SO_4)_3$ (Oelkrug *et al.*, 1988) and cubic $K_2Fe_2(SO_4)_3$ (Lander *et al.*, 2017) are known among synthetic compounds. Synthetic sulfates $K_2Cu_2(SO_4)_3$ and $Rb_2Cu_2(SO_4)_3$, as well as so-called 'hydrolangbeinite' $Rb_2Cu_2(SO_4)_3(H_2O)$, having the langbeinite-type stoichiometry, differ from langbeinite-type compounds in both structure and unit-cell metrics (Lander *et al.*, 2017; Siidra *et al.*, 2021), due to the Jahn-Teller distortion of the Cu^{2+}-centred polyhedra. It is also noteworthy that such Cu-bearing sulfates are described as synthetic analogues of fumarolic minerals (Siidra *et al.*, 2021).

In terms of crystal structure, the difference between calciolangbeinite-*C* and calciolangbeinite-*O* is mainly in the configuration of the langbeinite-type 3D heteropolyhedral *M*–S–O framework: it is distorted in calciolangbeinite-*O* in comparison with the cubic modification (see above) (Fig. 9). Such distortion was reported for synthetic $K_2Ca_2(SO_4)_3$ by Speer and Salje (1986) who noticed, in particular, that in the orthorhombic modification the average Ca–O distances become longer in heavily distorted octahedra in comparison with the cubic form whereas the average K–O distances become shorter and SO_4 tetrahedra shift and rotate during the phase transition. In the discussed natural pair, we see the same situation: the average *M*–O distances in calciolangbeinite-*O* are longer but it is not possible to compare these values correctly due to the presence of a significant Mg admixture in both *M* sites in calciolangbeinite-*C* whereas the *M* sites in calciolangbeinite-*O* are occupied only or almost only by Ca cations. Considering the distance ranges in MO_6 octahedra, the orthorhombic mineral demonstrates a greater range of values: from 2.319 to 2.389 Å and from 2.308 to 2.366 Å in calciolangbeinite-*O*, whereas in calciolangbeinite-*C* these values vary from 2.202 to 2.204 Å and from 2.194 to 2.198 Å, respectively. The values of the distortion index of the *M*-centred octahedra (calculated using the *Vesta* program: Momma and Izumi, 2011) in calciolangbeinite-*O* are 0.013 and 0.005 whereas in calciolangbeinite-*C* these values are 0.000 and 0.001. At the same time, SO_4 tetrahedra are more distorted in calciolangbeinite-*C*, with the S–O distances in the range from 1.430 to 1.458 Å and distortion index 0.006, whereas in calciolangbeinite-*O* three crystallographically non-equivalent tetrahedra have S–O distances in the ranges from 1.463 to

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Table 3. Powder X-ray diffraction data (*d* in Å) of calciolangbeinite-*O* and calciolangbeinite-*C* from the Tolbachik volcano.

