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ORIGINAL PAPER

Jörgkellerite, $Na_3Mn^{3+}{}_3(PO_4)_2(CO_3)O_2 \cdot 5H_2O$, a new layered phosphate-carbonate mineral from the Oldoinyo Lengai volcano, Gregory rift, northern Tanzania

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Abstract Jörgkellerite, ideally $Na_3Mn^{3+}{}_3(PO_4)_2(CO_3)O_2 \cdot 5H_2O$, is a new layered phosphate-carbonate from the Oldoinyo Lengai volcano in the Gregory Rift (northern Tanzania). The mineral occurs as spherulites, up to 200 µm in diameter, consisting of plates up to 10 µm in thickness in shortite-calcite and calcite carbonatites. Jörgkellerite is brown with a vitreous lustre and has a perfect micaceous cleavage on {001}, Mohs hardness is 3. The calculated density is 2.56 g/cm^3. Jörgkellerite is uniaxial (-), $\omega = 1.700(2)$, $\varepsilon = 1.625(2)$ (Na light, 589 nm) with distinct pleochroism: O = dark brown, E = light brown. The empirical formula of the mineral (average of 10 electron microprobe analyses) is $(Na_{2.46}K_{0.28}Ca_{0.08}Sr_{0.04}Ba_{0.02})_{\Sigma 2.88}(Mn^{3+}{}_{2.39}Fe^{3+}{}_{0.56})_{\Sigma 2.95}((PO4)_{1.95}(SiO_4)_{0.05}))_{\Sigma 2.00}(CO_3)(O_{1.84}(OH)_{0.16})_{\Sigma 2.00} \cdot 5H_2O$. The oxidation state of Mn has been determined by XANES. Jörgkellerite is trigonal, space group *P*-3, $a = 11.201(2)$ Å, $c = 10.969(2)$ Å, $V = 1191.9(7)$ Å^3 and $Z = 3$. The five strongest powder-diffraction lines [*d* in Å, (I/I_o), (*hkl*)] are: 10.970 (100) (001), 5.597 (15) (002), 4.993 (8) (111), 2.796 (14) (220) and 2.724 (20) (004). The crystal structure is built up of the layers composed of disordered edge-sharing [MnO_6] octahedra. Each fourth Mn site in octahedral layer is vacant that results in appearance of ordered system of hexagonal "holes" occupied by (CO_3) groups. The overall composition of the layer can be expressed as [$Mn_3O_8(CO_3)$]. These manganese-carbonate layers are linked in the third dimension by (PO_4) tetrahedra and Na-polyhedra. The origin of jörgkellerite is related to low-temperature oxidative alteration of gregoryite-nyerereite carbonatites.

Keywords Jörgkellerite · Phosphate-carbonate mineral · Carbonatite · Oldoinyo Lengai

Introduction

Oldoinyo Lengai is a well-known volcano in northern Tanzania owing to eruptions of highly alkaline gregoryite-nyerereite carbonatites and nephelinites from northern crater (e.g., Dawson 1962; Donaldson et al. 1987; Peterson 1989, 1990; Klaudius and Keller 2006; Keller and Zaitsev 2012). The volcano also contains phonolites, which form the older southern cone (Donaldson et al. 1987; Klaudius and Keller 2006), and olivine melilitites are known from several cones and craters on the lowest slopes and in the vicinity of Oldoinyo Lengai (Keller et al. 2006).

The carbonatites of Oldoinyo Lengai, occurring as lavas, lapilli and dykes (e.g., Dawson 1962; Church and Jones 1994; Keller and Zaitsev 2006; Zaitsev et al. 2009b), consist of four major minerals. Three are water-soluble: gregoryite

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$Na_2(CO_3)$, nyerereite $Na_2Ca(CO_3)_2$ and sylvite KCl, while fluorite CaF_2 is the only stable carbonatitic mineral under normal atmospheric conditions (Dawson et al. 1987; Keller and Zaitsev 2006; Mitchell 2006b; Zaitsev and Keller 2006).

Silicate-carbonate liquid immiscibility is considered to be a major process in the evolution of the Oldoinyo Lengai volcano and the formation of alkaline carbonatites and silicate rocks (e.g., Mitchell 2009; Sharygin et al. 2012; Sekisova et al. 2015). Radiogenic and stable isotope studies point to a mantle source for a primary carbonate-bearing silicate melt, and large variations in radiogenic isotope ratios are explained by a mixing of different mantle sources (Bell and Dawson 1995; Keller and Hoefs 1995; Bell and Simonetti 1996; Keller and Zaitsev 2006; Keller et al. 2006). A Sr-Nd-Pb isotope study of both unaltered and altered Oldoinyo Lengai carbonatites, including a calcite carbonatite xenolith described by Dawson (1993) and Zaitsev et al. (2013), and a calcite carbonatite dyke (Keller and Zaitsev 2006), suggests eruption of isotopically different batches of carbonatite magma at Oldoinyo Lengai (Zaitsev et al. 2009a).

