Hatertite, Na$_2$(Ca, Na)(Fe^{3+}, Cu)$_2$(AsO$_4$)$_3$, a new alluaudite-group mineral from Tolbachik fumaroles, Kamchatka peninsula, Russia

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Abstract: Hatertite, ideally Na$_2$(Ca, Na)(Fe^{3+}, Cu)$_2$(AsO$_4$)$_3$, was found in a fumarole of the North Breach of the Great fissure Tolbachik volcano eruption (1975–1976), Kamchatka Peninsula, Russia. The mineral occurs as individual, prismatic and tabular, honey-yellow crystals up to 0.3 mm across. It has a vitreous luster and yellow streak. Hatertite is monoclinic, $C2/c$, $a = 12.590(2)$, $b = 12.993(3)$, $c = 6.700(2)$ Å, $\beta = 113.72(2)^o$, $V = 1003.4(3)$ Å^3, $Z = 4$, $D_{calc} = 4.06$ g/cm^3. The eight strongest lines of the powder X-ray diffraction pattern are [d_{obs} in Å (I) (hkl)]: 6.493(25)(020); 3.628 (25)($\bar{1}$31); 3.204(39)($\bar{1}$12,131); 3.065(18)(002); 2.976(28)($\bar{3}$12, $\bar{2}$22); 2.830(100)(240), 2.632(36)($\bar{1}$32); 1.647(19)($\bar{2}$04,640). Hatertite is optically positive, $\alpha = 1.820(3)$, $\beta = 1.825(3)$, $\gamma = 1.833(3)$, $2V_{meas.} = 60(10)^o$, $2V_{calc.} = 77^o$. The orientation is $Y = b$. The chemical composition determined by the electron-microprobe analysis is as follows (wt.%): Na$_2$O 8.49, K$_2$O 2.41, MnO 1.64, CaO 7.06, Fe$_2$O$_3$ 11.15, ZnO 2.05, CuO 8.10, Al$_2$O$_3$ 2.22, As$_2$O$_5$ 55.67, total 98.79. The empirical formula (based on 12 O $apfu$) is (Na$_{0.47}$K$_{0.32}$)(Na$_{0.84}$Ca$_{0.16}$) (Ca$_{0.62}$Na$_{0.19}$Zn$_{0.16}$Mn$_{0.14}$) (Fe$^{3+}_{0.44}$Cu$_{0.32}$Al$_{0.13}$Na$_{0.11}$)$_2$(As$_{1.01}$O$_4$)$_3$. A general crystal chemical formula for hatertite should be written as NaNa(Ca$_{1-x}$M^+_x)(Fe$^{3+}_{1+x}$M$^{2+}_{1-x}$)(AsO$_4$)$_3$, where $0.5 > x > 0$, M$^+$ is an unspecified monovalent cation, and M^{2+} is an unspecified divalent cation. The crystal structure was solved by direct methods and refined to an agreement index $R1 = 0.028$ on the basis of 751 independent observed reflections. Hatertite is a new arsenate member of the alluaudite group. Its structure is based upon chains of edge-sharing octahedra running along [–101] and linked by $T(2)$O$_4$ tetrahedra into layers parallel to (010). The layers are further interlinked through $T(1)$O$_4$ tetrahedra to form a three-dimensional octahedral-tetrahedral framework with the $A(1)$ and $A(2)$' sites in the interstices. The mineral was named in honor of Prof. Frédéric Hatert (b. 1973), University of Liège, Belgium, for his contributions to the mineralogy and crystal chemistry of alluaudite-group minerals.

Key-words: hatertite, new mineral, arsenate, alluaudite group, volcanic fumaroles, Tolbachik, Kamchatka peninsula, Russia, crystal structure.

Introduction

Arsenates constitute one of the most diverse and rich classes of minerals, which has been studied intensively within the last few years (Chukanov *et al.,* 2011; Pekov *et al.,* 2011, 2012; Yang *et al.,* 2011; Callegari *et al.,* 2012; Cooper *et al.,* 2012; Hawthorne *et al.,* 2012; Meisser *et al.,* 2012; Mills *et al.,* 2012; Neuhold *et al.,* 2012; Starova *et al.,* 2012). Most arsenates found in nature are secondary minerals formed in oxidation zones of mineral deposits, where arsenic is derived from alteration of primary sulphides. There are more than 400 natural arsenates, of which about 350 contain water as an essential mineral-forming component. A diverse association of anhydrous arsenate minerals had been described from fumaroles of the Great Fissure Tolbachik Eruption (GFTE; 1975–76, Kamchatka peninsula, Russia). Six novel arsenate

mineral species have been first reported from this locality: alarsite, AlAsO$_4$ (Semenova *et al.,* 1994), bradaczekite, NaCu$_4$(AsO$_4$)$_3$ (Filatov *et al.,* 2001), coparsite, Cu$_4$O$_2$[(As, V)O$_4$]Cl (Vergasova *et al.,* 1999), filatovite, K[(Al, Zn)$_2$(As, Si)$_2$O$_8$] (Vergasova *et al.,* 2004), lammerite-β, Cu$_3$(AsO$_4$)$_2$ (Starova *et al.,* 2012), and urusovite, CuAlAsO$_5$ (Vergasova *et al.,* 2000).

