Calciolangbeinite, $K_2Ca_2(SO_4)_3$, a new mineral from the Tolbachik volcano, Kamchatka, Russia

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ABSTRACT

The new mineral calciolangbeinite, ideally $K_2Ca_2(SO_4)_3$, is the Ca-dominant analogue of langbeinite. It occurs in sublimates at the Yadovitaya fumarole on the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure eruption, Tolbachik volcano, Kamchatka, Russia. The mineral is associated with langbeinite, piypite, hematite, rutile, pseudobrookite, orthoclase, lyonsite, lammerite, cyanochroite and chlorothionite. Calciolangbeinite occurs as tetrahedral to pseudo-octahedral crystals, which are bounded by {111} and {11$\bar{1}$}, and as anhedral grains up to 1 mm in size, aggregated into clusters up to 2 mm across, and forming crusts covering areas of up to 1.5×1.5 cm on the surface of volcanic scoria. Late-stage calciolangbeinite occurs in complex epitaxial intergrowths with langbeinite. Calciolangbeinite is transparent and colourless with white streak and vitreous lustre. Its Mohs' hardness is $3-3\frac{1}{2}$. It is brittle, has a conchoidal fracture and no obvious cleavage. The measured and calculated densities are $D_{meas} = 2.68(2)$ and $D_{calc} = 2.74$ g cm^{-3}, respectively. Calciolangbeinite is optically isotropic with $n = 1.527(2)$. The chemical composition of the holotype specimen is Na_2O 0.38, K_2O 21.85, MgO 6.52, CaO 16.00, MnO 0.27, FeO 0.08, Al_2O_3 0.09, SO_3 55.14, total 100.63 wt.%. The empirical formula, calculated on the basis of twelve oxygen atoms per formula unit, is $K_{2.01}(Ca_{1.24}Mg_{0.70}Na_{0.05}Mn_{0.02}Fe_{0.01}Al_{0.01})_{\Sigma2.03}S_{3.00}O_{12}$. Calciolangbeinite is cubic, space group $P2_13$, $a = 10.1887(4)$ Å, $V = 1057.68(4)$ Å^3 and $Z = 4$. The strongest reflections in the X-ray powder pattern [listed as $(d,\text{Å}(I)(hkl)$] are 5.84(8)(111); 4.54(9)(120); 4.15(27)(211); 3.218(100)(310,130); 2.838(8)(230,320), 2.736(37)(231,321), 2.006(11)(431,341), 1.658(8)(611,532,352). The crystal structure was refined from single-crystal X-ray diffraction data to $R = 0.0447$. The structure is based on the langbeinite-type three-dimensional complex framework, which is made up of $(Ca,Mg)O_6$ octahedra (Ca and Mg are disordered) and SO_4 tetrahedra. Potassium atoms occupy two sites in voids in the framework; K(1) cations are located in ninefold polyhedra whereas K(2) cations are sited in significantly distorted octahedra. Calciolangbeinite and langbeinite are isostructural and form a solid-solution series.

Introduction

THE fumarole fields produced by the Great Tolbachik Fissure eruption of the Tolbachik volcano on the Kamchatka Peninsula, Russia in 1975−76 (Fedotov and Markhinin, 1983) are still active. They are famous for their great mineral diversity: to date, more than 100 mineral species have been identified as fumarole sublimates or their low-temperature alteration products, and the volcano is the type locality for 38 of these. Sulfates and oxides dominate the fumarole assemblages; chlorides, fluorides, carbonates, arsenates, vanadates, selenites, molybdates, silicates are subordinate; and sulfides and gold occur in minor amounts (Vergasova and Filatov, 1993).

Langbeinite, ideally $K_2Mg_2(SO_4)_3$, is one of the most common sulfate minerals in the Tolbachik fumaroles. During our studies of sulfate crusts (primarily langbeinite) a langbeinite analogue with Ca > Mg was discovered. It was named calciolangbeinite as a result of its chemical composition and relationship to langbeinite, with which it forms a solid-solution series.

The new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2011−067). The type specimen has been deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow under registration number 4153/1.