Alteration of the gregoryite-nyerereite carbonatites begins immediately after their eruption and they transform to pirssonite and calcite carbonatites with significant loss of sodium, potassium, chlorine and sulphur (Zaitsev and Keller 2006). During mineralogical study of altered carbonatites, a new mineral was found in one of the samples. It is a layered hydrous sodium manganese phosphate-carbonate belonging to a new structure type. The mineral was named in honour of Prof. Dr. Jörg Keller (born 1938), Emeritus Professor of Institut für Geo- und Umweltnaturwissenschaften, Albert-Ludwigs-Universität, Freiburg, Germany. The name, jörgkellerite, honours valuable contributions of Prof. Dr. Jörg Keller to the study of the origin and evolution of alkaline rocks and carbonatites, and particularly the Oldoinyo Lengai volcano (e.g., Keller and Krafft 1990; Bell and Keller 1995; Klaudius and Keller 2006; Keller et al. 2010). Both the mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2015-020). A polished mount with jörgkellerite spherulites extracted from the holotype sample OL 124 is deposited in the mineral collection at Mineralogy Department, St. Petersburg State University, St. Petersburg, Russia - catalogue number 19640/1).

Occurrence and morphology

Jörgkellerite was found during mineralogical study of an older, pre-1917, carbonatite platform (see Fig. 1 in Zaitsev et al. 2008) in a highly altered carbonatite sample (sample OL 124). This rock has been described in several publications (Zaitsev and Keller 2006; Zaitsev et al. 2008) and it consists of two mineral assemblages. The first is composed of relics of the primary carbonatite minerals fluorite, khanneshite, baryte, magnetite and rare nyerereite, and the second is composed of secondary minerals formed during low-temperature carbonatite alteration, such as calcite, shortite, nahcolite, trona, jacobsite and barytocalcite (see Fig. 2c in Zaitsev and Keller 2006, and Figs. 2b, 4, 6, 8–10 in Zaitsev et al. 2008).

Jörgkellerite occurs as spherulites, up to 200 μm in diameter, consisting of plates up to 10 μm in thickness (Fig. 1). Spherulites contain relics of fluorite, magnetite and khanneshite. Macroscopically jörgkellerite is brown, with vitreous luster and white streak. In thin section, the mineral is yellow to red-brown in cross-polarised light with undulose extinction and brown in plane-polarised light. The mineral is transparent, with perfect micaceous cleavage on {001}, Mohs hardness is 3. Density could not be measured due to lack of sufficiently large inclusion-free crystals; the density,

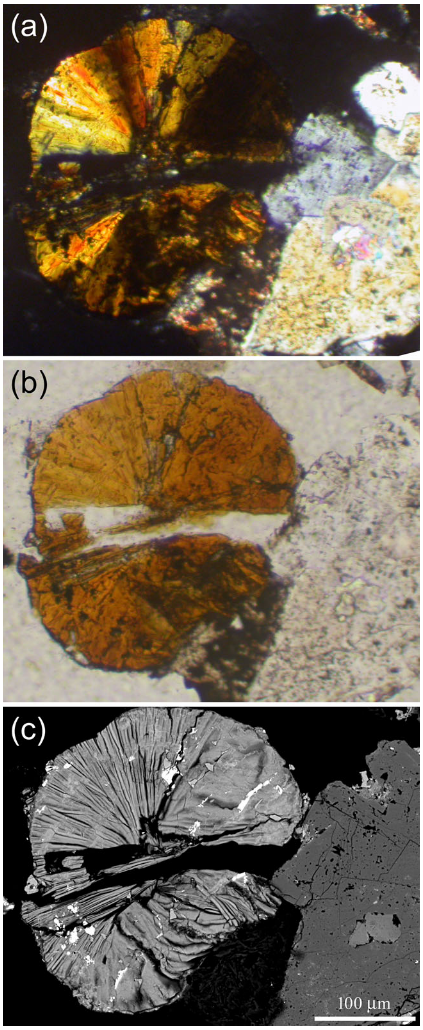

Fig. 1 Jörgkellerite spherulite (colour online), sample OL 124. **a** - cross-polarised light, **b** - plane-polarised light, **c** - BSE image. Light gray grains in shortite – calcite, white grains in jörgkellerite – magnetite-jacobsite and khanneshite, light gray grains in jörgkellerite (similar in colour to calcite) – fluorite

calculated on the basis of the empirical formula, is 2.56 g/cm^3. Jörgkellerite is uniaxial (-), $\omega = 1.700(2)$, $\varepsilon = 1.625(2)$ (Na light, 589 nm) with distinct pleochroism: O = dark brown, E = light brown. The mineral is non-fluorescent. The Gladstone-Dale compatibility index, $1 - (K_p/K_c)$ calculated using 112empirical formula and the unit cell parameters refined from XRD powder data, is -0.034 (excellent).

General mineralogical characterization

Infrared spectroscopy

Infrared spectra of jörgkellerite were collected from four spherulites mounted in epoxy resin using a Perkin Elmer Auto IMAGE microscope and a Perkin Elmer Spectrum FTIR spetrometer with a CsI beam splitter and a narrow-band MCT (mercury cadmium telluride) detector (Natural History Museum, London). The micro ATR objective has a germanium crystal with a 100 μm diameter tip that fixes the maximum diameter of the area sampled. The spectral resolution was set at 4 cm^{-1}. The microscope optics and detector restrict the wavelength range used to 4000–700 cm^{-1}. Atmospheric background adsorption was compensated for by subtraction of a blank (air) spectrum from the sample spectrum.