Calciolangbeinite-*O*					Calciolangbeinite-*C* (Pekov *et al.*, 2012)				
I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*	I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
5	7.44	4	7.366	110					
5	7.35	4	7.308	011					
11	5.97	14	5.967	111	8	5.84	8	5.882	111
7	4.577	5	4.579	012					
5	4.560	6	4.565	102	9	4.54	3	4.556	120
36	4.250	41	4.253	121					
23	4.205	29	4.219	211	27	4.15	31	4.159	211
18	4.188	23	4.186	112					
3	3.651	1	3.654	022					
12	3.465	21, 2	3.463, 3.445	221, 122					
86	3.315	89, 79	3.316, 3.310	130, 031					
75	3.270	83	3.273	310					
56	3.261	80	3.263	301					
100	3.228	100, 96	3.228, 3.223	013, 103	100	3.218	98, 100	3.222, 3.222	310, 130
27	3.156	25	3.153	131					
24	3.121	29	3.116	311					
17	2.882	10, 21	2.884, 2.880	032, 320	8	2.838	13, 2	2.826, 2.826	230, 320
6	2.854	2, 3	2.852, 2.849	302, 023					
51	2.783	53	2.787	231					
47	2.774	41, 39	2.778, 2.771	132, 321					
45	2.751	39, 45	2.753, 2.747	312, 123	37	2.736	31, 47	2.723, 2.723	231, 321
32	2.739	15	2.738	213					
5	2.545	5, 4	2.545, 2.542	140, 041	5	2.476	3, 2, 4	2.471, 2.471, 2.471	410, 140, 322
6	2.499	3, 7	2.506, 2.497	322, 223					
5	2.475	6	2.473	014					
4	2.434	3	2.436	411					
4	2.389	5	2.387	331					
7	2.374	12	2.371	133	3	2.333	4	2.337	331
4	2.343	4	2.341	240					
3	2.336	3	2.333	042					
3	2.308	2	2.303	402	1	2.284	1	2.278	420
6	2.279	1, 8	2.281, 2.276	241, 142					
5	2.251	6	2.250	412					
5	2.233	1, 3	2.235, 2.230	124, 214	1	2.227	2	2.223	421
7	2.213	5	2.211	332					
5	2.210	7	2.203	233					
12	2.199	20	2.195	323	4	2.183	8	2.172	332
5	2.127	3	2.127	242					
17	2.110	34	2.109	422					
23	2.095	42	2.093	224	7	2.087	19	2.080	422
9	2.058	4, 2, 5, 3	2.058, 2.058, 2.057, 2.055	150, 034, 051, 403					
15	2.038	15, 13	2.037, 2.036	431, 143					
21	2.018	21, 3, 15	2.018, 2.018, 2.017	134, 151, 413	11	2.006	12, 11	1.998, 1.998	431, 341
14	2.010	18	2.009	314					
10	1.991	7, 2	1.989, 1.989	333, 511	4	1.963	2	1.961	333
3	1.943	2	1.942	052					
4	1.936	4	1.932	342					
6	1.925	4, 8	1.924, 1.923	432, 520					
7	1.915	12, 2	1.914, 1.912	423, 234	3	1.898	3, 4, 1	1.892, 1.892, 1.892	250, 432, 342
3	1.894	5	1.894	205					
3	1.860	1	1.864	215	2	1.854	1	1.860	251
5	1.814	2, 2, 11	1.817, 1.813, 1.812	252, 404, 441	3	1.778	7, 1	1.774, 1.774	441, 522
3	1.800	5	1.799	144					
4	1.785	4, 4	1.786, 1.786	414, 053					
2	1.765	5	1.766	351					
3	1.754	2, 2	1.753, 1.752	531, 305	3	1.739	3, 1	1.747, 1.747	350, 530
3	1.727	2, 3	1.728, 1.726	315, 160					
6	1.701	12, 6	1.702, 1.698	161, 601					
10	1.691	14, 13	1.691, 1.688	352, 253					
5	1.678	6, 6	1.680, 1.676	532, 611					
5	1.663	4, 8	1.666, 1.662	235, 325					
7	1.655	3, 3, 9	1.657, 1.655, 1.653	260, 062, 116	8	1.658	10, 7, 9	1.653, 1.653, 1.653	611, 532, 352
4	1.634	1, 2, 2, 2	1.636, 1.636, 1.634, 1.631	620, 261, 162, 602					
10	1.613	3, 6, 2, 7	1.614, 1.614, 1.612, 1.611	344, 026, 612, 206	6	1.616	3, 4	1.611, 1.611	260, 620
6	1.603	1, 5, 7	1.604, 1.604, 1.600	504, 541, 154					
4	1.594	3, 2	1.594, 1.593	126, 216	2	1.582	1, 2, 1	1.591, 1.591, 1.591	621, 261, 443
4	1.581	1, 4	1.585, 1.580	353, 415	2	1.569	4, 2	1.572, 1.572	451, 541
6	1.555	5, 3, 8	1.558, 1.556, 1.552	622, 063, 452					
5	1.545	2, 6, 5	1.546, 1.545, 1.542	254, 630, 361					

(*Continued*)

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Table 3. (*Continued.*)

