New minerals with a modular structure derived from hatrurite from the pyrometamorphic Hatrurim Complex. Part I. Nabimusaite, $KCa_{12}(SiO_4)_4(SO_4)_2O_2F$, from larnite rocks of Jabel Harmun, Palestinian Autonomy, Israel

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ABSTRACT

The new mineral nabimusaite, $KCa_{12}(SiO_4)_4(SO_4)_2O_2F$ ($R\overline{3}m$, a = 7.1905(4), c = 41.251(3) Å, V =1847.1(2) Å³, Z=3), has been discovered in larnite-ye'elimite nodules of pyrometamorphic rocks of the Hatrurim Complex. Nabimusaite is colourless, transparent with a white streak, has a vitreous lustre and does not show luminescence. It is brittle, but shows pronounced parting and imperfect cleavage along (001). Nabimusaite is uniaxial (-), $\omega = 1.644(2)$, $\varepsilon = 1.640(2)$ (589 nm), nonpleochroic. Mohs' hardness is ~ 5 and the calculated density is 3.119 g cm⁻³. The crystal structure has been solved and refined to R1 = 0.0416. Its artificial analogue is known. The nabimusaite structure may be derived from that of hatrurite, also known as the clinker phase 'alite' ($C_3S = Ca_3SiO_5$), and is built up by an intercalation of three positively charged hatrurite-like modules of composition $[Ca_{12}(SiO_4)_4O_5F]^{3+}$ with inserted modules of $[K(SO_4)_2]^{3-}$. The hatrurite-like modules in nabimusaite are characterized by octahedrally coordinated anion sites and tetrahedrally coordinated cation sites. The structure is representative of the intercalated antiperovskite type. In contrast to its synthetic analogue. nabimusaite is P-bearing. The shortened bond T-O lengths for one tetrahedral site indicates P preference at the Si2 site, located at the border of the hatrurite-like modules. Significant variations of isomorphous substitutions in nabimusaite suggest the possibility of other isostructural minerals occurring in Nature. It also seems likely that nabimusaite could serve as a prototype for new advanced synthetic materials, given the discovery of two other new minerals in the Hatrurim Complex with related modular structures, placed in the nabimusaite group. These are zadovite and aradite, as described in a companion paper (Galuskin et al., 2015a).

The mineral assemblage and paragenesis of nabimusaite suggests that nabimusaite formed as a result of the reaction of potassium-enriched, sulfate-bearing melt with larnite and ellestadite. This contradicts the isochemical model that pyrometamorphic rocks of the Hatrurim Complex formed relatively fast in a practically dry system.

* E-mail: evgeny.galuskin@us.edu.pl DOI: 10.1180/minmag.2015.079.5.03 **Keywords:** nabimusaite, $KCa_{12}(SiO_4)_2O_2F$, antiperovskite, new mineral, structure, Raman spectrum, Hatrurim Complex, Palestine Autonomy.

Introduction

NABIMUSAITE, KCa₁₂(SiO₄)₄(SO₄)₂O₂F ($R\bar{3}m$, a = 7.1905(4), c = 41.251(3) Å, V = 1847.1(2) Å³, Z = 3), was discovered in pyrometamorphic rock of the Hatrurim Complex ("Mottled zone"; Bentor, 1960; Gross, 1977; Vapnik *et al.*, 2007) on Jabel Harmun (Mount Harmun). The type locality, near the village Nabi Musa, lies close to a historical place with the eponymous name (probably Tomb of Moses), situated in the Judea Desert, West Bank, Palestinian Autonomy (31°46′N 35°26′E).

Nabimusaite, KCa12(SiO4)4(SO4)2O2F, is the first of a series of minerals discovered in pyrometamorphic rocks of the Hatrurim Complex with a modular layered structure derived from the hatrurite, Ca₃SiO₅, structure. The compound Ca₃SiO₅ has also been known in industry and material science by the unofficial name 'alite'; it is an important clinker phase in Portland cement (de Noirfontaine et al., 2012). 'Alite' exists in various polymorphous forms but all are strongly pseudo-rhombohedral $(R\overline{3}m)$ with $a \approx 7.0$, $c \approx 25$ Å (Jeffery, 1952). The rhombohedral approximation of the 'alite' or hatrurite structure is sufficient to show the modular relation between Ca₃SiO₅ and the newly described minerals nabimusaite, zadovite and aradite. Zadovite, BaCa₆[(SiO₄)(PO₄)](PO₄)₂F ($R\overline{3}m$, a = 7.09660(10) Å, c = 25.7284(3), V = 1122.13(3) Å³, Z = 3) and aradite, BaCa₆[(SiO₄)(VO₄)](VO₄)₂F ($R\overline{3}m$, a = 7.1300(1), c = 26.2033(9) Å, V = 1153.63(6) Å³, Z=3), also discovered in the Hatrurim Complex (Galuskin et al., 2015a) are related structurally to nabimusaite and together form a new mineral group.