Tentative assignments of absorption bands in the IR spectrum of jörgkellerite (Fig. 2) have been made via comparison with the IR spectra of other phosphates and carbonates, including sidorenkite (Frost et al. 2015), shortite (Frost and Dickfos 2008) and vivianite-group minerals (Frost et al. 2002). The spectrum of jörgkellerite (Fig. 2) is characterised by the following absorption bands (cm^{-1}): 821 (water librational mode); 861 (ν_2 $(CO_3)^{2-}$ out-of-plane bending mode); 939, 1035 and 1075 (ν_3 $(PO_4)^{3-}$ antisymmetric stretching mode and ν_1 $(CO_3)^{2-}$ symmetric stretching mode); 1404 and 1443 (ν_3 $(CO_3)^{2-}$ antisymmetric stretching mode; 1629 (water HOH bending mode) and 3260–3300 (hydroxyl stretching vibrations) (not shown on the picture).

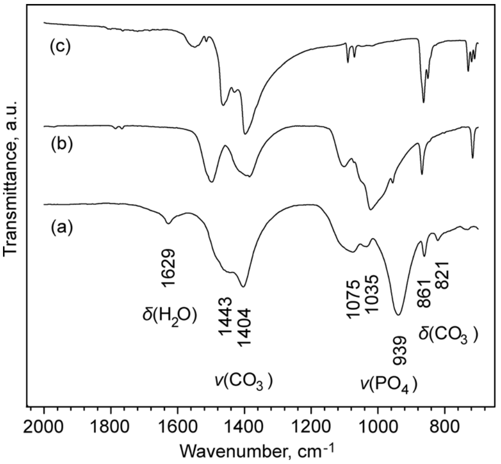

Fig. 2 IR absorption spectrum of jörgkellerite (*a*) in the region 2000–700 cm^{-1}. IR spectra of (*b*) sidorenkite $Na_3Mn^{2+}(PO_4)(CO_3)$ and (*c*) shortite $Na_2Ca_2(CO_3)_3$ are given for comparison purposes

Chemical analysis

The chemical composition of jörgkellerite was studied by electron probe X-ray microanalysis techniques (wavelength dispersive X-ray and energy dispersive X-ray spectrometries - WDS and EDS, respectively). The EDS analyses were performed using a JEOL 5900LV SEM equipped with an Oxford Instruments X-sight Si(Li) detector (Natural History Museum, London). Spectra were acquired for 50 s (live time) with an accelerating voltage of 20 kV and a beam current of 2 nA determined in a Faraday cup. For calibration, we used well-characterized mineral standards, with optimization of gain and current on a Co standard. A defocused beam, 5–8 μm in diameter, was used for analyses. The spectra were processed with the extended Pouchou and Pichoir (XPP) model in the INCA Oxford Instruments software package. To confirm the presence of carbon and to determine element content, the mineral was also studied using a JEOL 8900 Superprobe operated in WDS mode (Tübingen University). The carbon peak is clearly visible on a qualitative spectrum recorded by a LDE2 crystal spectrometer (Online Resource 1). The WDS analyses (15 kV, 7.5 nA and 2 μm beam diameter, sidorenkite as C standard, gold coating) gave 12.5–16.0 CO_2 wt.% (6 analyses). These values are much higher than the calculated CO_2 content (7.34 wt.%) probably due to mineral instability under the electron beam, uneven grain surfaces and microporosity; because of this, these values were not used in discussion of the analytical results. Determination of water content by means of conventional thermogravimetric analysis was not possible due to lack of sufficiently large inclusion-free crystals, but the presence of water was confirmed by spatially resolved IR spectroscopy (see the previous section) and X-ray single-crystal structure analysis.

The composition of jörgkellerite (average, standard deviation and range from 10 analyses) is given in Table 1. The oxidation state of manganese has been determined by means of X-ray near-edge absorption spectroscopy (XANES) at the Mn-*K* edge (Fig. 3). XANES spectra of jörgkellerite, $MnCO_3$ and Mn_2O_3 were recorded in transmission mode on the beamline A1, DORIS III ring, DESY, Hamburg. It is well known that XANES spectra of manganese are valence-sensitive: the position of white line at Mn *K*-edge allows to distinguish between Mn^{2+}, Mn^{3+} and Mn^{4+} (e.g., Manceau et al. 1992; Soldati et al. 2010). Our data (Fig. 3) are consistent with Mn being predominantly in the 3+ oxidation state in jörgkellerite, therefore microprobe data were recalculated based on Mn^{3+}. All iron was also assumed to be ferric as the oxidation potential of Fe^{3+} is lower than that of Mn^{3+}.