Occurrence and general appearance

Specimens with calciolangbeinite were collected in 2008 and 2009 by one of the authors (MEZ) at the Yadovitaya [Poisonous] fumarole in the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure eruption. This scoria cone was formed in 1975 (Fedotov and Markhinin, 1983) and is 300 m high with a volume of approximately 0.1 km³. In 2010, many fumaroles with gas temperatures of up to 480ºC were active at the top of the scoria cone. The gases are close to atmospheric air in composition, and contain <1% water vapour and <0.1% acid species, mainly CO_2, HF and HCl (MEZ, unpublished data). The Yadovitaya fumarole is an open cave which is 1.5 m across at the entrance and about 2 m deep. The rocks inside the cave are thickly coated in volcanic sublimates which have been partially altered by meteoric water. The temperature inside the

fumarole is still high, at up to 340ºC in 2010, but several years of detailed observation suggest that all (or almost all) of the volcanic sublimates were deposited at even higher temperatures, when the fumarole was younger.

Mineral assemblages in the sublimate crusts are significantly variable in different areas of the fumarole. Calciolangbeinite is a rare mineral which is found in association with abundant langbeinite (including its Ca-bearing variety, see below). Langbeinite occurs as colourless to pale yellowish translucent crusts, typically up to 1 mm and rarely up to 2 mm thick, covering areas of up to several dozens of square centimetres. Associated minerals include piypite, hematite, rutile (an Fe- and Sb-bearing variety), pseudobrookite, orthoclase [typically the As- and Zn-bearing variety, $K(Al,Zn)(Si,As)_3O_8$, which forms a solid-solution series with filatovite, $K(Al,Zn)(As,Si)_3O_8$], lyonsite, lammerite, and late secondary cyanochroite and chlorothionite.

Calciolangbeinite occurs as crystals and almost anhedral grains, typically up to 0.5 mm, and rarely up to 1 mm across. The crystals are tetrahedral, but if the faces of the positive and negative tetrahedron, $\{111\}$ and $\{11\bar{1}\}$, are equally developed the habit is pseudo-octahedral (Figs 1 and 2). Calciolangbeinite crystals are typically coarse and/or distorted; they may be flattened, curved or skeletal; some individuals have uneven surfaces. Crystals and/or grains of the new mineral occur in clusters up to 2 mm across and in crusts (Fig. 1) which cover areas of up to 1.5×1.5 cm on the surface of volcanic scoria.

FIG. 1. Crystals of calciolangbeinite on the holotype specimen. The field of view is 1.7 mm. Photo: I.V. Pekov and A.V. Kasatkin.
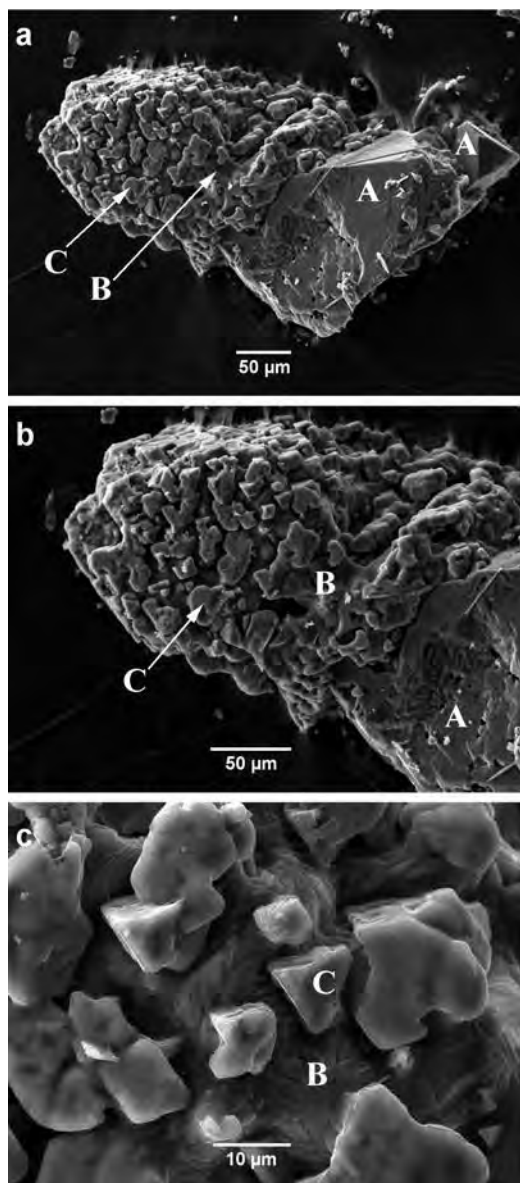
FIG. 2. Complex epitaxial intergrowths of langbeinite and calciolangbeinite: (*a*) general view; (*b,c*) smaller areas. Phase A is langbeinite with a composition close to $(K_{1.9}Na_{0.1})(Mg_{1.8}Ca_{0.2})(SO_4)_3$ (Table 1, column 4); phase B is an intermediate member of the langbeinite–calciolangbeinite solid-solution series with a composition close to its midpoint $(K_{1.6}Na_{0.2}Ca_{0.1})(Mg_{1.0}Ca_{1.0})(SO_4)_3$ (Table 1, column 3); phase C is calciolangbeinite with a composition close to $K_{2.0}(Ca_{1.5}Mg_{0.5})(SO_4)_3$ (Table 1, column 2).