In this paper, we report on the occurrence, properties and crystal structure of hatertite, another new arsenate mineral from Tolbachik fumaroles. Hatertite is a new member of the alluaudite group. The mineral was named in honor of Prof. Frédéric Hatert (b. 1973), Chercheur qualifié du FNRS, University of Liège, Belgium, for his contributions to the mineralogy and crystal chemistry of alluaudite-group minerals (Hatert *et al.,* 2000, 2005; Hatert *et al.,* 2006; Hatert, 2004, 2006, 2008; Rondeux & Hatert, 2010). Both the mineral and the mineral name were approved

by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (proposal 2012-048). Type material is deposited at the Mineralogical Museum, St. Petersburg State University, St. Petersburg, Russia (catalogue no. 1/19536).

Locality and occurrence

The GFTE is the largest basaltic eruption in modern history; its geology had been described in detail by Fedotov (1984). The GFTE was active in 1975–1976 and consisted of two breaches (North and South) and seven cones. Beginning in the late 1970s, fumarolic activity of the GFTE resulted in the crystallization of a unique mineral assemblage, with 39 new mineral species discovered to date. Crystals of hatertite were found in 1983 in products of fumarolic activity on the second cinder cone of the North breach of GFTE. The gas temperature in the fumarole where it was found was 410–420 °C.

Hatertite was found in close association with ponomarevite, piypite, dolerophanite, euchlorine, sylvite, lammerite, johillerite, urusovite, bradaczekite, filatovite, hematite and tenorite. The mineral occurs as well-formed transparent yellow crystals up to 0.3 mm in maximal dimension, slightly elongated along [101] and flattened on {010} (Fig. 1a, b). The dominant forms are {010}, {100}, {001}, {011}, and {-201} (Fig. 1c).

Chemical composition

The chemical composition of hatertite was studied on three grains by means of a Cameca SX-50 electron microprobe

Table 1. Chemical composition of hatertite.

Constituent	wt.%	Range	Stand. dev.	Standard used
Na_2O	8.49	8.20–8.70	0.16	plagioclase
K_2O	2.41	2.14–2.74	0.20	sanidine
MnO	1.64	1.52–1.76	0.09	rhodonite
CaO	7.06	6.30–8.86	0.87	plagioclase
Fe_2O_3	11.15	9.60–11.95	0.64	magnesioferrite
ZnO	2.05	1.76–2.75	0.26	gahnite
CuO	8.10	6.65–9.68	0.87	dolerophanite
Al_2O_3	2.22	1.93–2.43	0.22	plagioclase
As_2O_5	55.67	54.29–56.42	0.78	lammerite
Total	98.79	98.02–99.38	0.37	

operated at 20 kV and 30 nA, with a 5 μm beam diameter. The results of the analyses are summarized in Table 1. No elements other than those mentioned in Table 1 were detected.

The empirical formula of hatertite, calculated on the basis of 12 oxygens, is $(Na_{0.47}K_{0.32})$ $(Na_{0.84}Ca_{0.16})$ $(Ca_{0.62}Na_{0.19}Zn_{0.16}Mn_{0.14})$ $(Fe^{3+}_{0.44}Cu_{0.32}Al_{0.13}Na_{0.11})_2$ $(As_{1.01}O_4)_3$. The simplified formula is $Na_2(Ca, Na)$ $(Fe^{3+}, Cu)_2(AsO_4)_3$.

Physical and optical properties

Hatertite is honey-yellow, with a vitreous luster and a yellow streak. The mineral is very brittle and transparent. No cleavage had been observed. Hardness could not be measured due to the extreme brittleness of the mineral. The calculated density is 4.060 g/cm^3 (based on the empirical
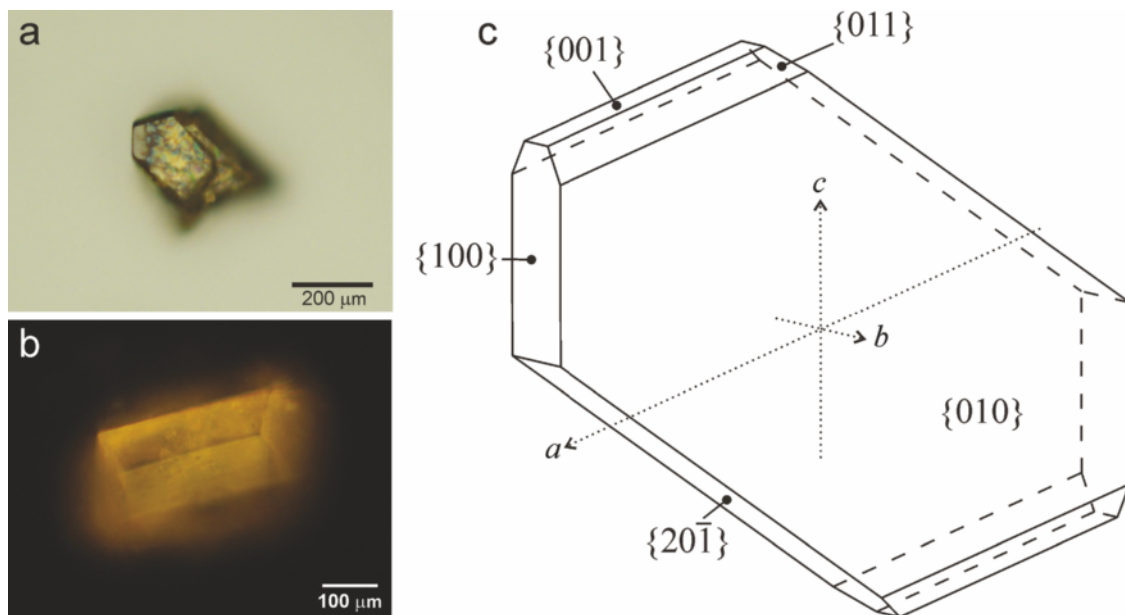