Table 1 Composition of jörgkellerite

Component	wt%	Range	Stand. Dev.	Probe standard
Na_2O	12.71	11.15–13.90	1.00	Sidorenkite
SiO_2	0.51	0.35–0.74	0.12	Orthoclase
P_2O_5	23.07	21.18–23.95	1.08	Apatite
K_2O	2.17	1.67–2.83	0.44	Orthoclase
CaO	0.76	0.40–1.35	0.33	Apatite
Mn_2O_3[a]	31.46	28.61–33.11	1.57	Manganese
Fe_2O_3[a]	7.52	6.52–9.00	0.74	Iron
SrO	0.76	0.40–1.04	0.21	Celestite
BaO	0.47	0.37–0.75	0.15	Baryte
CO_2[b]	7.34			
H_2O[c]	15.22			
Total	102.03			

[a] all Mn and Fe were calculated as Mn^{3+} and Fe^{3+}

[b] calculated assuming one $(CO_3)^{2-}$ group in the formula

[c] calculated assuming 5 H_2O groups and 2(O,OH) positions

Back-scattered electron images (Fig. 4) show that jörgkellerite spherulites are typically quite heterogeneous in composition. The heterogeneity of the mineral is revealed by the presence of spotty and cloudy areas within spherulites (light gray areas in Fig. 4). These areas are enriched in Na, Ca, Sr and Ba, evidence for the presence of micron-size inclusions of shortite, fluorite and strontium-barium carbonates intimately intergrown with jörgkellerite platelets. The analyses with high content of these elements, were not used for calculation of average composition.

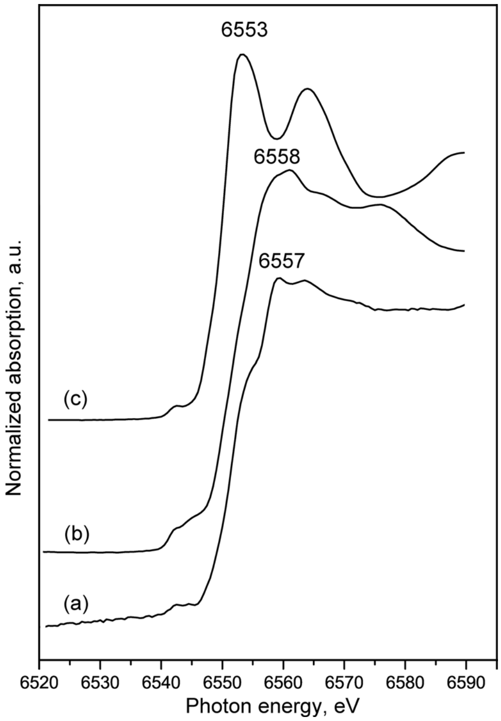

Fig. 3 Mn-*K* edge XANES spectra of (*a*) jörgkellerite, (*b*) synthetic Mn_2O_3 (Mn^{3+}) and (*c*) synthetic $MnCO_3$ (Mn^{2+}). The position of white line in jörgkellerite spectrum (6557 eV) coincide with that of Mn_2O_3 evidencing that manganese is represented by Mn^{3+}

Jörgkellerite is a complex hydrated phosphate-carbonate mineral with Na and Mn as major cations and subordinate Fe, K, Ca, Sr and Ba (Table 1). The analytical total, with calculated CO_2 and H_2O contents, somewhat exceeds 100 wt.% that can be accounted for partial loss of hydrate water under electron beam or insignificant amount of Mn^{2+} in the chemical composition. The empirical mineral formula, calculated for (P + Si) = 2 and O = 18, is $(Na_{2.46}K_{0.28}Ca_{0.08}Sr_{0.04}Ba_{0.02})_{\Sigma 2.88}(Mn^{3+}{}_{2.39}Fe^{3+}{}_{0.56})_{\Sigma 2.95}((PO4)_{1.95}(SiO_4)_{0.05}))_{\Sigma 2.00}(CO_3)(O_{1.84}(OH)_{0.16})_{\Sigma 2.00}\cdot 5H_2O$. The CO_2 and H_2O contents (Table 1) were assumed to be one $(CO_3)^{2-}$ and five H_2O per formula unit, on the basis of results of X-ray structure analysis (see below). The simplified formula can be expressed as $(Na,\square)_3Mn^{3+}{}_3(PO_4)_2(CO_3)(O,OH)_2\cdot 5H_2O$ or ideally $Na_3Mn^{3+}{}_3(PO_4)_2(CO_3)O_2\cdot 5H_2O$.

X-ray powder diffraction and description of the crystal structure

The spherulites of jörgkellerite are always contaminated with the microinclusions of various minerals (Fig. 4); therefore, the clear platelets suitable for X-ray powder diffraction study have been cautiously selected in the immersion liquid. A small micro-batch of disintegrated platelets has been pinned up onto glass fiber for powder data acquisition. X-ray powder diffraction pattern (Table 2) has been obtained by means of Stoe IPDS II image plate diffractometer (Gandolfi geometry, Mo*K*α-radiation, 50 kV, 40 mA, *d* = 200 mm, exposure 30 min).

In spite of relatively large size of jörgkellerite spherulites, the severely curved habit of the platelets (Fig. 1) imposed substantial difficulties for selection of the crystals appropriate for X-ray structural study. Despite these issues, a relatively small crystal of the mineral did provide data sufficient for the structure solution and subsequent refinement that has been carried out using *SHELX*-97 software via Olex2 v.2.1 graphical user interface (Sheldrick 2008; Dolomanov et al. 2009). The details of data collection routine, structure solution and refinement are summarized in Table 3; fractional atomic coordinates and selected interatomic bond distances are given in Tables 4 and 5, respectively. The listing of anisotropic displacement parameters can be obtained from the supplementary CIF file (Online Resource 2). The relatively high values of R_1 and wR_2 (Table 3) are accounted for the imperfectness of the even best crystal which could be selected for the study.