Langbeinite and calciolangbeinite occur as epitaxial intergrowths on some specimens (Fig. 2). Crystals of langbeinite with the approximate composition $(K_{1.9}Na_{0.1})(Mg_{1.8}Ca_{0.2})(SO_4)_3$ (Fig. 2, phase A; Table 1, column 4) are overgrown by framboidal aggregates of Ca-rich members of the langbeinite−calciolangbeinite series. The compositions of the centres of these aggregates are typically close to the midpoint of the solid-solution series with formulae approximating $(K_{1.6}Na_{0.2}Ca_{0.1})(Mg_{1.0}Ca_{1.0})(SO_4)_3$ (Fig. 2, phase B; Table 1, column 3), whereas small crystals on their surfaces (Fig. 2, phase C; Table 1, column 2) are near to endmember calciolangbeinite with formulae close to $K_{2.0}(Ca_{1.5}Mg_{0.5})(SO_4)_3$. These phases are commonly in the same crystallographic orientation as the underlying material, forming complex epitaxial intergrowths.

Physical properties and optical data

Calciolangbeinite is transparent and colourless. The streak is white and the lustre vitreous. The mineral is not fluorescent in ultraviolet radiation or when exposed to cathode rays. Calciolangbeinite is brittle. Its Mohs' hardness is $3-3\frac{1}{2}$. Cleavage and parting were not observed, but the fracture is conchoidal. The density measured by flotation in heavy liquids ($CHBr_3$ + ethanol) is 2.68(2) g cm^{-3} and the calculated density is 2.74 g cm^{-3} (both values are for the holotype specimen). Calciolangbeinite is optically isotropic with n = 1.527(2).

Infrared spectroscopy

Calciolangbeinite powder was mixed with anhydrous KBr, pelletized, and the spectrum was recorded using an ALPHA Fourier transform infrared spectrometer (Bruker Optics) at a resolution of 4 cm^{-1} (average of 16 scans). The infrared (IR) spectrum of a pellet of pure KBr was used as a reference.

The IR spectrum of calciolangbeinite is shown in Fig. 3. Absorption bands and their assignments are (s, strong band; w, weak band; sh, shoulder): 1144(s) (S−O stretching vibrations of SO_4^{2-} groups); 645(sh), 630, 612 (bending vibrations of SO_4^{2-} groups); 473(w), 446(w) (lattice modes involving mainly Mg−O and Ca−O stretching and motion of SO_4^{2-} anions as a whole). Bands corresponding to H-, B-, C- and N-bearing groups (1200−3800 cm^{-1}) are absent in the IR spectrum,

TABLE 1. Chemical compositions of langbeinite−calciolangbeinite series minerals from the Yadovitaya fumarole, Tolbachik volcano, Kamchatka, Russia.

Oxide (wt.%)	1	2	3	4
Na_2O	0.38 (0.3−0.5)	0.30	1.37	0.48
K_2O	21.85 (21.2−22.4)	21.03	17.78	21.37
MgO	6.52 (5.7−7.2)	4.78	9.53	17.71
CaO	16.00 (15.2−17.7)	19.45	15.13	2.87
MnO	0.27 (0.2−0.3)	0.32	0.26	0.29
FeO	0.08 (0.00−0.15)	0.15	0.13	0.05
Al_2O_3	0.09 (0.00−0.15)	0.06	0.05	0.07
SO_3	55.14 (53.0−56.8)	54.42	55.10	57.52
Total	100.63	100.51	99.35	100.36
Formula calculated on the basis of 12 oxygen atoms				
Na	0.05	0.04	0.19	0.06
K	2.01	1.95	1.62	1.89
Mg	0.70	0.52	1.02	1.83
Ca	1.24	1.52	1.16	0.21
Mn	0.02	0.02	0.02	0.02
Fe	−	0.01	0.01	−
Al	0.01	0.01	−	0.01
S	3.00	2.98	2.96	2.99
ΣMe*	4.03	4.07	4.02	4.02