Nabimusaite has a synthetic analogue described from fluorine-bearing cement clinker (Fayos et al., Cr^{6+} 1985). Germanium and analogues, $KCa_{12}(GeO_4)_4(SO_4)_2O_2F$ and KCa₁₂(SiO₄)₄ $(Cr^{6+}O_4)_2O_2F$ were also synthesized (Navarro and Glasser, 1985). The phosphate mineral arctite, BaCa₇Na₅(PO₄)₆F₃, ($R\overline{3}m$, a = 7.094, c = 41.320 Å; Sokolova et al., 1984) and the synthetic phase $Ca_{5,45}Li_{3,55}[SiO_4]_3O_{0,45}F_{1,55}$ (R3m, a=7.137, c= 41.459 Å; Krüger, 2010) are isostructural with nabimusaite. Arctite, BaCa7Na5(PO4)6F3, and the synthetic phases KCa₁₂(SiO₄)₄(SO₄)₂O₂F and Ca_{5.45} Li_{3.55}[SiO₄]₃O_{0.45}F_{1.55} are considered to have intercalated antiperovskite structures (Krivovichev, 2008; Krüger, 2010) for which octahedra are anion-centred and tetrahedra are cation-centred. The structures contain triplets of F- and O-centred octahedra intercalated with layers of cations and tetrahedra.

Nabimusaite is a key mineral for understanding the genesis of the Hatrurim Complex as its formation is associated with high-temperature syn-pyrometamorphic alteration of primary ye'elimite-larnite rocks during combustion events (see below). Such metasomatic processes with participation of both melt and gas are not usually taken into consideration. In general, most authors assume that the formation of larnite rocks is very fast and takes place under dry isochemical conditions (Geller *et al.*, 2012; Sokol *et al.*, 2014).

Here we describe holotype nabimusaite from Jabel Harmun, proposal IMA2012-057 approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA) in 2012. In a second paper (Galuskin et al., 2015a), the related new minerals zadovite (IMA2013-031) and aradite (IMA2013-047) are described. After the approval of nabimusaite we found this mineral as a rock-forming component at many locations of larnite pyrometamorphic rocks of the Hatrurim Complex in the Judean Mountains (Ma'ale-Adummin, Nabi Musa and Nahal Darga localities) and in the Negev Desert (Har Parsa Mountain). The name nabimusaite is given after the type locality, near the village of Nabi Musa. Type material is deposited in the collections of the Museum of Natural History in Bern, Bernastrasse 5, CH-3005 Bern, Switzerland, catalogue number NMBE 41598.

Methods

The crystal morphology and chemical composition of nabimusaite and associated minerals were examined using optical microscopy, a Philips XL30 ESEM/EDAX analytical scanning electron microscope (Faculty of Earth Sciences, University of Silesia) and CAMECA SX100 electron microprobe (Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw). Electron probe microanalyses of nabimusaite were performed at 15 kV and 20 nA using the following lines and standards: BaL\alpha, $SK\alpha$ – barite; $PK\alpha$ – apatite; CaK\alpha – wollastonite; MgK\alpha, SiK\alpha – diopside; AlK\alpha, KK\alpha – orthoclase; TiK\alpha – rutile; NaK\alpha – albite, SrL\alpha – SrTiO₃, FKα –fluorphlogopite.

The Raman spectrum of nabimusaite was recorded on a WITec confocal CRM alpha 300 Raman microscope (Jagiellonian Centre for Experimental Therapeutics, Cracow, Poland) equipped with an air-cooled solid state laser (488 nm) and a CCD camera operating at -82°C. The laser radiation was coupled to a microscope through a single-mode optical fibre with a diameter of 50 µm. An air Olympus MPLAN (100/0.90NA) objective was used. Raman scattered light was focused on a multi-mode fibre (50 µm diameter) and monochromator with a 600 mm^{-1} grating. The power of the laser at the sample position was 44 mW. Some 15-20 scans with integration time of 10–15 s and a resolution of 3 cm^{-1} were collected and averaged. The monochromator was calibrated using the Raman scattering line of a silicon plate $(520.7 \text{ cm}^{-1}).$

A single-crystal X-ray study of nabimusaite was carried out using a Bruker APEX II SMART diffractometer (MoK α radiation, $\lambda = 0.71073$ Å) (University of Bern, Switzerland). Data were processed using *SAINT* (Bruker, 1999). An empirical absorption correction using *SADABS* (Sheldrick, 1996) was applied. The structure was solved by direct methods, with subsequent analyses of difference-Fourier maps, and refined with neutral atom scattering factors using *SHELXL* (Sheldrick, 2008).

Occurrence and description of nabimusaite

The Jabel (Mount) Harmun is one of many locations where the unusual pyrometamorphic

rocks of the Hatrurim Complex are exposed in the Judean Mountains, close to the Jerusalem-Jericho highway (Novikov *et al.*, 2013; Galuskina *et al.*, 2014*a*). Outcrops of high-temperature rocks are represented by spurrite-, larnite- and gehlenite-bearing rocks, and also by unusual ternesite- and jasmundite-bearing rocks. High-temperature mineral assemblages are commonly altered and hosted by low-temperature calcium hydrosilicate rocks often enriched in secondary carbonate.