Jörgkellerite represents the only known example of a phosphate-carbonate having layered architecture (Fig. 5). The basic unit of its structure is an infinite $[Mn_3O_8(CO_3)]$ layer: a two-dimensional lattice composed of triplets of disordered $[MnO_6]$ octahedra (Fig. 5) arranged so that pseudo-

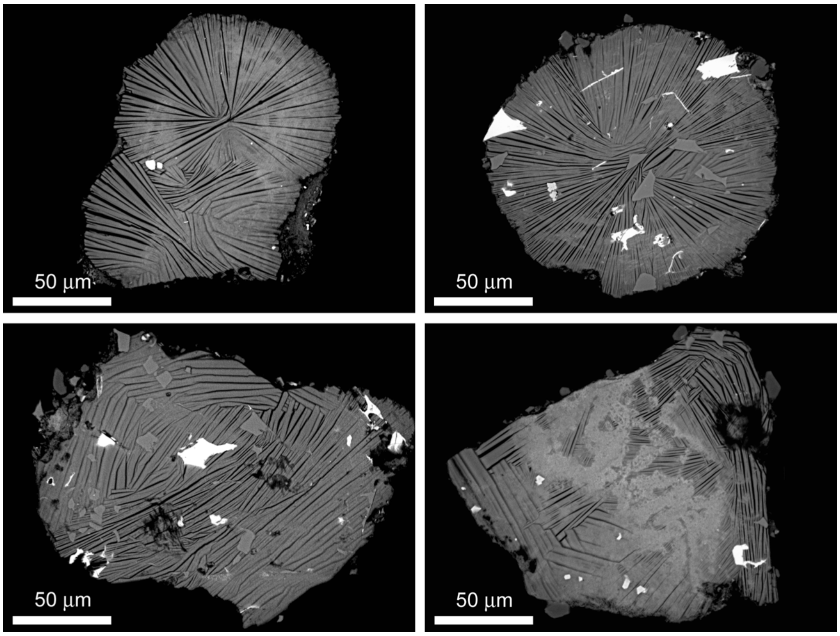

Fig. 4 Back-scattered electron images of jörgkellerite sperulite showing heterogeneous composition of the mineral and inclusions of khanneshite (*white*), calcite and fluorite (*gray*)

fourfold axis of each octahedron is directed outwards of the layer (Fig. 6). Each pair of symmetrically independent octahedra share common oxygen atom O3 (Fig. 6, Tables 4 and 5) whereas oxygen sites lying in equatorial positions are half-occupied (O12) or asymmetrically split between two mutually exclusive sites O13 and O14 (Table 4, Fig. 6). [MnO_6] octahedra are somewhat compressed along ***Z*** axis due to Jahn-Teller effect (Table 5). Such compressive distortion rather than elongation of [MnO_6] octahedra, albeit rare, is known both in mineral structures (Moore 1967; Armbruster et al. 1993; Hawthorne et al. 1995) and inorganic Mn(III) compounds (Tregenna-Piggott 2008). Each fourth Mn site in the layer is vacant; the latter results in appearance of ordered hexagonal "holes" (Fig. 4) occupied by (CO_3) groups. The resulting [$Mn_3O_8(CO_3)$] layers are arranged into 3D structure via the slabs composed of corner or edge sharing (PO_4) tetrahedra and Na polyhedra (Fig. 5b, Table 4). Note that all Na polyhedra are partially occupied (Table 5) and we suggest that the Na site occupation may vary from crystal to crystal and even inside the same crystal. That could result in some differences in the chemical composition observed for different crystals.

The unique layered structure of jörgkellerite and occurrence of redox-sensitive component (manganese) in its composition makes this mineral promising prototype for further studies of sodium ions mobility. Recently, the library of perspective phosphate cathode materials suitable for Na-ion batteries (Yabuuchi et al. 2014; Kim et al. 2016) have been expanded with synthetic analogue of the mineral sidorenkite $Na_3Mn(PO_4)(CO_3)$ (Chen et al. 2013; Hassanzadeh et al. 2014). The studies aimed at the synthesis of synthetic analogue of jörgkellerite could result in discovery of new phosphate matrices for sodium-ion batteries.