Fig. 1. Photographs of crystals of hatertite taken in plane-polarized light (a) and with crossed polars (b), and a scheme of hatertite crystal morphology (c).

chemical formula). The mineral does not fluoresce in either short- or long-wave ultraviolet radiation.

Hatertite is optically positive, $\alpha = 1.820(3)$, $\beta = 1.825(3)$, $\gamma = 1.833(3)$, $2V_{meas.} = 60(10)°$, $2V_{calc.} = 77°$. The orientation is $Y = b$, further measurements were not possible. No pleochroism has been observed. The value of compatibility constant is –0.082 (poor). The reasons for the poor compatibility are unclear. Mandarino (2006) discussed the Gladstone-Dale compatibility relationships for arsenates and noted 16 species with fair and 13 species with poor compatibility, bradaczekite among the latter.

Powder X-ray diffraction data

Powder X-ray diffraction data were collected using a STOE Image Plate Diffraction System II (Gandolfi mode with Mo-$K\alpha$). Data (in Å) are listed in Table 2. Unit-cell parameters refined from the powder data are as follows: monoclinic, $a = 12.590(2)$, $b = 12.993(3)$, $c = 6.700(2)$ Å, $\beta = 113.72(2)°$, $V = 1003.4(3)$ Å^3, $Z = 4$. The diagnostic lines of the X-ray powder diffraction pattern are [d_{obs} in Å (I) (hkl)]: 6.493(25)(020); 3.628 (25)($\bar{1}$31); 3.204(39) ($\bar{1}$12,131); 3.065(18)(002); 2.976(28)($\bar{3}$12, $\bar{2}$22); 2.830 (100)(240), 2.632(36)($\bar{1}$32); 1.647(19)($\bar{2}$04,640).

Crystal structure

Experimental procedure

The crystal of hatertite was mounted on a Bruker SMART APEX CCD diffractometer with a crystal-to-detector distance of 5 cm. A hemisphere of three-dimensional data was collected using Mo-$K\alpha$ X-radiation and frame widths of 0.3° in ω, with 90 s used to acquire each frame. The unit-cell dimensions were refined on the basis of 2776

Table 2. X-ray powder-diffraction pattern for hatertite*.

I	d_{meas}, Å	d_{calc}, Å	$h\,k\,l$	I	d_{meas}, Å	d_{calc}, Å	$h\,k\,l$
25	**6.493**	**6.503**	**0 2 0**	4	2.157	2.156	3 5 0
16	5.754	5.781	2 0 0	8	2.053	2.073	5 3 $\bar{2}$
14	4.329	4.321	2 2 0	8	1.993	1.987	3 5 $\bar{2}$
11	3.882	3.903	3 1 $\bar{1}$	8	1.964	1.951	6 2 $\bar{2}$
5	3.692	3.695	3 1 0	5	1.862	1.875	1 5 2
25	**3.628**	**3.630**	**1 3 $\bar{1}$**	12	1.829	1.84	3 3 2
39	**3.204**	**3.210**	**1 1 $\bar{2}$**	2	1.789	1.789	1 7 $\bar{1}$
		3.183	**1 3 1**	5	1.726	1.732	6 4 $\bar{2}$
18	**3.065**	**3.065**	**0 0 $\bar{2}$**	19	**1.647**	**1.658**	**6 4 0**
28	**2.976**	2.997	3 1 $\bar{2}$			1.656	2 0 $\bar{4}$
		2.956	2 2 $\bar{2}$	7	1.589	1.591	3 7 $\bar{2}$
100	**2.830**	**2.834**	**2 4 0**	9	1.548	1.555	5 1 2
4	2.715	2.722	4 0 $\bar{2}$	7	1.525	1.531	1 7 2
36	**2.632**	**2.632**	**1 3 $\bar{2}$**	9	1.467	1.478	4 4 $\bar{4}$
1	2.505	2.511	4 2 $\bar{2}$	3	1.441	1.445	8 0 0
4	2.323	2.323	2 4 $\bar{2}$	6	1.382	1.386	0 4 $\bar{4}$
5	2.261	2.277	5 1 0				

*Eight most intense lines are shown in bold.