(1) The holotype specimen of calciolangbeinite (mean data for 5 analyses with ranges in parentheses).
(2−4) Different parts of a complex epitactic intergrowth; (2) calciolangbeinite; (3) an intermediate member of the series (a Ca-rich variety of langbeinite with some of the Ca located in the K sites); (4) langbeinite. The compositions in columns 2, 3 and 4 correspond to the phases marked C, B and A, respectively, in Fig. 2.
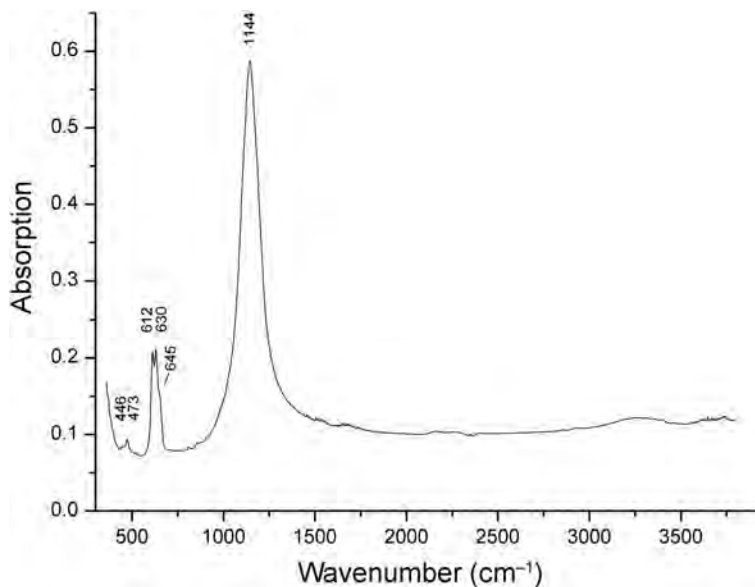* ΣMe is the sum of all metal cations.

FIG. 3. The infrared spectrum of calciolangbeinite.

as are bands that could belong to Be−O modes (700−800 cm^{-1}). The IR spectra of calciolangbeinite and langbeinite are very similar.

Chemical composition

Chemical data (Table 1) were obtained using a JEOL JSM-6480LV scanning electron microscope equipped with an INCA-Energy 350 energy-dispersive spectrometer. The accelerating voltage was 20 kV, beam current 1 nA and beam diameter 3 μm. The standards used for calibration were albite (Na), orthoclase (K), olivine (Mg), $CaWO_4$ (Ca), Mn (Mn), $CuFeS_2$ (Fe), Al_2O_3 (Al) and ZnS (S).

The empirical formula of the holotype specimen of calciolangbeinite (Table 1, column 1), calculated on the basis of 12 oxygen atoms per formula unit (a.p.f.u.) is $K_{2.01}(Ca_{1.24} Mg_{0.70}Na_{0.05}Mn_{0.02}Fe_{0.01}Al_{0.01})_{\Sigma 2.03}S_{3.00}O_{12}$. The simplified formula is $K_2(Ca,Mg)_2(SO_4)_3$. The ideal endmember formula is $K_2Ca_2(SO_4)_3$; this requires K_2O 21.10, CaO 25.11, SO_3 53.79, total 100.00 wt.%.

The values of the Gladstone−Dale compatibility index $[1 - (K_p/K_c)]$ (Mandarino, 1981) for the holotype specimen are: −0.014 (which is rated as superior), using the calculated density; and −0.037 (which is rated as excellent), using the

TABLE 2. X-ray powder diffraction data for calciolangbeinite.