Calciolangbeinite-*O*					Calciolangbeinite-*C* (Pekov *et al.*, 2012)				
I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*	I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
3	1.534	2, 2	1.536, 1.534	245, 524	2	1.519	2, 2, 1	1.519, 1.519, 1.519	360, 542, 452
2	1.529	2	1.529	425					
3	1.520	5	1.519	613					
3	1.510	4	1.510	136					
5	1.492	3, 9, 4	1.492, 1.492, 1.489	362, 444, 263	2	1.470	3	1.471	444
2	1.478	3	1.479	632					
1	1.475	2	1.474	623					
2	1.465	3	1.464	236					
2	1.456	1, 3	1.457, 1.454	345, 435					
2	1.443	1	1.442	064					
2	1.440	1, 3	1.441, 1.439	270, 072					
5	1.427	3, 2, 2, 5	1.427, 1.426, 1.426, 1.426	271, 117, 604, 641					
3	1.417	1, 3, 2, 3	1.418, 1.418, 1.418, 1.415	406, 702, 363, 552	1	1.414	1, 1	1.413, 1.413	640, 460
4	1.406	1, 3, 3, 5	1.407, 1.406, 1.406, 1.405	721, 255, 633, 712					
3	1.398	2, 4, 3	1.399, 1.398, 1.395	207, 525, 336					

* For the calculated pattern, only reflections with intensities ≥1 are given; ** for the unit-cell parameters calculated from single-crystal data.

Table 4. Crystal data, data collection information and structure refinement details for calciolangbeinite-*O* from Tolbachik.

Crystal data	
Formula	$K_2Ca_2(SO_4)_3$
Formula weight	446.54
Temperature (K)	293(2)
Radiation and wavelength, Å	Mo*Kα*; 0.71073
Crystal system; space group; *Z*	Orthorhombic; $P2_12_12_1$; 4
Unit cell dimensions (Å)	*a* = 10.3330(2)
	b = 10.5027(2)
	c = 10.1763(2)
V (Å^3)	1104.37(4)
Absorption coefficient μ (mm^{-1})	2.414
F_{000}	888
Data collection	
Crystal size (mm)	0.07 × 0.15 × 0.24
Diffractometer	Xcalibur S CCD
θ range for data collection (°)	2.77–34.86
Index ranges	$-16 \le h \le 15$, $-16 \le k \le 16$, $-16 \le l \le 16$
Reflections collected	30,225
Independent reflections	4608 (R_{int} = 0.0517)
Independent reflections with $I > 2\sigma(I)$	4405
Structure solution	Direct methods
Refinement	
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	173
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0275, wR_2* = 0.0517
R indices (all data)	R_1 = 0.0303, wR_2* = 0.0526
GoF	1.091
Largest diff. peak and hole (e^-/Å^3)	0.440 and −0.357

* $w = 1/[\sigma^2(F_o^2) + (0.0176P)^2 + 0.2728P]$; $P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$

Table 5. Coordinates, equivalent displacement parameters (U_{eq}, in Å^2) of atoms in and bond-valence sums (BVS) calciolangbeinite-*O* from Tolbachik. Parameters for BVS were taken from Gagné and Hawthorne (2015).