Nabimusaite is one of five new minerals described from Jabel Harmun. In addition to nabimusaite the following new minerals have been defined: harmunite, CaFe₂O₄, a mineral with the post-spinel structure type (Galuskina et al., 2014a); vapnikite, Ca₃UO₆ (Galuskin et al., 2014), the first natural uranian double perovskite; dzierżanowskite, CaCu₂S₂ (Galuskina et al., 2014b), a natural thiocuprate; and fluormayenite, Ca₁₂Al₁₄O₃₂F₂ (Galuskin et al., 2015b), a new mineral of the mayenite supergroup. The geological setting and also the main hypotheses for the formation of the Hatrurim Complex and the Jabel Harmun location were presented by Kolodny and Gross (1974), Burg et al. (1999), Sokol et al. (2007, 2008), Geller et al. (2012), Novikov et al. (2013) and Galuskina et al. (2014a).

Nabimusaite with the end-member crystal chemical formula $KCa_{12}(SiO_4)_4$ (SO_4)₂ O_2F was found in larnite-ye'elimite nodules of pyrometamorphic rocks locally termed 'pseudo-conglomerates' (Gross, 1977). Nabimusaite forms xenomorphic, poikilitic crystals 0.1–0.2 mm in size, filled with inclusions of larnite and ye'elmite (Figs 1 and 2). Very rarely nabimusaite grains reach 0.5 mm in size. Grains show



FIG. 1. Nabimusaite in larnite pyrometamorphic rock. Nmb = nabimusaite, Ell = fluorellestadite, Lrn = larnite, Brm = brownmillerite. (a) Polarized light, (b) crossed polarizers.



FIG. 2. (a) Xenomorphic nabimusaite in larnite-ye'elimite rock; (b) fresh surfaces, parting and imperfect cleavage are easily visible in nabimusaite, section sub-perpendicular to (0001). Nmb = nabimusaite, Ell = fluorellestadite, Lrn = larnite, Brm = brownmillerite, Prc = periclase, Ye = ye'elimite.

parting along (001) (Fig. 2b), creating difficulties in separating monocrystalline fragments for structural investigation and in the selection of uncontaminated mineral concentrates. Nabimusaite is associated with larnite, ye'elimite, brownmillerite, P-bearing fluorellestadite and minerals of the fluormayenite-fluorkyuygenite series. Less common are associations with gehlenite, periclase, oldhamite, covellite, dzierżanowskite, shulamitite, magnesioferrite and spinel. Usually, nabimusaite is confined to linear zones in rocks that are characterized by high porosity



FIG. 3. Porous zones in larnite-ye'elimite rocks, in which coarsening of larnite, ye'elimite and fluorellestadite grains is observed. These zones also contain nabimusaite, jasmundite and ternesite. Nmb = nabimusaite, Ell = fluorellestadite, Lar = larnite, Brm = brownmillerite, Trn = ternesite, Ye = ye'elimite, Jsm = jasmundite.

and coarsening of grain size of fluorellestadite, ye'elimite and larnite (Fig. 3). In porous zones ternesite and jasmundite appear (Fig. 3). The pore space is partially filled by minerals of the ettringite group and Ca hydrosilicates. On fresh fracture surfaces within pores, calciolangbeinite, sylvite and aphthitalite were established. Nabimusiate is usually developed after fluorellestadite, but also replaces larnite. Along the rims, nabimusaite grains are substituted by a mixture of uncharacterized Ca hydrosilicates, minerals of the ettringite group and barite.

Nabimusaite is colourless, transparent with a white streak and has a vitreous lustre; it shows no UV luminescence. Nabimusaite is brittle and shows pronounced parting and imperfect cleavage along (001); it is uniaxial (–), $\omega = 1.644(2)$, $\varepsilon = 1.640(2)$ (589 nm), nonpleochroic; Mohs' hardness is ~ 5; VHN load 50 g, range 370–500 kg mm⁻², mean (of 12 measurements) 420 kg mm⁻². Density could not be measured because of abundant tiny inclusions of ye'elmite and larnite; the calculated density is 3.119 g cm⁻³.