Table 3. Crystal data, data collection, and structure refinement parameters for hatertite.

Crystal data	
Temperature	293 K
Radiation, wavelength	Mo-$K\alpha$, 0.71073 Å
Crystal system	monoclinic
Space group	$C2/c$
Unit-cell dimensions a, b, c (Å), β (°)	12.640(2), 13.007(2), 6.700(1) 113.828(3)
Unit-cell volume (Å^3)	1007.6(3)
Z	4
Calculated density (g/cm^3)	4.06
Absorption coefficient (mm^{-1})	13.66
Crystal size (mm^3)	$0.18 \times 0.14 \times 0.10$
Data collection	
θ range (°)	2.36 – 28.11
h, k, l ranges	−9 → 16, −16 → 16, −8 → 8
Total reflections collected	2869
Unique reflections (R_{int})	1137 (0.046)
Unique reflections $F > 4\sigma(F)$	751
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting coefficients a, b	0.0005, 0
Extinction coefficient	0.00000(5)
Data/restraints/parameters	1137/0/99
R_1 [$F > 4\sigma(F)$], wR_2 [$F > 4\sigma(F)$],	0.028, 0.038
R_1 all, wR_2 all	0.037, 0.039
Goodness-of-fit on F^2	0.753
Largest diff. peak and hole (e Å^{-3})	0.659, −0.691

reflections (Table 3). The systematic absences of reflections are consistent with the space-group $C2/c$. The data were reduced using the Bruker program SAINT. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was applied using the Bruker program SADABS, and the data were corrected for Lorentz, polarisation, and background effects.

The Bruker SHELXTL system of programs was used for the refinement of the crystal structure on the basis of F^2. The structure was refined on the basis of atom coordinates determined by Hatert *et al.* (2000) for the structure of $Na_{0.5}Li_{0.5}MnFe_2(PO_4)_3$. Occupancies of the cation positions were refined from the experimental site-scattering factors in accordance with the empirical chemical composition. Refinement of all atom-position parameters, allowing for the anisotropic displacement of all atoms, and the inclusion of a refinable weighting-scheme of the structure factors, resulted in a final agreement index ($R1$) of 0.028, calculated for the 751 unique observed reflections (|Fo| > $4\sigma F$), and a goodness-of-fit (S) of 0.753. The final atom parameters are listed in Table 4, and selected interatomic distances are given in Table 5. Site-scattering factors and assignment of cation positions are listed in Table 6. Observed and calculated structure factors are available as Supplementary Material attached to this article on the

Table 4. Fractional coordinates, displacement parameters (Å^2), and bond-valence sums (BVS, valence units) for atoms in the structure of hatertite.

Atom	BVS*	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
A(1)	1.12	½	0	0	0.0321(11)	0.0394(19)	0.0189(17)	0.0205(16)	0.003(1)	−0.0061(14)	−0.0042(13)
A(2)'	0.56	0	−0.00080(2)	¼	0.0466(13)	0.0217(19)	0.047(2)	0.052(2)	0	−0.0049(16)	0
M(1)	2.14	0	0.264401(12)	¼	0.0219(6)	0.0239(11)	0.0180(10)	0.0284(11)	0	0.0154(9)	0
M(2)	2.49	0.27324(7)	0.65670(6)	0.35841(12)	0.0147(3)	0.0162(5)	0.0148(5)	0.0130(4)	−0.0004(4)	0.0058(4)	0.0006(4)
T(1)	5.12	0	−0.27594(6)	¼	0.0166(2)	0.0221(5)	0.0149(4)	0.0102(4)	0	0.0038(4)	0
T(2)	5.04	0.24467(5)	−0.10591(4)	0.13632(8)	0.01722(16)	0.0228(3)	0.0146(3)	0.0116(3)	0.0006(3)	0.0043(3)	0.0021(3)
O(1)	2.05	0.4476(3)	0.7007(2)	0.5259(4)	0.0208(9)	0.027(2)	0.024(2)	0.0107(18)	−0.0049(15)	0.0066(18)	0.0000(18)
O(2)	1.96	0.0971(3)	0.6447(2)	0.2211(5)	0.0308(10)	0.033(3)	0.024(2)	0.034(2)	−0.0136(17)	0.013(2)	0.0025(18)
O(3)	2.04	0.3262(3)	0.6661(2)	0.1044(5)	0.0235(9)	0.032(2)	0.016(2)	0.0160(18)	−0.0015(15)	0.0038(18)	−0.0053(17)
O(4)	2.11	0.1161(3)	0.4083(2)	0.3061(4)	0.0235(9)	0.027(2)	0.023(2)	0.0193(19)	0.0061(17)	0.0087(18)	0.0052(19)
O(5)	1.91	0.2306(3)	0.8200(2)	0.3333(5)	0.0214(9)	0.031(2)	0.022(2)	0.0159(18)	0.0035(16)	0.0144(19)	0.0018(17)
O(6)	2.01	0.3187(3)	0.5072(2)	0.3732(5)	0.0322(10)	0.044(3)	0.024(2)	0.0260(19)	−0.0005(17)	0.011(2)	−0.0178(19)