Site	*x*	*y*	*z*	U_{eq}	BVS
Ca(1)	0.30646(3)	0.33955(3)	0.32452(4)	0.01174(7)	2.04
Ca(2)	0.59881(4)	0.59419(3)	0.57522(3)	0.01379(7)	2.10
S(1)	0.21130(4)	0.37189(4)	0.01926(4)	0.01151(8)	6.04
S(2)	0.38717(4)	0.00445(4)	0.25074(4)	0.01170(8)	6.07
S(3)	−0.00078(4)	0.21750(4)	0.36978(4)	0.01103(8)	6.09
K(1)	0.83094(4)	0.81292(4)	0.81090(5)	0.02194(9)	0.97
K(2)	0.03409(5)	0.05682(5)	0.06159(5)	0.02683(11)	0.91
O(1)	0.30735(15)	0.26988(14)	0.03485(17)	0.0250(3)	1.91
O(2)	0.08639(13)	0.31918(14)	0.97614(16)	0.0227(3)	2.03
O(3)	0.25765(14)	0.46297(13)	0.92121(14)	0.0205(3)	2.08
O(4)	0.19325(18)	0.43431(15)	0.14783(14)	0.0271(3)	1.90
O(5)	0.30484(14)	0.93202(14)	0.34154(13)	0.0204(3)	2.13
O(6)	0.39283(15)	0.13806(13)	0.29046(15)	0.0233(3)	2.01
O(7)	0.51910(15)	0.95175(15)	0.25996(17)	0.0267(3)	2.03
O(8)	0.33691(17)	0.99023(16)	0.11691(14)	0.0270(3)	1.98
O(9)	0.06215(16)	0.10116(15)	0.32186(16)	0.0265(3)	2.06
O(10)	0.90678(15)	0.18733(15)	0.47317(14)	0.0247(3)	2.02
O(11)	0.92976(14)	0.27780(16)	0.26029(16)	0.0273(4)	2.03
O(12)	0.09891(15)	0.30466(14)	0.42077(15)	0.0231(3)	2.04

1.475 Å, from 1.462 to 1.474 Å and from 1.456 to 1.473 Å with distortion indices 0.003, 0.003 and 0.004, respectively. The *M*–O–S angles in calciolangbeinite-*C* are 3 × 142.3 and 3 × 157.8° [*M*1] and 3 × 129.9 and 3 x 161.5° [*M*2]. In calciolangbeinite-*O* six different values of *M*–O–S angles vary from 115.1 to 163.7° [*M*1] and from 116.2 to 157.3° [*M*2]. The change of K-centred polyhedra is close in the pairs calciolangbeinite-*O*–calciolangbeinite-*C* and orthorhombic–cubic synthetic $K_2Ca_2(SO_4)_3$. In both natural and synthetic orthorhombic sulfates, the K(1) site centres a ten-fold polyhedron while the K(2) site is coordinated by nine O atoms with average K–O distances 2.991 [K(1)] and 3.006 Å [K(2)] in calciolangbeinite-*O* and 2.986 [K(1)] and 3.000 [K(2)] in synthetic $K_2Ca_2(SO_4)_3$. In cubic sulfates, both K sites centre nine-fold polyhedra [in calciolangbeinite-*C* the K(2) polyhedra can be also considered as distorted octahedra, not taking into account strongly elongated K(2)–O bonds: 3.273(6) Å]. The average K–O distances in cubic forms are longer than in orthorhombic ones: in calciolangbeinite-*C* they are 3.012 [K(1)] and 3.034 Å [K(2)] (Pekov *et al.*, 2012) and in synthetic high-temperature $K_2Ca_2(SO_4)_3$ they are 3.073 [K(1)] and 3.091 Å [K(2)] (Speer and Salje, 1986).

It is noteworthy that, regardless of the topological similarity of the crystal structures and similar unit-cell dimensions between calciolangbeinite-*C* [*a* = 10.1887(4) Å, *V* = 1057.68(4) Å^3] and calciolangbeinite-*O* [*a* = 10.3330(2), *b* = 10.5027(2), *c* = 10.1763(2) Å, *V* = 1104.37(4) Å^3] (Table 7), these varieties of calciolangbeinite differ strongly from one another in powder XRD patterns and some physical properties. They can be distinguished easily using powder XRD diagrams, Raman or IR spectra and optical data. Due to the difference in systematic absences and unequal lattice

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Table 6. Selected interatomic distances (Å) in the crystal structure of calciolangbeinite-*O* from Tolbachik.