Discussion of the formation of jörgkellerite

Jörgkellerite is a rare mineral at Oldoinyo Lengai; it occurs in two samples of highly altered carbonatites including shortite-

Table 2 X-ray powder diffraction data for jörgkellerite

I_{obs}	d_{obs}	I_{calc}	d_{calc}	*h*	*k*	*l*
100	10.970	100	10.969	0	0	1
15	5.597	5	5.601	1	1	0
		15	5.485	0	0	2
8	4.993	5	4.988	1	1	1
4	3.659	4	3.656	0	0	3
6	3.234	6	3.234	0	3	0
		2	3.102	3	0	1
2	3.060	1	3.062	1	1	3
14	2.796	6	2.800	2	2	0
		6	2.785	3	0	2
20	2.724	8	2.742	0	0	4
		8	2.713	2	2	1
4	2.496	1	2.494	2	2	2
		1	2.463	1	1	4
5	2.189	5	2.194	0	0	5
3	2.120	2	2.117	4	1	0
4	2.080	2	2.078	4	1	1
2	1.837	1	1.840	3	3	1
2	1.828	1	1.828	0	0	6
2	1.768	1	1.767	3	3	2
3	1.729	1	1.727	2	2	5
4	1.616	5	1.617	0	6	0
2	1.597	2	1.599	6	0	1
3	1.529	2	1.531	2	2	6
1	1.478	1	1.479	6	0	3
3	1.394	2	1.393	6	0	4
2	1.358	1	1.357	4	4	2
2	1.302	2	1.302	6	0	5

Calculated data were obtained based on atomic coordinates taken from structural refinement and lattice parameters refined from powder data

Table 3 Crystal parameters, data collection and structure refinement details for jörgkellerite

Structural Formula	$(Na_{2.18}\square_{0.82})_{3.00}(Mn^{3+}_{2.43}Fe^{3+}_{0.57})_{3.00}(PO_4)_2(CO_3)$ = = $[O_{1.18}(OH)_{0.82}]_{2.00}(H_2O)_{5.43}$
Crystal size, mm	0.02 × 0.02 × 0.005
Crystal system; space group	Trigonal; *P*3
a, Å; *c*, Å; *V*, $Å^3$; *Z*	11.2021(9); 10.875(1); 1181.8(2); 3
D_x, g/cm^3	2.51
Instrument and X-ray optics	Bruker Kappa APEX DUO (CCD), microfocus tube
Radiation; temperature (K)	Mo$K\alpha$ (0.71073 Å); 293
2Θ range, degrees	3.74–50.00
Total; unique; unique observed reflections	2347; 1397; 846
$R_{int.}$; R_σ	0.037; 0.059
hkl range	$-13 < h < 10$; $-11 < k < 9$; $-8 < l < 12$
R_1 ($\lvert F_o \rvert \geq 4\sigma_F$); R_1 (all data); wR_2; *S*=*GooF*	0.088; 0.137; 0.231; 1.184

calcite (sample OL 124) and calcite (sample OL 329) carbonatites. The latter is from the Northern Flank and collected about 50 m below the pre-2007 eruption crater rim. Here altered carbonatites immediately overlying the truncated combeite-wollastonite nepelinites of Lengai IIb and they can belong to an earliest pre-1917 carbonatite platform in the crater area. Formation of calcitic carbonatites at the Oldoinyo Lengai volcano is a result of multi-stage alteration of gregoryite-nyerereite carbonatites due to reactions with atmosphere and meteoric water at temperatures between 8 and 43 °C with variable fugacity of CO_2 and H_2O and relatively high pH values (Dawson et al. 1987; Mitchell 2006b; Zaitsev and Keller 2006; Zaitsev et al. 2008; Perova and Zaitsev 2016). An experimental study of shortite formation shows mineral formation via reaction pirssonite + calcite = shortite + H_2O at temperature above 55 ± 2 °C (P = 1 atm) (Jagniecki et al. 2013). Addition of NaCl to the system lowered equilibrium temperature to 52 ± 2 °C (P = 1 atm).

Although hydrothermal phosphate minerals (except apatite-group minerals) are common in a several carbonatite

Table 4 Fractional atomic coordinates, site occupancies and isotropic displacement parameters (U_{iso}) in the crystal structure of jörgkellerite

Site	Occupancy	*x/a*	*y/b*	*z/c*	U_{iso}
*M*1	$Mn_{0.81}Fe_{0.19}$	0.33326(14)	0.17792(14)	−0.00039(14)	0.0135(6)
*M*2	$Mn_{0.81}Fe_{0.19}$	1/2	1/2	0	0.0194(8)
Na1	$Na_{0.84}$	0.3269(6)	0.3409(6)	0.2623(6)	0.042(3)
Na2	$Na_{0.54}$	0	0	1/2	0.056(11)
Na3	$Na_{0.46}$	1/3	2/3	−0.5066(16)	0.043(8)
P1	$P_{1.00}$	0.3249(3)	0.3413(3)	−0.2238(3)	0.0236(8)
C1	$C_{1.00}$	2/3	1/3	−0.0223(13)	0.034(5)
C2	$C_{1.00}$	0	0	0	0.044(9)
O1	$O_{1.00}$	0.3417(8)	0.1476(7)	0.1739(7)	0.0287(19)
O2	$O_{1.00}$	0.3252(8)	0.2102(8)	−0.1774(6)	0.0247(18)
O3	$O_{0.59}(OH)_{0.41}$	0.3252(7)	0.3423(7)	0.0408(7)	0.0243(18)
O4	$O_{1.00}$	0.4551(8)	0.4724(8)	−0.1764(6)	0.0239(18)
O5	$O_{1.00}$	0.3234(9)	0.3416(9)	−0.3615(8)	0.041(2)
O6	$(H_2O)_{0.63}$	0.455(4)	0.334(5)	0.435(2)	0.18(3)
O7	$(H_2O)_{0.64}$	0.212(5)	0.195(5)	0.432(3)	0.26(4)
O8	$(H_2O)_{0.94}$	2/3	1/3	0.255(2)	0.061(9)
O9	$(H_2O)_{0.55}$	0	0	0.248(4)	0.069(17)
O10	$(H_2O)_{0.78}$	2/3	1/3	−0.254(5)	0.26(4)
O11	$(H_2O)_{0.69}$	0.664(8)	0.521(5)	0.575(5)	0.40(6)
O12	$O_{0.50}$	0.1157(15)	0.1201(14)	−0.0069(13)	0.021(3)
O13	$O_{0.87}$	0.5501(8)	0.3358(8)	−0.0101(6)	0.020(3)
O14	$O_{0.13}$	0.534(8)	0.220(9)	−0.0155(15)	0.06(3)