I_{obs}	d_{obs} (Å)	I_{calc}*	d_{calc}** (Å)	Miller indices
8	5.84	8	5.882	111
9	4.54	3	4.556	120
27	4.15	31	4.159	211
100	3.218	98, 100	3.222, 3.222	310, 130
8	2.838	13, 2	2.826, 2.826	230, 320
37	2.736	31, 47	2.723, 2.723	231, 321
5	2.476	3, 2, 4	2.471, 2.471, 2.471	410, 140, 322
3	2.333	4	2.337	331
1	2.284	1	2.278	420
1	2.227	2	2.223	421
4	2.183	8	2.172	332
7	2.087	19	2.080	422
11	2.006	12, 11	1.998, 1.998	431, 341
4	1.963	2	1.961	333
3	1.898	3, 4, 1	1.892, 1.892, 1.892	250, 432, 342
2	1.854	1	1.860	251
3	1.778	7, 1	1.774, 1.774	441, 522
3	1.739	3, 1	1.747, 1.747	350, 530
8	1.658	10, 7, 9	1.653, 1.653, 1.653	611, 532, 352
6	1.616	3, 4	1.611, 1.611	260, 620
2	1.582	1, 2, 1	1.591, 1.591, 1.591	621, 261, 443
2	1.569	4, 2	1.572, 1.572	451, 541
2	1.519	2, 2, 1	1.519, 1.519, 1.519, 1.519	360, 542, 452
2	1.470	3	1.471	444
1	1.414	1, 1	1.413, 1.413	640, 460
2	1.387	3, 2, 2	1.387, 1.387, 1.387	721, 271, 552
3	1.361	1, 2	1.362	462, 642
2	1.328	2	1.327	731
2	1.299	2	1.294	561
1	1.266	1	1.264	562
1	1.245	1	1.245	733
1	1.223	1	1.227	742
1	1.198	2	1.201	822

* For the calculated X-ray powder pattern, only reflections with $I_{calc} \geqslant 1$ are given.
** Calculated for unit-cell parameters obtained from single-crystal data.

TABLE 3. Crystal data, data collection and structure refinement details for calciolangbeinite.

Formula, from structure refinement	$K_2(Ca_{1.33}Mg_{0.67})(SO_4)_3$
Formula weight	435.9
Temperature (K)	293(2)
Radiation and wavelength (Å)	Mo$K\alpha$; 0.71073
Crystal system, space group	Cubic, $P2_13$
Unit cell dimensions (Å)	a = 10.1887(2)
Volume (Å^3)	1057.69(4)
Z	4
Calculated density (g cm^{-3})	2.737
Absorption coefficient μ (mm^{-1})	2.234
$F(000)$	866
Diffractometer	Xcalibur S CCD
θ range for data collection (º)	2.83−30.44
Index ranges	$-14 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 14$, $-14 \leqslant l \leqslant 14$
Reflections collected	35,541
Independent reflections	1086 (R_{int} = 0.0624)
Reflections with $I > 2\sigma(I)$	1034
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	60
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0447, wR_2 = 0.1159
Goodness-of-fit on F^2	1.118
Largest diff. peak and hole (e$^-$ Å^{-3})	0.496 and −0.296

measured density. Calciolangbeinite dissolves slowly in water at room temperature.

X-ray crystallography and crystal structure

X-ray powder diffraction data for calciolangbeinite (Table 2) were obtained using a STOE IPDS II single-crystal diffractometer equipped with an image plate detector (Mo$K\alpha$ radiation; sample–detector distance 200 mm) using the Gandolfi method. All reflections were indexed on the langbeinite-type cubic unit cell obtained in the single-crystal study (see below). The unit-cell dimension and volume refined from the powder data are a = 10.192(4) Å and V = 1059(1) Å^3.

Single-crystal X-ray studies of the holotype specimen of calciolangbeinite were carried out using an Xcalibur S diffractometer equipped with a CCD detector. The mineral is cubic, space group $P2_13$, a = 10.1887(4) Å, V = 1057.68(4) Å^3 and Z = 4. The structure was solved by direct methods and refined using the *SHELX* software package (Sheldrick, 2008) to R = 0.0447 for 1034 unique reflections with $I > 2\sigma(I)$. Crystal data, data collection and structure refinement details are provided in Table 3, atom coordinates and equivalent displacement parameters are listed in Table 4 and selected interatomic distances in Table 5. A crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available at www.minersoc.org/pages/e_journals/dep_mat.html.

The crystal structure of calciolangbeinite (Fig. 4) is based on a langbeinite-type 3D complex framework formed by $M(1)O_6$ and $M(2)O_6$ octahedra (M = Ca,Mg) and SO$_4$ tetrahedra. Each MO_6 octahedron shares all of its vertices with SO$_4$ tetrahedra and thus there is no direct linkage between the M polyhedra. Potassium atoms occupy two sites that are not crystallographically equivalent in voids in the framework. The K(1) cations occur in ninefold polyhedra whereas the K(2) cations occur in distorted octahedra. The structural formula of calciolangbeinite can be presented (according to Pushcharovsky *et al.*, 1998) as $K_\infty^{[9/6]3}[Ca_2^oS_3^tO_{12}]$.