Composition, structure and results of the Raman spectroscopy study of nabimusaite

Nabimusaite is characterized by a variable chemical composition. In the central part of the grains light spots in backscattered electron (BSE) images indicate increasing Ba content (Table 1, Fig. 2). In this study of holotype nabimusaite we tried to exclude areas of grains enriched in barium. The

3		4			5			6	
Mean	Mean	S.D.	Range	Mean	S.D.	Range	Mean	S.D.	Range
(n = 3)	(<i>n</i> = 7)			(n = 6)			(n = 7)		
12.85	< 0.03			13.99	0.22	13.22-13.84	14.83	0.23	14.67-15.32
< 0.07				< 0.07			0.10	0.04	0.05-0.18
2.09	0.82	0.16	0.69-1.19	2.02	0.21	1.63-2.20	3.26	0.22	2.93-3.57
0.24	0.50	0.13	0.32 - 0.74	0.18	0.05	0.13-0.24	0.31	0.04	0.26-0.38
18.64	24.95	0.47	23.92-25.34	18.80	0.14	18.53-18.93	22.70	0.34	22.41-23.37
0.45	0.95	0.24	0.73-1.49	0.18	0.04	0.10-0.24	0.30	0.04	0.25-0.38
5.67	0.05	0.07	0-0.19	1.22	0.47	0.73-2.01	< 0.08		
0.33	< 0.08			0.41	0.02	0.37-0.45	0.13	0.03	0.09-0.19
0.13				0.13	0.09	0-0.28	0.12	0.05	0.04-0.19
	1.02	0.10	0.84-1.15						
57.28	67.03	0.97	64.71-67.73	59.00	0.48	58.19-59.45	58.00	0.54	57.14-58.87
0.12	1.03	0.04	0.97 - 1.09	0.08	0.01	0.07 - 0.10	< 0.02		
	0.29	0.06	0.14-0.35	< 0.06			< 0.06		
1.83	< 0.03			3.43	0.16	3.15-3.65	< 0.03		
0.10	< 0.02			0.17	0.02	0.14-0.19	0.16	0.05	0.08-0.26
0.70	< 0.10			1.23	0.18	0.96-1.53	< 0.10		
	3.82	0.06	3.69-3.92						
0.29	1.43			0.52					
100.13	99.03			100.33			99.91		

TABLE 1. Chemical composition of holotype nabimusaite (1); Ba-analogue of nabimusaite (2); intermediate phase nabimusaite-'Ba-nabimusaite' (3); jasmundite (4); low-Ba nabimusaite (5); and ternesite (6) from altered larnite rock, wt.%.

NABIMUSAITE FROM LARNITE ROCKS OF JABEL HARMUN

(continued)

 SO_3

 V_2O_5

 P_2O_5

TiO₂

SiO₂

 Al_2O_3

BaO

SrO

Fe₂O₃*

FeO** CaO

MgO

ZnO

 K_2O

Na₂O

Total

F

S -O = F/S 1

0.17

0.04

0.07

0.89

0.04

0.06

0.02

0.27

0.03

0.27

Range

1.51-2.21

0.04-0.21

0.23 17.93-18.85 18.01

0.25-0.48

2.01 - 4.91

0.13-0.29

0-0.28

0.58 56.39-59.21 56.87

2.05 - 3.02

0.08-0.20

0.53 - 1.54

0.06-0.13 0.12

13.85 0.43 12.59-14.70 12.69

Mean S.D.

(n = 24)

< 0.07

1.80

0.10

18.44

0.34

3.60

0.21

0.13

57.95

0.10

< 0.06.

2.52

0.14

1.05

0.44

99.79

2

Mean

(n = 15)

< 0.07

2.23

0.28

0.74

7.09

< 0.08

< 0.06

1.53

0.13

0.77

0.33

100.27

0.14

S.D.

0.16

0.07

0.27

0.64

0.08

0.02

0.23

0.04

0.27

Range

2.05-2.64

0.13-0.39

0.35-1.24

6.13-8.38

0-0.25

0.09-0.16

1.13-2.02

0.06-0.26

0.24-1.29

0.37 12.13-13.41

0.40 17.23-18.67

0.54 55.57-57.96

Table	1.	(contd.)
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		1			2		3		4			5			6
	Mean	S.D.	Range	Mean	S.D.	Range	Mean	Mean	S.D.	Range	Mean	S.D.	Range	Mean	S.D. Range
	(<i>n</i> = 24)			(<i>n</i> = 15)			(n = 3)	(n = 7)			(n = 6)			(n = 7)	
K	0.62			0.38			0.46				0.83				
Ba	0.27			0.55			0.43				0.09				
Na	0.05			0.05			0.04				0.06			0.02	
Sr	0.02						0.04				0.05			0.01	
Fe ²⁺								0.13							
Mg	0.03			0.03			0.04	0.23			0.02				
Zn								0.03							
Ca	11.98			11.97			11.99	10.62			11.98			4.99	
$\operatorname{Sum} X(+A)$	12.97			12.98			13.00	11.01			13.03			5.02	
Si	3.56			3.54			3.64	3.69			3.56			1.82	
Al	0.08			0.17			0.10	0.17			0.04			0.03	
Р	0.29			0.23			0.22	0.10			0.32			0.11	
Ti ⁴⁺	0.01			0.04			0.03	0.06			0.03			0.02	
Fe ³⁺	0.02			0.02			0.02				0.02			0.01	
V ⁵⁺	0.02			0.02			0.02				0.02			0.01	
Sum $T1$	3.96			4.00			4.01	4.02			3.97			2.00	
S ⁶⁺	2 01			1.87			1.88				1 99			0.89	
р	2.01			0.14			0.13				1.77			0.05	
Sum T2	2.01			2.01			2.01				1 99			1.00	
F ⁻	0.64			0.48			0.43				0.74			1.00	
S^{2-}	0.04			0.70			0.45	1.06			0.74				

*All Fe as Fe^{3+} . **All Fe as Fe^{2+} . Compositions 1, 2, 3 and 5 were calculated on 27(O + F); 4 was calculated on 18(O + S²⁻); and 6 on calculated on 12 O.