Table 5 Interatomic bond distances (Å) and coordination of cations in the crystal structure of jörgkellerite

Site1	Site2	Distance	Notes
*M*1	O1	1.936(8)	Octahedron
	O2	1.969(7)	compressed along
	O3	1.906(7)	*z*-axis
	O3	1.940(7)	
	O12	2.188(14)–2.201(13)	
	O13-O14	2.178(8)–2.06(8)	
*M*2	O3	2 × 1.922(7)	Octahedron
	O4	2 × 1.968(7)	compressed along
	O13-O14	2.178(8)–2.30(9)	*z*-axis
Na1	O1	2.450(9)	Polyhedron
	O2	2.470(9)	$NaO_3(H_2O)_4$
	O3	2.409(10)	
	O4	2.471(10)	
	O6	2.38(3)	
	O7	2.38(4)	
	O11	2.32(4)	
Na2	O7	6 × 2.40(4)	Cube $Na(H_2O)_8$
	O9	2 × 2.74(4)	
Na3	O6	3 × 2.50(3)	Cube $Na(H_2O)_8$
	O8	2.73(3)	
	O10	2.61(6)	
	O11	3 × 2.24(4)	
P1	O1	1.564(8)	
	O2	1.555(7)	
	O4	1.551(8)	
	O5	1.498(9)	
C1	O13	3 × 1.326(8)	sof(O13) = 0.87
	O14	3 × 1.39(8)	sof(O14) = 0.13
C2	O12	6 × 1.323(15)	sof(O12) = 1/2

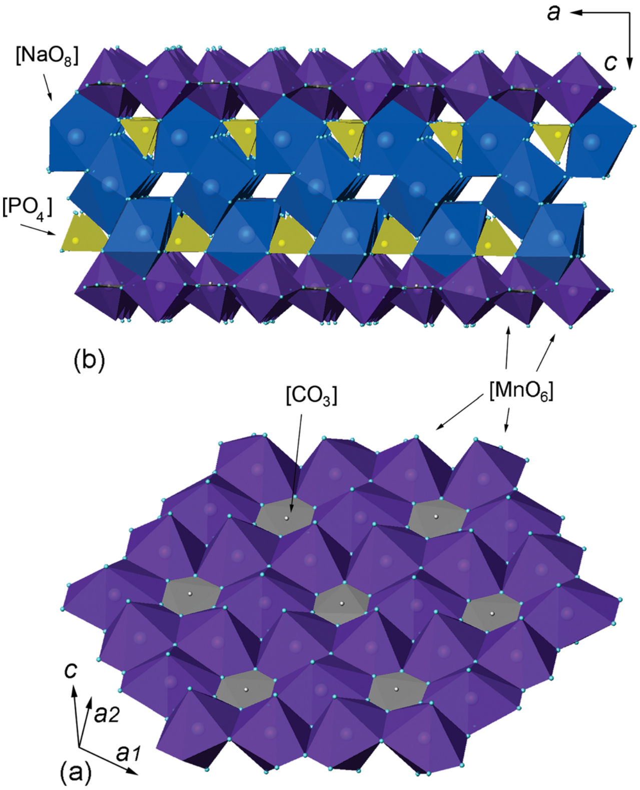

Fig. 5 Crystal structure of jörgkellerite (colour online). **a** $[Mn_3O_8(CO_3)]$ layer composed of disordered edge-sharing $[MnO_6]$ octahedra (*violet*) with hexagonal "holes" inhabited by disordered slightly non-planar (CO_3) groups (grey). **b** $[Mn_3O_8(CO_3)]$ layers (*violet*) linked by (PO_4) tetrahedra (*yellow*) and Na-polyhedra (*blue*)

complexes such as Kovdor massif (Britvin et al. 1990, 1991, 2002; Krivovichev et al. 2002, 2013), phosphate-carbonate species are practically unknown in these associations. Jörgkellerite has no similarity in both composition and structure with any of known minerals and synthetic compounds. Only sidorenkite, $Na_3Mn(PO_4)(CO_3)$ (Khomyakov et al. 1980; Kurova et al. 1980), and girvasite $NaCa_2Mg_3(PO_4)_3(CO_3)\cdot 6H_2O$ (Britvin et al. 1990; Krivovichev et al. 2015) show similarity in composition, but sidorenkite is anhydrous and contains Mn^{2+}, while girvasite does not contain Mn. An un-named sodium phosphate-carbonate mineral with an approximate formula "$Na_{5\text{-}4.5}PO_4(CO_3,F,Cl)$" has been described from altered carbonatite lapilli at Oldoinyo Lengai (Mitchell 2006a). Unfortunately, only compositional data have been reported for this mineral, and lack of structural and/or spectroscopic data does not allow for precise identification of this phase. High sodium content (51.3–55.8 wt.% Na_2O), lack of manganese and presence of fluorine and chlorine (4.9–5.1 and 1.0–1.1 wt.% respectively) clearly show that this mineral is not jörgkellerite.