*calculated using bond-valence parameters taken from Brese & O'Keeffe (1991); the Na$^+$-O^{2-} curve was used for the A(1)-O and A(2)-O bonds; the Ca^{2+}-O^{2-}, Fe^{3+}-O^{2-} and As^{5+}-O^{2-} curves were used for the M(1)-O, M(2)-O, and T-O bonds, respectively. Relatively low BVS values for the A(2)' and M(2) sites are explained by their mixed-cation occupancies (Table 6).

Table 5. Selected bond lengths (Å) in the structure of hatertite.

T(1)-O(2)	1.674(3) 2x	A(1)-O(4)	2.313(3) 2x
T(1)-O(1)	1.688(3) 2x	A(1)-O(2)	2.403(3) 2x
<T(1)-O>	1.681	A(1)-O(4)	2.608(3) 2x
		<A(1)-O>	2.441
T(2)-O(4)	1.653(3)		
T(2)-O(6)	1.664(3)	A(2)'-O(6)	2.636(3) 2x
T(2)-O(3)	1.688(3)	A(2)'-O(6)	2.738(4) 2x
T(2)-O(5)	1.700(3)	A(2)'-O(1)	2.858(4) 2x
<T(2)-O>	1.676	A(2)'-O(3)	3.029(4) 2x
		< A(2)'-O>	2.816
M(2)-O(6)	2.019(3)		
M(2)-O(2)	2.042(4)	M(1)-O(4)	2.318(3) 2x
M(2)-O(3)	2.068(3)	M(1)-O(1)	2.350(3) 2x
M(2)-O(5)	2.108(3)	M(1)-O(3)	2.381(3) 2x
M(2)-O(1)	2.108(3)	<M(1)-O>	2.350
M(2)-O(5)	2.182(3)		
<M(2)-O>	2.088		

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Structure description

The structure of hatertite contains six symmetrically independent cation sites, numbered in this work according to the nomenclature proposed by Hatert *et al.* (2000). The A(1) and A(2)' sites are predominantly occupied by Na. All the K present in the mineral is found in the A(2)' site; this is reflected in a rather large coordination polyhedron, which can be described as an octahedron flattened along one of its threefold axes (Fig. 2d). The A(1) site, which contains 13 % Ca, is coordinated by O atoms to form a coordination polyhedron known as a gyrobifastigium (Fig. 2e) (Casanova *et al.*, 2005). The M(1) and M(2) sites have octahedral coordination. Two adjacent M(2)O$_6$ octahedra share an edge to form a [M(2)$_2$O$_{10}$] dimer. The dimers are linked by the M(1)O$_6$ polyhedra to form chains running along [–101] (Fig. 2c). The chains are linked by T(2)O$_4$ tetrahedra into layers parallel to (010) (Fig. 2a). The layers are further interlinked through T(1)O$_4$ tetrahedra into a three-dimensional octahedral-tetrahedral framework with the A(1) and A(2)' sites in the framework cavities (Fig. 2b).

Crystal-chemical formula

The crystal-chemical formula derived from the crystal-structure analysis and calculated on the basis of a comparison between the site-scattering of cation sites (Table 6) and results of microprobe analysis can be written as $(Na_{0.55}K_{0.30})(Na_{0.87}Ca_{0.13})(Ca_{0.60}Na_{0.27}Mn_{0.13})$ $(Fe^{3+}_{0.45}$ $Cu_{0.20}Al_{0.19}Zn_{0.16})_2(AsO_4)_3$. This formula is in reasonably good agreement with the empirical chemical formula of hatertite given above. Hatertite is defined as a mineral with Ca dominant in the M(1) site and Fe^{3+} dominant in

Table 6. Refined site-scattering factors and assignment for cation sites in the structure of hatertite*.

Site	SC	SOF	SSF_{exp} [e^-]	Assigned occupancy	SSF_{calc} [e^-]
$A(1)$	Na	1.134(8)	12.47(9)	$Na_{0.87}Ca_{0.13}$	12.17
$A(2)$'	Na	1.104(8)	12.14(9)	$Na_{0.55}K_{0.30}$	11.76
$M(1)$	Ca	0.943(4)	18.86(8)	$Ca_{0.60}Na_{0.27}Mn_{0.13}$	18.22
$M(2)$	Fe	0.919(2)	23.89(5)	$Fe^{3+}_{0.45}Cu_{0.20}Al_{0.19}Zn_{0.16}$	24.32