FIG. 4. The crystal structures of nabimusaite (left) and hatrurite (right) projected along [010]. Calcium atoms are shown as yellow spheres, SiO₄ tetrahedra are in red, SO₄ tetrahedra in blue and KO₆ octahedra in orange. Both structures are characterized by modules of three face-sharing, antiperovskite type [ACa₆] octahedra where A is either oxygen (grey spheres) or fluorine (blue spheres). The module is labelled AP. In both structures the triplets extend along the threefold axis at (0, 0, z), (1/3,1/3, z) and (2/3, 2/3, z). Compared to hatrurite the antiperovskite modules in nabimusaite [Ca₁₂(SiO₄)₄FO₂]³⁺ are intercalated with K(SO₄)₂³⁻ slices. In addition all tetrahedra in hatrurite point down [001], while those in nabimusaite alternate in an up and down sequence. The Si1 tetrahedra (more opaque) in nabimusaite point towards the intercalated K(SO₄)₂³⁻ module while the Si2 tetrahedra (translucent red) point to the centre of the antiperovskite module.

average composition of holotype nabimusaite (Table 1, analysis 1) is (K_{0.62}Ba_{0.27}Na_{0.05}Mg_{0.03} $Sr_{0.02})_{\Sigma 0.99}Ca_{11.98}(Si_{3.56}P_{0.29}Al_{0.08}Fe_{0.02}^{3+}Ti_{0.01}^{4+})_{\Sigma 3.96}$ $S_{2,01}O_{26,36}F_{0,64}$, which may be simplified to (K,Ba) $Ca_{12}(SiO_4)_4(SO_4)_2O_2(F,O)$ reflecting the endmember formula $KCa_{12}(SiO_4)_4(SO_4)_2O_2F.$ Chemically speaking, the nabimusaite holotype represents a complex solid-solution member with predominance (~75%) of the series (K,Ba) $Ca_{12}(SiO_4)_4(SO_4)_2O_2(F,O),$ with subordinate KCa₁₂[(SiO₄)₃(PO₄)](SO₄)₂O₃ (19%) and (K,Ba) $Ca_{12}[(PO_4)_2(AlO_4)_2](SO_4)_2O_2(F,O)$ (5%).

The average chemical composition of light BSE spots in nabimusaite corresponds to the formula $(Ba_{0.55}K_{0.38}Na_{0.05}Mg_{0.03})_{\Sigma1.01}Ca_{11.97}(Si_{3.54}P_{0.23}Al_{0.17}Fe_{0.02}^{3.4}Ti_{0.40}^{4.4}X_{1.87}P_{0.14})_{\Sigma2.01}O_{26.52}F_{0.48}$. Thus

the solid solution is dominated by the Ba-rich component of the nabimusaite series, (Ba,K) $Ca_{12}(SiO_4)_4(SO_4)_2O_2(F,O)$ (~62%) containing 4% $KCa_{12}[(SiO_4)_3(PO_4)](SO_4)_2O_3$, 10% (K,Ba) $Ca_{12}[(PO_4)_2(AIO_4)_2](SO_4)_2O_2(F,O)$ and 14% of the end-member BaCa₁₂(SiO₄)₄[(PO₄)(SO₄)] O₂F. The average composition of light spots leads to another potentially new mineral species with the end-member formula BaCa₁₂(SiO₄)₄(SO₄)₂O₂O (Table 1, analysis 2).

The composition of nabimusaite from the part of the holotype specimen in which jasmundite, $Ca_{11}(SiO_4)_4O_2S$, was also detected (second find in Nature), is on the compositional boundary between nabimusaite (as defined in this paper) and the Baanalogue of nabimusaite (Table 1, analysis 3),

Unit-cell dimensions	<i>a</i> = 7.1905(4) Å
(11)	c = 41,251(3) Å
Space group	$R\overline{3}m$
$V(Å^3)$	1847 07(19)
7 (A) 7	3
Chemical formula	K _{0.73} Ba _{0.27} Ca ₁₂ (SO ₄) ₂ (SiO ₄) ₄ O ₂ F
Intensity Measurement	
Crystal shape	prism
Crystal size (mm)	$0.1 \times 0.08 \times 0.03$
Diffractometer	APEX II SMART
X-ray radiation	ΜοΚα
X-ray power	50 kV 30 mA
Monochromator	Graphite
Temperature	293 K
Measurement method	Phi and Omega scans
Time per frame	60 s
Max. θ° range for data collection	30.51
Index ranges	-8 < h < 9
0	$-8 \le k \le 10$
	$-51 \le l \le 57$
No. of measured	7610
reflections	
No. of unique	764
reflections	
No. of observed	547
reflections $[I > 2\sigma(I)]$	
No. of parameters used	57
in refinement	
R _{int}	0.077
$R1, I > 2\sigma(I)$	0.0416
R1 all data	0.0678
wR2 on (F^2)	0.0986
Goof	1.050
$\Delta \rho_{\min} (e \text{ Å}^{-3})$	-0.72 close to Si1
$\Delta \rho_{\text{max}} (e \text{ Å}^{-3})$	0.80 close to Si1