Ca(1)–O(7)	2.3187(15)	S(3)–O(10)	1.4559(14)
Ca(1)–O(10)	2.3222(14)	S(3)–O(9)	1.4675(15)
Ca(1)–O(6)	2.3227(14)	S(3)–O(11)	1.4690(15)
Ca(1)–O(4)	2.3648(15)	S(3)–O(12)	1.4726(15)
Ca(1)–O(12)	2.3860(15)	<S(3)–O>	1.466
Ca(1)–O(3)	2.3892(14)		
<Ca(1)–O>	2.351	K(1)–O(12)	2.8265(16)
		K(1)–O(11)	2.9033(16)
Ca(2)–O(5)	2.3078(14)	K(1)–O(6)	2.9079(17)
Ca(2)–O(11)	2.3327(15)	K(1)–O(10)	2.9598(16)
Ca(2)–O(9)	2.3345(16)	K(1)–O(7)	2.9629(17)
Ca(2)–O(8)	2.3358(16)	K(1)–O(3)	2.9834(16)
Ca(2)–O(2)	2.3466(15)	K(1)–O(5)	3.0161(16)
Ca(2)–O(1)	2.3663(15)	K(1)–O(4)	3.0410(18)
<Ca(2)–O>	2.337	K(1)–O(2)	3.0441(16)
		K(1)–O(8)	3.2681(17)
S(1)–O(3)	1.4629(14)	<K(1)–O>	2.991
S(1)–O(1)	1.4691(14)		
S(1)–O(2)	1.4714(14)	K(2)–O(9)	2.7048(17)
S(1)–O(4)	1.4752(15)	K(2)–O(5)	2.7925(15)
<S(1)–O>	1.470	K(2)–O(3)	2.8694(16)
		K(2)–O(2)	2.9395(16)
S(2)–O(6)	1.4616(14)	K(2)–O(12)	2.9890(17)
S(2)–O(8)	1.4651(15)	K(2)–O(7)	3.1196(18)
S(2)–O(5)	1.4683(14)	K(2)–O(1)	3.1250(17)
S(2)–O(7)	1.4743(15)	K(2)–O(8)	3.2553(18)
<S(2)–O>	1.467	K(2)–O(11)	3.2616(19)
		<K(2)–O>	3.006

parameters *a*, *b* and *c* between space groups $P2_12_12_1$, and $P2_13$, the powder XRD pattern of calciolangbeinite-*O* contains many more reflections in comparison with that of calciolangbeinite-*C*, including the most informative low-angle region ($d > 2.5$ Å). In particular, six strong, well-resolved reflections present in the powder XRD pattern of calciolangbeinite-*O* instead of a narrow singlet in the powder XRD pattern of calciolangbeinite-*C* in the region of $3.0 < d < 3.5$ Å and four strong reflections instead of a singlet in the region of $2.7 < d < 2.8$ Å (Table 3). The Raman spectra of orthorhombic and cubic varieties of calciolangbeinite are different, first of all, in the number of bands (Table 1 and Fig. 6). Calciolangbeinite-*C*, a cubic form, is optically isotropic and has a refractive index distinctly higher in comparison with calciolangbeinite-*O* which is optically anisotropic and demonstrates significant birefringence: 0.033 (Table 7).

For the natural cubic modification described as calciolangbeinite, the idealised, end-member formula $K_2Ca_2(SO_4)_3$ was suggested originally (Pekov *et al.*, 2012), by analogy with synthetic cubic ($P2_13$) high-temperature langbeinite-type modification of $K_2Ca_2(SO_4)_3$, reported by Speer and Salje (1986). However, all the studied samples of cubic calciolangbeinite (now calciolangbeinite-*C*) from its type locality, the Yadovitaya fumarole, contain a significant admixture of Mg: 4.8–9.5 wt.% MgO = 0.5–1.0 apfu Mg (Pekov *et al.*, 2012). As the present work has shown, calciolangbeinite-*C* from the Arsenatnaya fumarole contains not less than *ca.* 1 wt.% MgO = 0.1 apfu Mg,