Manganese-bearing minerals are known in the Oldoinyo Lengai carbonatites. Unaltered carbonatites contain between 0.32 and 0.87 wt.% MnO with an average value of 0.46 wt.% (Keller and Zaitsev 2012). At low levels, Mn is present in the major minerals nyerereite (852–1750 ppm) and gregoryite (478–1838 ppm) (Zaitsev et al. 2009b; Mitchell and Kamenetsky 2012). Much higher concentrations are found in accessory magnetite (10.5–16.6 wt.% MnO), monticellite (10.9–14.1 wt.% MnO), sphalerite (9.2–20.3 wt.% Mn) and pyrrhotite (up to 3 wt.% Mn) (Mitchell and Belton 2004). Accessory alabandite is the only mineral in the Oldoinyo Lengai carbonatites that contains Mn as an essential element (35.8–49.1 wt.% Mn) (Mitchell and Belton 2004 and references herein).

Altered pirssonite carbonatites contain similar levels of Mn (0.51–0.88 wt.% MnO) and calcite carbonatites show slight enrichment in Mn with MnO content between 0.80 and 1.34 wt.% (sample OL 329 contains 1.25 wt.% MnO) (Zaitsev and Keller 2006). While gregoryite, nyerereite and alabandite are unstable minerals that completely dissolve

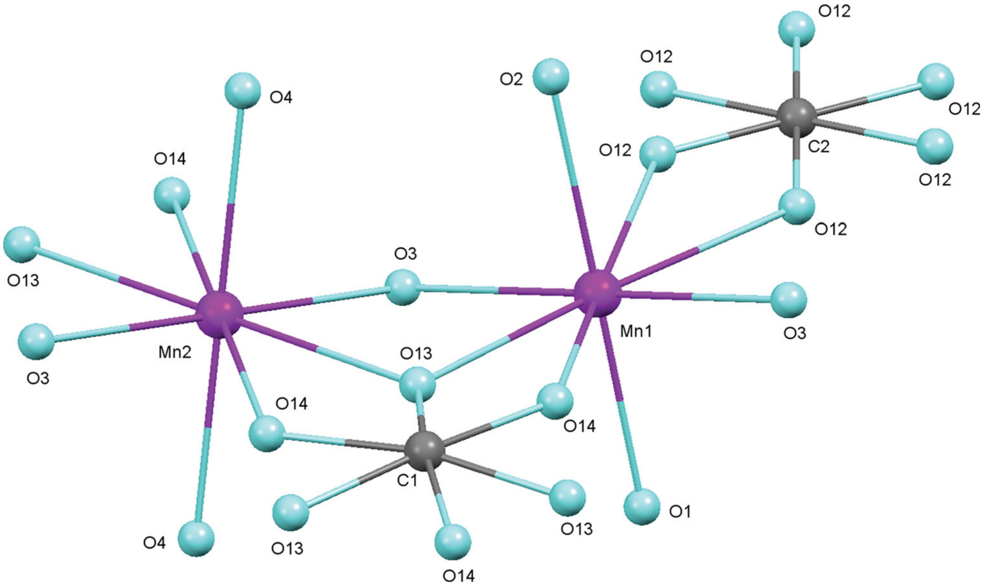

Fig. 6 Fragment of $[Mn_3O_8(CO_3)]$ layer of jörgkellerite structure in skeletal representation (colour online). Two symmetrically independent distorted $[MnO_6]$ octahedra share common O3 oxygen-hydroxyl site (fully occupied position). Positions of apical oxygen atoms O1, O2 and O4 are also fully occupied whereas oxygen sites O12 is half-occupied and mutually exclusive sites O13 and O14 are occupied in a 87:13 ratio (Table 3)

during alteration, secondary pirssonite and calcite carbonatites contain abundant relic magnetite, which may act as a Mn reservoir (Keller and Zaitsev 2006; Zaitsev et al. 2008). Other primary Mn-bearing minerals were not observed in calcite carbonatites, but their possible presence could not be excluded. Jacobsite, $Mn^{2+}Fe^{3+}{}_2O_4$, a spinel-group mineral, occurs in some highly altered carbonatites at Oldoinyo Lengai and contains up to 22.4 wt.% MnO (Zaitsev et al. 2008, 2013). However, the Mn oxidation state may vary as a result of incorporating Mn^{3+} from a hausmannite component in solid solution. The crystallisation of Mn^{3+}-rich jörgkellerite requires specific local conditions, namely high Eh and pH values, which are favourable for the stability of Mn^{3+} (Garrels and Christ 1965).

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