TABLE 2. Parameters for X-ray data collection and crystal-structure refinement for nabimusaite.

 $\begin{array}{l} (K_{0.46}Ba_{0.43}Na_{0.04}Sr_{0.04}Mg_{0.04})_{\Sigma_{1.01}}Ca_{11.99}(Si_{3.64}P_{0.22}\\ Al_{0.10}Fe_{0.02}^{3+}Ti_{0.03}^{4+})_{\Sigma_{4.01}}(S_{1.88}P_{0.13})_{\Sigma_{2.01}}O_{26.57}F_{0.43}\approx\\ (Ba_{0.5}K_{0.5})Ca_{12}(SiO_{4})_4(SO_{4})_2O_2(O_{0.5}F_{0.5}). \ This jasmundite has minor Zn and P (Table 1, analysis 4), which distinguishes it from the type material from Eifel, Germany (Hentschel$ *et al.* $, 1983). Nabimusaite with the maximum K₂O content of 3.65 wt.% (Table 1, analysis 6) was found intergrown with P-bearing ternesite (Table 1, analysis 7). The average composition of this nabimusaite is (K_{0.83}Ba_{0.09}Na_{0.06}Sr_{0.05}Mg_{0.02})_{\Sigma_{1.05}}Ca_{11.98}(Si_{3.56}P_{0.32}Al_{0.04}Ti_{0.04}^{4+}G_{0.02}O_{0.5}S_{1.99}O_{26.26}F_{0.74}. \end{array}$

The crystal structure of nabimusaite corresponds to the synthetic phase $KCa_{12}(SiO_4)_4(SO_4)_2O_2F$ (Fayos et al., 1985). The structure is derived from that of hatrurite, Ca₃SiO₅, and is characterized by the presence of rows containing oxide, sulfate, silicate and fluoride anions and six- (or twelve- with 6×2.90 Å + 6×3.34 Å bonds) coordinate potassium ions, together with seven-coordinate calcium ions at sites between the rows, connecting them with Ca-O and Ca-F bonds (Fig. 4; Fayos et al., 1985). Details of X-ray data collection and structure refinement are given in Table 2. Final atom coordinates, displacement parameters, refined site occupancies and selected bond lengths are listed in Tables 3 to 5. With the refined formula $(K_{0.73}Ba_{0.27})^{\sim 28.99e}$ -Ca $^{\sim 240e}_{12}$ -Si $^{\sim 56e}_{4}$ -S $^{\sim 32e}_{2}$ -O₂₆(F,O) the resulting structure is well within the composition calculated on the basis of microprobe analyses, $(K_{0.62}Ba_{0.27}Na_{0.05}Mg_{0.03}Sr_{0.02})_{\Sigma 0.99}^{\sim 28.57e-}Ca_{11.98}^{\sim 239.6e-}$ $(Si_{3,56}P_{0,29}Al_{0,08}Fe_{0,02}^{3+}Ti_{0,01}^{4+})\tilde{\Sigma}_{3,96}^{55,97e-}S_{2,01}^{\sim 32.16e-}$ O26.36F0.64.

The following main bands in the Raman spectrum of nabimusaite were observed (Fig. 5, cm⁻¹): 129 (Ba–O vibration); 403 ($v_2 \operatorname{SiO}_{4}^{-1}$); 463 ($v_2 \operatorname{SO}_{2}^{-1}$); 524 and 563 ($v_4 \operatorname{SiO}_{4}^{+1}$); 637($v_4 \operatorname{SO}_{2}^{-1}$); 831, 849 and 885($v_1 \operatorname{SiO}_{4}^{+1}$); 930 and 948 ($v_3 \operatorname{SiO}_{4}^{-1}$); 993 ($v_1 \operatorname{SO}_{2}^{-1}$); 1121($v_3 \operatorname{SO}_{2}^{-1}$). Doubling of the lines related to SiO₄⁴⁻ vibrations is striking. This is due to two symmetry-independent Si sites in the structure. The $v_1 \operatorname{PO}_{4}^{-1}$ vibrations also contribute to the band at 948 cm⁻¹.

Because of difficulties in the selection of uncontaminated nabimusaite concentrates, powder X-ray diffraction data have been calculated from the refined crystal structure (Table S1, supplementary material which has been deposited with the Principal Editor of *Mineralogical Magazine* and is available from www.minersoc.org/pages/e_ journals/dep mat mm.html).