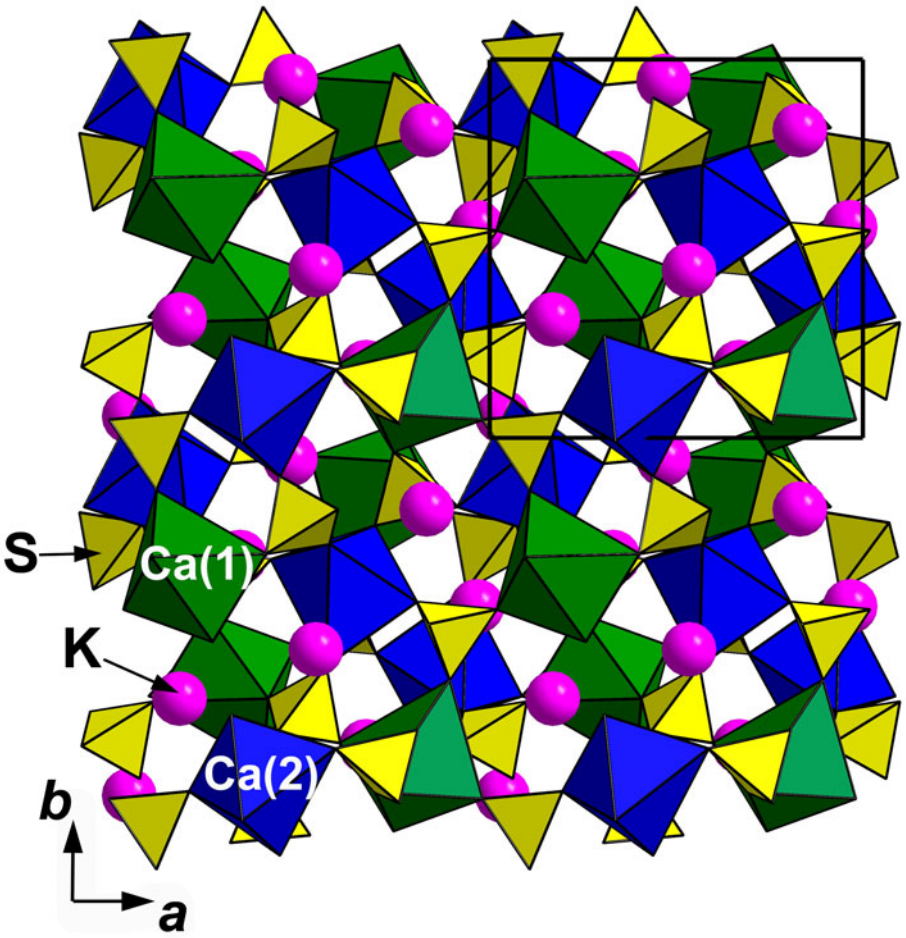


Fig. 8. The crystal structure of calciolangbeinite-*O* in the *ab* projection. The unit cell is outlined.

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Table 7. Comparative data of two modifications of calciolangbeinite and their synthetic counterparts.

Mineral / Compound	Calciolangbeinite-*O*	Synthetic low-temperature $K_2Ca_2(SO_4)_3$*	Calciolangbeinite-*C*	Synthetic high-temperature $K_2Ca_2(SO_4)_3$**
Empirical formula	$(K_{1.95}Rb_{0.03})_{\Sigma 1.98}$ $(Ca_{1.97}Na_{0.02})_{\Sigma 1.99}$ $S_{3.01}O_{12}$***	$K_2Ca_2(SO_4)_3$	$K_{2.01}(Ca_{1.24}Mg_{0.70}$ $Na_{0.05}Mn_{0.02}Fe_{0.01}$ $Al_{0.01})_{\Sigma 2.03}S_{3.00}O_{12}$****	$K_2Ca_2(SO_4)_3$
Structure type	$K_2Cd_2(SO_4)_3$	$K_2Cd_2(SO_4)_3$	Langbeinite	Langbeinite
Crystal system	Orthorhombic	Orthorhombic	Cubic	Cubic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_13$	$P2_13$
a (Å)	10.2828(2)	10.33	10.1887(4)	10.429
b (Å)	10.5027(2)	10.50		
c (Å)	10.1763(2)	10.18		
V (Å^3)	1104.37(4)	1104	1057.68(4)	1134.3
Z	4	4	4	4
Strong reflections of powder X-ray diffraction pattern (*d*, Å – *I*)	4.250–36	4.252–27	5.84–8	6.025–15
	4.205–23	4.218–21	4.54–9	4.257–40
	4.188–18	4.187–17	4.15–27	3.298–100
	3.315–86	3.315–89	3.218–100	3.146–50
	3.270–75	3.272–61	2.838–8	2.787–60
	3.261–56	3.262–77	2.736–37	2.459–22
	3.228–100	3.229–100		
	3.156–27	3.152–16		
	3.121–24	3.115–18		
	2.882–17	2.879–16		
	2.783–51	2.787–34		
	2.774–47	2.778–41		
	2.751–45	2.771–40		
	2.739–32	2.747–41		
Optical data (measured)	Biaxial (+) $\alpha = 1.475(3)$ $\beta = 1.490(2)$ $\gamma = 1.508(3)$ $2V = 85(5)°$	Not reported	Isotropic $n = 1.527(2)$	Not reported
Source	This work	Speer and Salje, 1986	Pekov *et al.*, 2012	Speer and Salje, 1986