Calciolangbeinite is a representative of the well-known langbeinite structure type. It is isostructural with langbeinite (Mereiter, 1979) and with numerous synthetic langbeinite-type sulfates with the general formula $K_2M_2^{2+}(SO_4)_3$, in which M^{2+} = Mg, Mn, Co, Ni, Zn, Cd, and Ca. The synthetic compound $K_2Ca_2(SO_4)_3$, corresponding to endmember calciolangbeinite, has space group $P2_13$, a = 10.43 Å and V = 1134 Å^3 (Speer and Salje, 1986).

TABLE 4. Final atom coordinates and equivalent displacement parameters (Å^2) for calciolangbeinite.

Site	x/a	y/b	z/c	U_{eq}
$M(1) = Ca_{0.625(8)}Mg_{0.37(1)}$	0.57913(9)	0.57913(9)	0.57913(9)	0.0260(5)
$M(2) = Ca_{0.700(7)}Mg_{0.30(2)}$	0.84035(9)	0.84035(9)	0.84035(9)	0.0287(5)
S	0.62413(10)	0.47372(11)	0.26097(10)	0.0282(3)
K(1)	0.06709(10)	0.06709(10)	0.06709(10)	0.0394(4)
K(2)	0.30130(11)	0.30130(11)	0.30130(11)	0.0426(4)
O(1)	0.6611(6)	0.5121(6)	0.3908(5)	0.0803(17)
O(2)	0.7383(5)	0.4833(6)	0.1768(6)	0.0856(18)
O(3)	0.5742(5)	0.3405(4)	0.2595(6)	0.0733(15)
O(4)	0.5276(5)	0.5632(5)	0.2048(6)	0.0813(17)

Discussion

Calcium and magnesium are almost completely disordered in calciolangbeinite from Tolbachik. The structure refinement on the holotype specimen gave cation ratios at the sites of $M(1)$ = $Ca_{0.63}Mg_{0.37}$ and $M(2)$ = $Ca_{0.70}Mg_{0.30}$ (Table 4). These values are close to those derived from the chemical data (Table 1,

column 1) and are confirmed by the cation–oxygen distances listed in Table 5. The dominance of Ca in both M sites defines calciolangbeinite as a new species.

At Tolbachik, we have found samples with compositions corresponding to intermediate members of a solid-solution series between langbeinite and calciolangbeinite. Representative compositions of the series, found in different parts of complex epitaxial intergrowths (Fig. 2), are listed in Table 1 (columns 2−4). The Ca:Mg ratio increases from early to later generations of the minerals in these intergrowths. Compositional variations in langbeinite−calciolangbeinite series minerals from the Yadovitaya fumarole (for bivalent cations and for Al in the M sites, from our electron microprobe data) are shown in Fig. 5. The compositions range from Ca-free langbeinite to a mineral with $Ca_{1.7}Mg_{0.3}$ in the M sites, although there is a gap between $Mg_{1.8}Ca_{0.2}$ and $Mg_{1.0}Ca_{1.0}$. Nonetheless, the existence of the continuous solid-solution series between langbeinite and calciolangbeinite, including the endmember $K_2Ca_2(SO_4)_3$, seems probable in nature. For this reason, we prefer to present the ideal formula of calciolangbeinite as $K_2Ca_2(SO_4)_3$, and not as $K_2(Ca,Mg)_2(SO_4)_3$, i.e. Mg is not considered to be an inalienable component of the mineral.

The existence of cation-ordered intermediate members of the langbeinite−calciolangbeinite series seems plausible when the significant difference in the sizes of Mg^{2+} and Ca^{2+} is considered. Of all the M^{2+} cations that have been reported in synthetic langbeinite-type potassium sulfates (Mg, Mn, Co, Ni, Zn, Cd and Ca; Speer and Salje, 1986), Ca^{2+} has the largest ionic radius. Partial ordering of the M^{2+} cations was reported in the compound $K_2Mn_{1.115}Cd_{0.845}(SO_4)_3$ ($P2_13$, $a =$

TABLE 5. Selected interatomic distances (Å) in the structure of calciolangbeinite.