*SC = scattering curve used to refine site occupancy; SOF = refined site-occupation factor; SSF_{exp} and SSF_{calc} = experimental and calculated site-scattering factors.
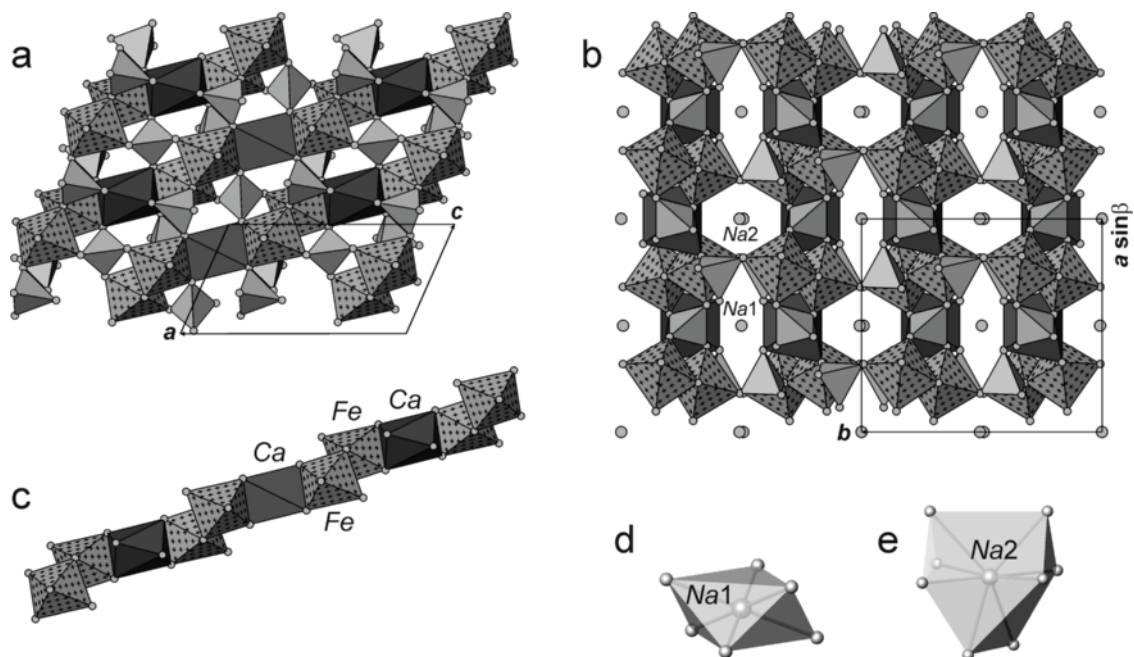

Fig. 2. Layer of FeO_6 (cross-hatched), CaO_6 (dark-gray) and AsO_4 (gray) polyhedra in the structure of hatertite (a) is based upon chains of FeO_6 and CaO_6 polyhedra (c). The layers are linked into three-dimensional framework with $Na1$ and $Na2$ (shown as circles) in channels (b). The $Na1$ and $Na2$ sites are coordinated by six and eight anions, respectively (c).

the $M(2)$ site. The charge-balancing mechanism in the studied sample is controlled by the coupled $Ca^{2+} \leftrightarrow Na^+$ and $Fe^{3+} \leftrightarrow Cu^{2+}$ substitutions. A general crystal chemical formula for hatertite should be written as $NaNa(Ca_{1-x}M^+_x)(Fe^{3+}_{1+x}M^{2+}_{1-x})(AsO_4)_3$, where $0.5 > x > 0$, M^+ is an unspecified monovalent cation, and M^{2+} is an unspecified divalent cation. Recently, we located another sample of hatertite, where $M^{2+} = Mg^{2+}$ and the content of Cu^{2+} is negligible. This sample is currently under investigation.

Discussion

Hatertite belongs to the alluaudite mineral group, which at present includes nine arsenate species (Table 7). Unfortunately, each of these minerals has been reported with different cell settings and atom names. In order to homogenize the coordinates setting and to allow for easy comparison between different structures, we have transformed all reported structure models for the alluaudite-group arsenate minerals to a reference model that corresponds to the set of coordinates determined by Hatert *et al.* (2000) for the structure of $Na_{0.5}Li_{0.5}MnFe_2(PO_4)_3$. The corresponding unit-cell transformation matrices, translation matrices and renumbering schemes for the O atoms are given in Table 8 (note that, after application of the corresponding matrices, atom coordinates still have to be transformed to a reference site by a symmetry operator of the $C2/c$ space group). Table 9 contains reference-model coordinates of atoms comprising octahedral-tetrahedral frameworks in the structures of minerals listed in Table 7. Transformation of the structure data to the reference models allowed to unambiguously assign extra-framework

Table 7. Crystallographic data for arsenate minerals from the alluaudite group.