*Calculated powder X-ray diffraction data are given; **all data were obtained at 260°C.
Samples with studied crystal structures are included: ***an. #14 in Table 2; ****an. #8 in Table 2.

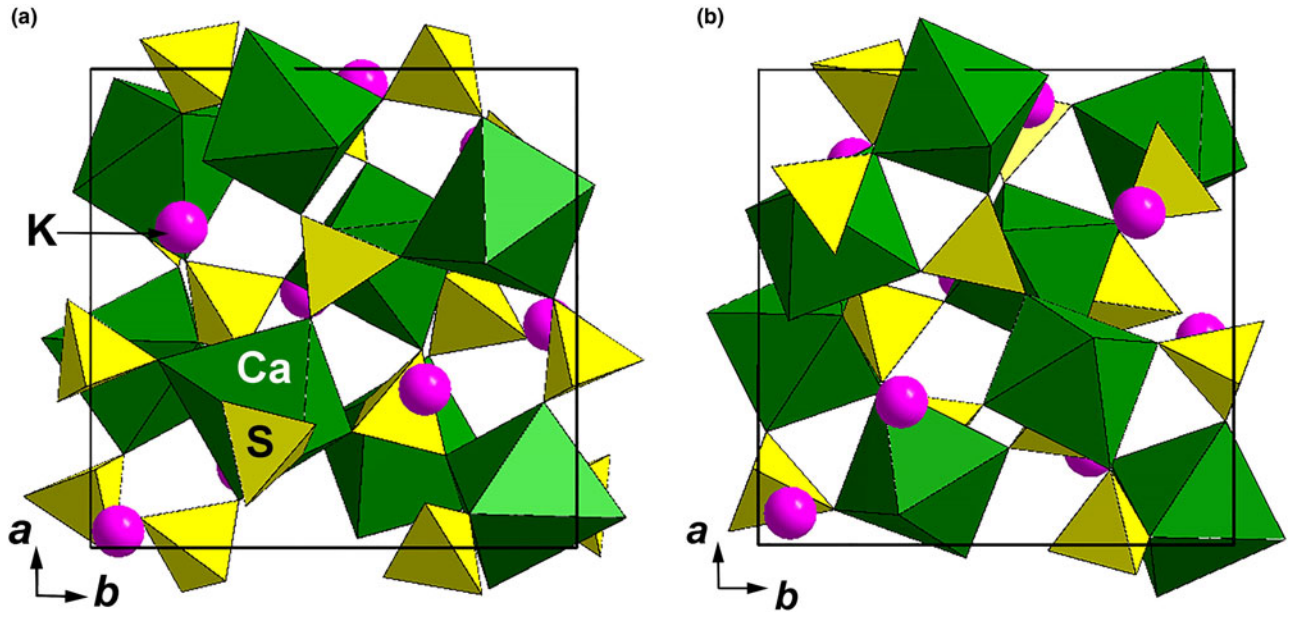


Fig. 9. The comparison of crystal structures of calciolangbeinite-*O* (a) and calciolangbeinite-*C* (b), in simplified form.