Discussion

The isotypic structures of nabimusaite, KCa_{12} (SiO₄)₄(SO₄)₂O₂F and arctite, BaCa₇Na₅(PO₄)₆F₃, may be considered as intercalated antiperovskite structures (Krivovichev, 2008). Linear face-sharing trimers of anion-centred octahedra have the composition [FO₂Ca₁₂]¹⁹⁺ in nabimusaite and [F₃Na₅Ca₇]¹⁶⁺ in arctite. Between the trimers there are SiO₄ tetrahedra in nabimusaite and PO₄ tetrahedra in arctite. The antiperovskite module in nabimusaite is represented by {[FO₂Ca₁₂](SiO₄)₄]³⁺ and by {[F₃Na₅Ca₇](PO₄)₄]⁴⁺ in arctite. Intercalated layers

NABIMUSAITE FROM LARNITE ROCKS OF JABEL HARMUN

	x/a	y/b	z/c	$U_{ m eq}$	Occupancy
K1	0	0	0	0.0323(6)	0.734(5)
Ba1				0.0323(6)	0.266(5)
Ca1	0.15831(8)	0.84169(8)	0.39825(2)	0.0223(3)	1
Ca2	0.15318(8)	0.84682(8)	0.53240(2)	0.0228(3)	1
S	0	0	0.67550(5)	0.0209(5)	1
Si1	0	0	0.20617(6)	0.0190(5)	1
Si2	0	0	0.08246(6)	0.0190(5)	1
01	0.5557(3)	0.4443(3)	0.64558(8)	0.0323(9)	1
O2	0.1248(3)	0.8752(3)	0.19426(9)	0.0279(8)	1
O3	0.1253(3)	0.8747(3)	0.07156(9)	0.0286(8)	1
04	0	0	0.36048(15)	0.0230(13)	1
05	0	0	0.75320(15)	0.0263(14)	1
06	0	0	0.12235(15)	0.0264(14)	1
07	0	0	0.43076(13)	0.0194(12)	1
F1	0	0	0.5000	0.0282(17)	1

TABLE 3. Atom coordinates, occupancies and equivalent isotropic displacement parameters (Å²) for nabimusaite.

TABLE 4. Anisotropic displacement parameters (Å²) for nabimusaite.

Site	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
K1, Ba1	0.0309(8)	0.0309(8)	0.0351(11)	0.000	0.000	0.0155(4)
Cal	0.0198(4)	0.0198(4)	0.0271(5)	-0.00127(19)	0.00127(19)	0.0098(4)
Ca2	0.0200(4)	0.0200(4)	0.0273(5)	0.0013(2)	-0.0013(2)	0.0093(4)
S	0.0210(6)	0.0210(6)	0.0208(10)	0.000	0.000	0.0105(3)
Si1	0.0166(7)	0.0166(7)	0.0238(12)	0.000	0.000	0.0083(3)
Si2	0.0164(7)	0.0164(7)	0.0242(12)	0.000	0.000	0.0082(3)
01	0.0426(19)	0.0426(19)	0.0269(19)	0.0021(8)	-0.0021(8)	0.033(2)
O2	0.0223(14)	0.0223(14)	0.043(2)	-0.0016(8)	0.0016(8)	0.0139(16)
03	0.0212(13)	0.0212(13)	0.042(2)	-0.0043(8)	0.0043(8)	0.0097(16)
04	0.0205(19)	0.0205(19)	0.028(3)	0.000	0.000	0.0102(10)
05	0.027(2)	0.027(2)	0.026(3)	0.000	0.000	0.0133(10)
O6	0.024(2)	0.024(2)	0.031(3)	0.000	0.000	0.0119(10)
07	0.0186(17)	0.0186(17)	0.021(3)	0.000	0.000	0.0093(9)
F1	0.026(2)	0.026(2)	0.032(4)	0.000	0.000	0.0131(12)

with large cations in nabimusaite are exemplified by $K(SO_4)_2^{3-}$ and by $Ba(PO_4)_2^{4-}$ in arctite. In zadovite, $BaCa_6[(SiO_4)(PO_4)](PO_4)_2F$ and aradite, $BaCa_6[(SiO_4)(VO_4)](VO_4)_2F$ the antiperovskite monolayer has the composition { $[FCa_6](R^{4.5+}O_4)_2$ }⁴⁺ (R = Si and P or V⁵⁺) and the Ba-bearing layer has the composition { $Ba[(P,V)O_4]_2$ }⁴⁻ (Galuskin *et al.*, 2015*a*).