$M(1)O_6$ octahedra
$M(1)-O(1)$ 2.202(5) $\times$ 3
$M(1)-O(2)$ 2.204(5) $\times$ 3
Mean   2.203

$M(2)O_6$ octahedra
$M(2)-O(4)$ 2.194(4) $\times$ 3
$M(2)-O(3)$ 2.198(5) $\times$ 3
Mean   2.196

$K(1)O_9$ polyhedra
$K(1)-O(1)$ 2.858(6) $\times$ 3
$K(1)-O(2)$ 3.079(7) $\times$ 3
$K(1)-O(4)$ 3.098(7) $\times$ 3
Mean   3.012

$K(2)O_6$ polyhedra
$K(2)-O(3)$ 2.841(5) $\times$ 3
$K(2)-O(4)$ 2.988(6) $\times$ 3
Mean   2.915

SO_4 tetrahedra
$S-O(1)$ 1.430(4)
$S-O(2)$ 1.448(4)
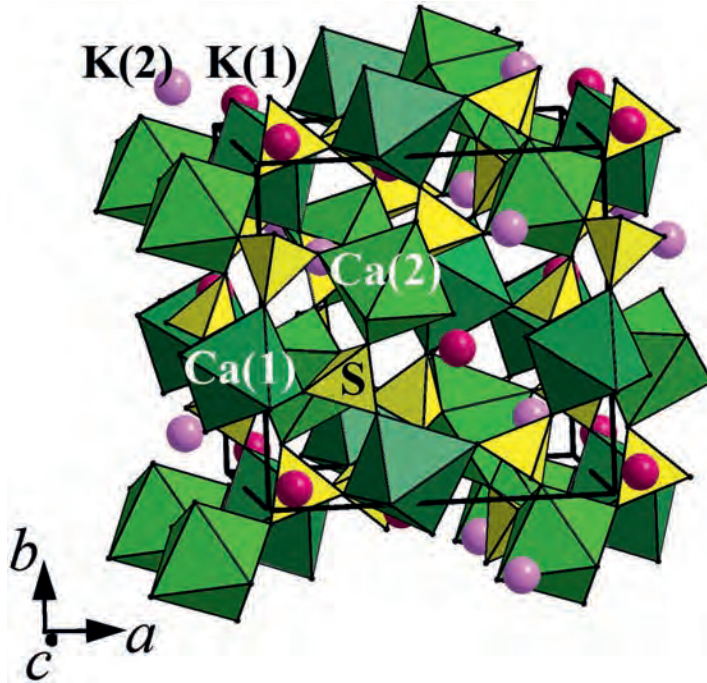$S-O(3)$ 1.450(4)
$S-O(4)$ 1.458(4)
Mean   1.447

FIG. 4. The crystal structure of calciolangbeinite. The framework is formed by $M(1)O_6$ and $M(2)O_6$ octahedra ($M =$ Ca), which are green, and SO_4 tetrahedra, which are yellow. The two K sites are represented by red and pink spheres.
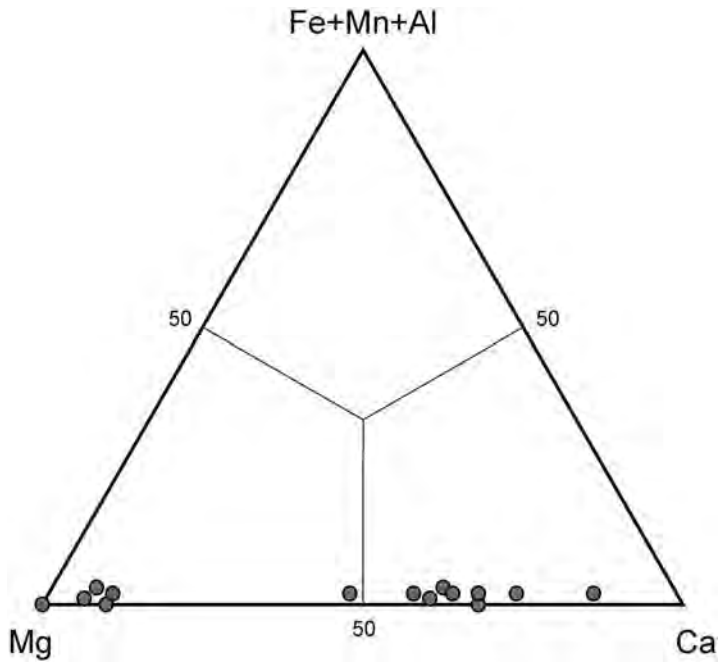

FIG. 5. A ternary diagram showing the ratios of M cations (divalent cations and Al) in the minerals of the langbeinite−calciolangbeinite series from the Yadovitaya fumarole, Tolbachik volcano, Kamchatka, Russia.