unlike calciolangbeinite-*O* in which Mg ≤ 0.1 apfu (Fig. 7); most typically, the Mg content in calciolangbeinite-*O* is below the detection limit and, thus, this modification is chemically close to the end-member $K_2Ca_2(SO_4)_3$ (an. 13–15 in Table 2). In some specimens from the Arsenatnaya fumarole, the association of Mg-bearing calciolangbeinite-*C* with Mg-free calciolangbeinite-*O* is observed and both structural varieties of calciolangbeinite in all cases demonstrate these individual chemical features.

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We believe that a significant admixture of Mg (> 0.1 apfu) in calciolangbeinite (Tables 2 and 7) stabilises its cubic structure at room temperature while Mg-free or Mg-poor (with Mg ≤ 0.1 apfu: Fig. 7) varieties of the mineral can only exist at room temperature in orthorhombic form. This suggestion is confirmed by the above-discussed clear correlation between the temperature of the transition of the cubic form of a langbeinite-type sulfate to the orthorhombic one and ionic radius of the *M* cation reported by Speer and Salje (1986). Based on this, the simplified formula of Tolbachik calciolangbeinite-*C* existing under room-temperature conditions could be written as $K_2(Ca,Mg)_2(SO_4)_3$. We cannot exclude the existence of calciolangbeinite-*C* varieties stabilised by other cations smaller than Ca. In any case, the idealised, end-member formula of calciolangbeinite-*C* remains $K_2Ca_2(SO_4)_3$.

Notes on genesis of calciolangbeinite

At the Tolbachik volcano, calciolangbeinite is a fumarolic mineral deposited directly from the gas phase as a volcanic sublimate or, more probably, formed as a result of the interaction between volcanic gas and basalt scoria. The latter could be a source of Ca which has a very low volatility in fumarolic systems at temperatures up to 400–500°C (Symonds and Reed, 1993). The temperature of formation of both varieties of calciolangbeinite in the Arsenatnaya fumarole was not lower than 380–400°C. In the Yadovitaya fumarole, we estimate, based on direct temperature measurements, that calciolangbeinite-*C* was formed at temperatures not lower than 300°C (Pekov *et al.*, 2012).

In pyrometamorphic rocks of the Hatrurim Complex, calciolangbeinite was presumably formed at temperatures ~800–900°C. We believe that it could crystallise from small portions of a specific Na–Ca–K-rich sulfate melt, one of the products of pyrometamorphism, which can be liquated to Na–K and K–Ca melts (Galuskina *et al.*, 2014). The temperature of the melt could be not lower than 1000–1020°C, i.e. not lower than the estimated melting point of $K_2Ca_2(SO_4)_3$ (Morey *et al.*, 1964; Tesfaye *et al.*, 2020 and references therein).

Thus, in all known cases in Nature the temperature of crystallisation of calciolangbeinite is higher than the point of phase transition found even for pure $K_2Ca_2(SO_4)_3$, 184°C (Speer and Salje, 1986). We can conclude that calciolangbeinite crystallises in cubic modification with the langbeinite-type structure and during cooling its 'fate' depends on the composition of M^{2+} cations. The chemical variety close to the calcium end-member $K_2Ca_2(SO_4)_3$ undergoes phase transition to the $K_2Cd_2(SO_4)_3$-type compound and becomes calciolangbeinite-*O*, whereas the Mg-enriched chemical varieties keep the langbeinite-type structure (stabilised in this case by Mg) and remain calciolangbeinite-*C*, a calciolangbeinite variety ('sub-species') with the most correct, for room-temperature conditions, simplified formula $K_2(Ca,Mg)_2(SO_4)_3$.

The high-temperature crystallisation favours Ca–Mg isomorphism (disorder) in calciolangbeinite-*C*. It is not excluded that the variety of calciolangbeinite-*C* richest in Ca existing at room temperature is in fact a quenched form of the cubic modification.

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Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2021.95

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