The nabimusaite structure may also be described as triplets of antiperovskite (hatrurite-like) modules with the formula $[Ca_{12}(SiO_4)_4O_2F]^{3+}$ where two anion octahedra have the composition $[OCa_6]$ and one octahedron is centred by F^- , $[FCa_6]$ (Fig. 4). However, the tetrahedral tips of SiO₄ units within the antiperovskite layer in hatrurite all point in the same direction along [001], while those in

Cal	$O1 \times 2$	2.630(3)
	O2	3.122(4)
	$O3 \times 2$	2.360(3)
	O4	2.513(4)
	O5	2.355(2)
	O7	2.384(3)
Ca2	$O2 \times 2$	2.339(3)
	O2	2.569(4)
	O3	2.676(4)
	O7	2.439(4)
	F	2.329(1)
	O6	2.297(2)
S	$O1 \times 3$	1.472(4)
	O4	1.484(6)
Si1	$O2 \times 3$	1.630(3)
	O5	1.676(6)
Si2	$O3 \times 3$	1.624(4)
	O6	1.645(7)
K1, Ba1	$O1 \times 6$	2.902(4)
	$O3 \times 6$	3.339(4)

TABLE 5. Selected interatomic distances(Å) in nabimusaite.

nabimusaite, zadovite and aradite alternate in an up and down sequence (Fig. 6). Structurally there is hardly any difference between nabimusaite and its synthetic analogue (Fayos *et al.*, 1985). The Si tetrahedra of nabimusaite are partly occupied by P, but slightly shorter Si–O bond lengths are only observed for Si2 [1.624(4) Si2–O3 compared to 1.630(4) and 1.645(7) Si2–O6 compared to 1.653 (6)] while Si1 tetrahedra are even larger in nabimusaite [1.630(3) Si1–O2 compared to 1.615 (4) and 1.676(6) Si1–O5 compared to 1.649(6)]. This indicates that P is accumulated at the Si2 site while Si1 is fully occupied by Si. This assumption is supported by the fact that the Si2 tetrahedra are closer to the adjacent negatively charged $K(SO_4)_2^{3-}$ module while Si1 is closer to the centre of the positively charged $[Ca_{12}(SiO_4)_4O_2F]^{3+}$ module. The additional positive charge of P⁵⁺ at Si2 as well as Ba²⁺ at the K site is balanced by incorporation of O^{2–} at the centre of the anion octahedra.

Our recent investigations showed that nabimusaite is a widespread mineral in larnite-ye'elimitebrownmillerite (\pm fluormayenite-chlormayenite, spinel, fluorapatite-fluorellestadite) and also in ternesite- and jasmundite-bearing rocks. Spot-like aggregates of nabimusaite, jasmundite and aggregates of elongated ternesite crystals are confined to linear porous zones in larnite rocks (Fig. 3). Investigation of fresh surfaces of altered larnite rock fragments showed that the pore space is filled with calciolangbeinite, aphthitalite, sylvite, small barite crystals or less frequently with fluorellestadite and ferrite inclusions (Galuskina et al., 2014a). The latter are interpreted as products of crystallization of residual sulfate-chloride (+ silicate) melt detached during a clinkerization process of primary sedimentary rocks as a result of interlayer combustion processes. Crystallization with the participation of sulfate melts explains the large poikilitic



FIG. 5. The Raman spectrum of nabimusaite.



FIG. 6. Projection of the nabimusaite (a,b) and hatrurite structure (c) along [001]. The layer in (a) is the intercalated $K(SO_4)_2^{3-}$ unit. The antiperovskite layer of hatrurite (c) is shown below the comparable layer in nabimusaite (b). The main difference is the orientation of the SiO₄ tetrahedra (red) which all point in the same direction in hatrurite while in nabimusaite the Si1 tetrahedron points towards the adjacent $K(SO_4)^{3-}$ module (shown in (a)), while the Si2 tetrahedron points to the centre of the antiperovskite module.

metacrystals (up to 1 cm) of ternesite, srebrodolskite and harmunite (Galuskin *et al.*, 2013; Galuskina *et al.*, 2014*a*) in cryptocrystalline larnite nodules of pseudo-conglomerates of the Hatrurim Complex. Nabimusaite formed as a result of the reaction of potassium-enriched sulfate melt with larnite and fluorellestadite. Fluormavenite, ve'elimite, spinel and brownmillerite were not subject to alteration and are thus characteristic inclusions in nabimusaite. A paragenesis of nabimusaite with ternesite indicates high crystallization temperatures. Ternesite from altered xenoliths in Eifel volcanites (Germany) formed at 1000-1300°C (Irran et al., 1997). A synthetic analogue of ternesite forms as an intermediate phase during production of calcium sulfoaluminate cement at 900°C and remains stable up to 1200-1280°C (Beretka et al., 1993). Participation of sulfate melts with variable chemical composition reflects the high heterogeneity of the sedimentary protoliths and results in a high diversity of mineral phases in the rocks of the Hatrurim Complex. This also invalidates the hypothesis that a typical 'clinker' system is a good model for these rocks. The mineral assemblages of larnite-ye'elimite rocks clearly did not form synchronously in a dry, chemically closed system. Thus, the 'clinker' models suggested by several authors (Gross, 1984; Geller et al., 2012; Sokol et al., 2014) are oversimplifications of the actual genesis of the Hatrurim Complex.

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