10.35 Å) in which $M(1) = Mn_{0.65}Cd_{0.35}$, $M(2) = Mn_{0.5}Cd_{0.5}$ (Magome *et al.*, 2004). Some synthetic langbeinite-type phosphates show significant or even complete M ordering. In $K_2Yb^{3+}Ti^{4+}(PO_4)_3$ ($P2_13$, $a = 10.09$ Å), $M(1) = Yb_{0.64}Ti_{0.36}$, $M(2) = Ti_{0.64}Yb_{0.36}$; in $K_2Cr^{3+}Ti^{4+}(PO_4)_3$ ($P2_13$, $a = 9.80$ Å), $M(1) = Cr_{0.61}Ti_{0.39}$, $M(2) = Ti_{0.61}Cr_{0.39}$ (Norberg, 2002); and in $K_2Pr^{3+}Zr^{4+}(PO_4)_3$ ($P2_13$, $a = 10.35$ Å), $M(1) = Pr_{1.0}$, $M(2) = Zr_{1.0}$ (Trubach *et al.*, 2004).

The Ca–Mg disorder in calciolangbeinite from Tolbachik is probably caused by the high temperature origin of the mineral. Both Ca and Mg have very low volatilities in volcanic gases at temperatures <400–500ºC (e.g. Symonds and Reed, 1993). Thus we assume that members of the langbeinite–calciolangbeinite series were deposited directly from the gas phase in the fumaroles at temperatures higher than 400ºC. However, the possibility that these minerals formed as a result of gas–rock interactions in which basalt served as a source of metals and sulfur originated from volcanic gases cannot be excluded. If this is the mechanism of formation, a lower temperature of crystallization for the langbeinite–calciolangbeinite series minerals (300–400ºC) can also be assumed.

Calciolangbeinite is a member of the langbeinite group of minerals, which includes langbeinite, manganolangbeinite and efremovite (Table 6). Manganolangbeinite (Zambonini and Carobbi, 1924; Bellanca, 1947) and calciolangbeinite are restricted in their occurrence to fumaroles at Vesuvius in Italy and at the Tolbachik volcanoes. Efremovite is more widely distributed, but has only been reported as a sublimate of coal fires (Shcherbakova and Bazhenova, 1989; Parafiniuk and Kruszewski, 2009; Shimobayashi *et al.*, 2011). Langbeinite is known from fumaroles (Vergasova and Filatov, 1993; this work) and from several localities as a sublimate formed in burning coal tips (Sejkora and Kotrlý, 2001; Naze-Nancy Masalehdani *et al.*, 2009). However, it is most common in marine evaporites, where it is an important ore of potash (Anthony *et al.*, 2003). Thus the most diverse

TABLE 6. Comparative data for langbeinite-group minerals.

Mineral	Efremovite		Langbeinite*		Manganolangbeinite*		Calciolangbeinite	
Endmember formula	$(NH_4)_2Mg_2(SO_4)_3$		$K_2Mg_2(SO_4)_3$		$K_2Mn_2(SO_4)_3$		$K_2Ca_2(SO_4)_3$	
Crystal system	Cubic		Cubic		Cubic		Cubic	
Space group	$P2_13$		$P2_13$		$P2_13$		$P2_13$	
a (Å)	9.99–10.03		9.92		10.01		10.19	
V (Å^3)	997–1010		977		1004		1058	
Z	4		4		4		4	
	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)
	5.76	35	4.05	25	5.84	10	5.84	8
	4.07	70	3.137	100	4.13	14	4.54	9
Strongest lines	3.15	100	2.992	16	3.198	100	4.15	27
in the X-ray	3.00	35	2.753	16	3.047	18	3.218	100
powder-	2.668	50	2.651	35	2.702	50	2.838	8
diffraction	1.855	20	2.405	12	2.064	14	2.736	37
pattern	1.741	20	1.946	10	1.984	14	2.006	11
	1.620	25	1.609	12	1.640	16	1.658	8
Refractive index	1.550		1.533–1.535		1.572		1.527	
Density (g cm^{-3})	2.52 (calc.)		2.77–2.83		3.02		2.68 (meas.) 2.737 (calc.)	
References	Shcherbakova and Bazhenova (1989); Shimobayashi *et al.* (2011)		Mereiter (1979); Anthony *et al.* (2003)		Zambonini and Carobbi (1924); Bellanca (1947)		This work	

* Unit cell and X-ray powder diffraction data are given for synthetic analogues of the endmember langbeinite and maganolangbeinite (from JCPDS-ICDD 19-974 and 20-909, respectively).

occurrences of langbeinite-group minerals are in sublimates related to volcanic fumaroles and in burning coal deposits or dumps; only langbeinite is known in other geological environments.

Acknowledgements

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