Mineral name	Chemical formula	Space group	a (Å)	b (Å)	c (Å)	β (°)	Ref.
arseniopleite	$(Ca, Na)(Na, Pb)Mn_3(AsO_4)_3$	$C2/c$	12.132	13.036	6.811	113.3	1
bradaczekite	$NaCu_4(AsO_4)_3$	$C2/c$	12.053	12.432	7.253	117.8	2
caryinite	$(Na, Pb)(Ca, Na)Ca(Mn, Mg)_2(AsO_4)_3$	$C2/c$	12.419	13.147	6.855	114.1	3
hatertite	$Na_2(Ca, Na)(Fe^{3+}, Cu)_2(AsO_4)_3$	$C2/c$	12.640	13.007	6.700	113.8	4
johillerite	$Na\ Cu(Mg, Zn)_3(AsO_4)_3$	$C2/c$	11.882	12.760	6.647	112.8	5
		$C2/c$	11.882	12.739	6.752	113.6	6
keyite	$Cd_2Cu_3(Zn, Cu)_4(AsO_4)_6(H_2O)_2$	$C2/c$	12.544	12.780	6.840	113.5	7
nickenichite	$NaCaCu(Mg, Fe)(AsO_4)_3$	$C2/c$	11.882	12.760	6.647	112.8	8
o'danielite	$Na(Zn, Mg)Zn_2H_2(AsO_4)_3$	$C2/c$	12.113	12.445	6.793	112.9	5
yazganite	$NaFe_2(Mg, Mn)(AsO_4)_3(H_2O)$	$C2/c$	12.181	12.807	6.6391	112.4	9

References: (1) Tait & Hawthorne (2003); (2) Krivovichev *et al.* (2001); (3) Ercit (1993); (4) this work; (5) Keller & Hess (1988); (6) Tait & Hawthorne (2004); (7) Cooper & Hawthorne (1996); (8) Auernhammer *et al.* (1993); (9) Sarp & Cerný (2005).

Table 8. Transformation modes of unit cells and atom coordinates for alluaudite-group arsenate minerals reported in the original works to the reference model that corresponds to the set of coordinates given by Hatert *et al.* (2000) for $Na_{0.5}Li_{0.5}MnFe_2(PO_4)_3$.

Mineral	Ref.	Cell transformation matrix	Translation matrix	Renumbering scheme for the O sites (old → new)
arseniopleite	1	−1 0 –1/0 –1 0/1 0 0	0 0 0	1→1, 2→2, 3→3, 4→4, 5→5, 6→6
bradaczekite	2	1 0 0/0 1 0/0 0 1	0 ½ 0	6→1, 2→2, 5→3, 3→4, 4→5, 1→6
caryinite	3	−1 0 –1/0 1 0/1 0 0	0 0 ½	1→1, 2 + 3*→2, 4→3, 5→4, 6→5, 7→6
johillerite	4	−1 0 –1/0 1 0/1 0 0	0 0 ½	6→1, 3→2, 4→3, 2→4, 5→5, 1→6
keyite	5	−1 0 –1/0 –1 0/0 0 1	¼ $^3/_4$ ½	5→1, 3→2, 4→3, 6→4, 1→5, 2→6
nickenichite	6	1 0 0/0 1 0/0 0 1	0 0 0	2→1, 1→2, 6→3, 3→4, 4→5, 6→6
o'danielite	7	1 0 0/0 –1 0/0 0 1	0 0 0	6→1, 3→2, 4→3, 2→4, 5→5, 1→6
yazganite	8	1 0 0/0 –1 0/0 0 1	0 0 0	6→1, 3→2, 4→3, 2→4, 5→5, 1→6

*Splitted site.
References: (1) Tait & Hawthorne (2003); (2) Krivovichev *et al.* (2001); (3) Ercit (1993); (4) Tait & Hawthorne (2004); (5) Cooper & Hawthorne (1996); (6) Auernhammer *et al.* (1993); (7) Keller & Hess (1988); (8) Sarp & Cerný (2005).

cations to the $A(1)$ and $A(2)$ positions according to the scheme developed by Hatert *et al.* (2000) (Table 10). The following conclusions concerning site preferences by different cations can be made. In alluaudite-group arsenate minerals, Na^+ obviously tends to occupy the $A(2)'$ site (as in hatertite), but can also be incorporated into the $A(1)$ site (similar observations were made by Hatert *et al.* (2000) for alluaudite-type phosphates). The Cu^{2+} cations demonstrate high affinity to the $A(1)'$ site, but can also be found in the $A(2)$ site (as in keyite). Calcium can be incorporated into the $A(1)$ and $A(1)''$ sites. The $A(2)'$ site is able to host H_2O groups, but in a disordered arrangement: in both hydrated alluaudite-type arsenates, keyite and yazganite, H_2O molecules are slightly shifted from the $A(2)'$ site to the 8f site with 50 %-occupancy. According to Hatert *et al.* (2000), H atoms of protonated phosphate anions in alluaudite-type structures occupy the $A(1)''$ sites, which is likely to be the case for arsenate members of the group as well. Unfortunately, the H atom coordinates for o'danielite, the only natural alluaudite-group arsenate with protonated arsenate groups, have not been reported in the literature.

From the data listed in Table 10, it can be seen clearly that hatertite has a unique distribution of dominant cations over structure sites, which is in total agreement with its status of a separate mineral species.

Among nine minerals listed in Table 7, four (johillerite, nickenichite, bradaczekite and hatertite) have been found in Tolbachik fumaroles. Johillerite, nickenichite and bradaczekite contain Cu as an essential mineral-forming component. Hatertite also contains significant but subordinate amount of Cu in the $M(2)$ site. Its formation is most probably associated with the increasing deficit of Cu in local geochemical environments.

Table 9. Reference-model sets of atom coordinates ($\times 10^4$) of the octahedral-tetrahedral framework in the structures of the alluaudite-group arsenate minerals compared to the coordinates reported by Hatert et al. (2000) for synthetic $Na_{0.5}Li_{0.5}MnFe_2(PO_4)_3$.

Site		NLM	AP	BZ	CY	JH	KY	NH	OD	YZ
M(1)	x	0	0	0	0	0	0	0	0	0
	y	2641	2649	2651	2650	2604	2464	2616	2807	2673
	z	2500	2500	2500	2500	2500	2500	2500	2500	2500
M(2)	x	2803	2834	2802	2771	2854	2746	2857	2926	2808
	y	6528	6559	6563	6575	6553	6428	6558	6588	6560
	z	3687	3719	3602	3620	3737	3663	3756	3796	3671
T(1)	x	0	0	0	0	0	0	0	0	0
	y	7127	7117	7228	7164	7144	7223	7118	6905	7201
	z	2500	2500	2500	2500	2500	2500	2500	2500	2500
T(2)	x	2418	2313	2275	2342	2305	2443	2327	2207	2427
	y	8919	8881	8829	8906	8856	8862	8871	8851	8929
	z	1330	1237	1215	1283	1250	1357	1243	1144	1290
O(1)	x	4525	4617	4570	4565	4636	4580	4614	4657	4532
	y	7164	7153	7029	7083	7145	7050	7160	7346	7044
	z	5324	5286	5365	5340	5232	5240	5200	5278	5241
O(2)	x	987	1042	1030	981/973**	1062	1000	1085	1141	1071
	y	6375	6255	6230	6272/6401**	6201	6280	6232	6059	6373
	z	2386	2523	2582	2572/2049**	2626	2600	2619	2681	2441
O(3)	x	3284	3393	3544	3356	3412	3190	3397	3462	3282
	y	6643	6696	6672	6674	6701	6690	6706	6768	6783
	z	1022	1164	1214	1201	1195	1100	1189	1243	1126
O(4)	x	1221	1202	1181	1214	1161	1120	1169	1304	1146
	y	3994	3970	3893	4076	3909	4000	3933	4076	4089
	z	3096	3165	3237	3116	3131	2990	3150	3343	3117
O(5)	x	2244	2183	2212	2227	2156	2250	2162	2122	2254
	y	8221	8179	8075	8208	8113	8150	8141	8122	8186
	z	3180	3202	3080	3246	3190	3280	3215	3161	3303
O(6)	x	3148	3391	3328	3365	3321	3200	3325	3506	3291
	y	5023	4989	5053	5021	5030	5040	5042	5033	5081
	z	3772	3943	3820	3885	3858	3820	3887	4033	3890

*Legend: NLM = $Na_{0.5}Li_{0.5}MnFe_2(PO_4)_3$; AP = arseniopleite; BZ = bradaczekite; CY = caryinite; JH = johillerite; KY = keyite; NH = nickenichite; OD = o'danielite; YZ = yazganite.
**Site is split into two half-occupied sites.

Table 10. Assignment of cation sites for arsenate minerals of the alluaudite group.

Site	$A(1)$	$A(1)'$	$A(1)''$	$A(2)$	$A(2)'$	$A(2)''$	$M(1)$	$M(2)*$
Wyckoff site	4b	4e	8f	4a	4e	8f	4e	8f
Coordinates	½ 0 0	$0\,y\,¼\,(y \sim ½)$	$x\,y\,z\,(x \sim ½, y, z \sim 0)$	0 0 0	$0\,y\,¼\,(y \sim 0)$	$x\,y\,z\,(x, y, z \sim 0)$	$0\,y\,¼$	$x\,y\,z$
Arseniopleite	□	□	Ca**	□	Na	□	Mn	Mn
Bradaczekite	□	Cu	□	□	Na	□	Cu	Cu
Caryinite	□	□	Ca**	□	Na	□	Ca	Mn
Hatertite	Na	□	□	□	Na	□	Ca, M^+	Fe^{3+}, M^{2+}
Johillerite	□	Cu	□	□	Na	□	Mg	Mg
Keyite	□	Cu	□	Cu**	H_2O***	□	Cd	Zn
Nickenichite	Ca**	Cu**	□	□	Na	□	Mg	Mg
O'danielite	□	□	□	□	Na	□	Zn	Zn
Yazganite	Na	□	□	□	H_2O***	□	Mg	Fe^{3+}

*M^+ and M^{2+} are unspecified mono- and divalent cations, respectively.

**Site-occupation factor is 50 % or less.

***Site is split into two adjacent half-occupied 8f sites.

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