

Vapnikite Ca_3UO_6 – a new double-perovskite mineral from pyrometamorphic larnite rocks of the Jabel Harmun, Palestinian Autonomy, Israel

E. V. GALUSKIN^{1,*}, I. O. GALUSKINA¹, J. KUSZ², T. ARMBRUSTER³, K. M. MARZEC⁴, P. DZIERŻANOWSKI⁵ AND M. MURASHKO⁶

¹ Faculty of Earth Sciences, Department of Geochemistry, Mineralogy and Petrography, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland

² Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland

³ Mineralogical Crystallography, Institute of Geological Sciences, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

⁴ Jagiellonian Centre for Experimental Therapeutics, Bobrzyńskiego 14, 30-348 Krakow, Poland

⁵ Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw, al. Żwirki i Wigury 93, 02-089 Warsaw, Poland

⁶ Systematic Mineralogy, 44, 11th line V.O., apt. 76, Saint-Petersburg 199178, Russia

[Received 22 December 2013; Accepted 6 February 2014; Associate Editor: G. D. Gatta]

ABSTRACT

The new mineral species vapnikite, Ca_3UO_6 , was found in larnite pyrometamorphic rocks of the Hatrurim Formation at Jabel Harmun in the Judean desert, Palestinian Autonomy, Israel. Vapnikite is an analogue of the synthetic ordered double-perovskite $\beta\text{-Ca}_3\text{UO}_6$ and is isostructural with the natural fluorperovskite – cryolite Na_3AlF_6 . Vapnikite Ca_3UO_6 ($P2_1/n$, $Z = 2$, $a = 5.739(1)$, $b = 5.951(1)$, $c = 8.312(1)$ Å, $\beta = 90.4(1)^\circ$, $V = 283.9(1)$ Å³) forms yellow-brown xenomorphic grains with a strong vitreous lustre. Small grains up to 20–30 µm in size are wedged between larnite, brownmillerite and ye'elimite. Vapnikite has irregular fracture, cleavage and parting were not observed. The calculated density is 5.322 g cm⁻³, the microhardness is $\text{VHN}_{25} = 534$ kg mm⁻² (mean of seven measurements) corresponding to the hardness of ~5 on the Mohs scale. The crystal structure of vapnikite Ca_3UO_6 differs from that of its synthetic analogue $\beta\text{-Ca}_3\text{UO}_6$ by having a larger degree of Ca, U disorder. Vapnikite formed at the high-temperature retrograde stage of pyrometamorphism when larnite rocks were altered by fluids/melts of high alkalinity.

KEYWORDS: vapnikite, Ca_3UO_6 , vorlanite, Raman, structure, pyrometamorphic rocks, Hatrurim Formation, Jabel Harmun.

Introduction

VAPNIKITE, Ca_3UO_6 (IMA2013-082), was discovered in pyrometamorphic larnite rocks of the Jabel (Mountain in Arabian) Harmun locality belonging to the Hatrurim Formation ('Mottled Zone'; Picard, 1931; Bendor, 1960; Gross, 1977; Vapnik

et al., 2007), situated in the Judean Desert, West Bank, Palestinian Autonomy, Israel (31°46'N 35°26'E). Vapnikite ($P2_1/n$, $Z = 2$, $a = 5.739(1)$, $b = 5.951(1)$, $c = 8.312(1)$ Å, $\beta = 90.4(1)^\circ$, $V = 283.9(1)$ Å³) is the first naturally occurring ordered double perovskite of the $A_2BB'\text{O}_6$ type ($A, B = \text{Ca}$; $B' = \text{U}^{6+}$) with the synthetic analogue named $\beta\text{-Ca}_3\text{UO}_6$ ($P2_1/n$, $Z = 2$, $a = 5.728(1)$, $b = 5.956(1)$, $c = 8.298(2)$ Å, $\beta = 90.55(3)^\circ$, $V = 283.1(1)$ Å³; Loopstra and Rietveld, 1969; van Duivenboden and IJdo, 1986; Mitchell, 2002;

* E-mail: evgeny.galuskin@us.edu.pl
DOI: 10.1180/minmag.2014.078.3.07

Read *et al.*, 2013). The synthetic low-temperature polymorph α -Ca₃UO₆ is trigonal ($R\bar{3}$, $a = 9.624(1)$, $c = 11.388(1)$ Å, $\gamma = 120^\circ$, $V = 913.3(1)$ Å³; Holc and Goli, 1983). Cryolite Na₃AlF₆ ($P2_1/n$, $Z = 2$; $a = 5.4024(2)$, $b = 5.5959(1)$, $c = 7.7564(3)$ Å, $\beta = 90.278(1)^\circ$, $V = 234.48(1)$ Å³; Hawthorne and Ferguson, 1975), a natural fluorperovskite, is isotypic with vapnikite.

Diaboleite Pb₂Cu(OH)₄Cl₂, originally described by Spencer and Mountain (1923), belongs to double defect $A_2B_2X_6$ perovskites (Mitchell, 2002). The crystal structure of diaboleite Pb₂(Cu□)(OH)₄Cl₂ ($P4mm$, $Z = 1$, $a = 5.880(1)$ Å, $c = 5.500(2)$ Å, $V = 190.1(1)$ Å³) was interpreted as a B-site defect double perovskite, in which half of the BX₆ octahedra are not occupied by cations (Rouse, 1971; Cooper and Hawthorne, 1995).

The name vapnikite is given in honour of Yevgeny Vapnik (Ben Gurion University of the Negev, Beer Sheva, Israel), who initiated a new program of geological, geophysical, petrological and mineralogical studies of the Hatrurim Formation in Israel and Jordan (Vapnik *et al.*, 2007; Sokol *et al.*, 2007, 2008, 2010; Novikov *et al.*, 2013; etc.). He took part in the discovery of 14 new minerals from the pyrometamorphic rocks of the Hatrurim Formation: barioferrite BaFe₁₂³⁺O₁₉ (Murashko *et al.*, 2010); murashkoite FeP, halamishite Ni₅P₄ (*H*), zuktamrurite Ni₅P₄ (*O*), negevite NiP₂, transjordanite Ni₃P (Britvin *et al.*, 2013*a–e*); harmunite CaFe₂O₄, gurimite BaCa₆[(SiO₄)(PO₄)](VO₄)₂F (Galuskina *et al.*, 2013*a,b*, 2014); nabimusaita KCa₁₂(SiO₄)₄(SO₄)₂O₃F, fluorkyuygenite Ca₁₂Al₁₄O₃₂[(H₂O)₄F₂], fluormayenite Ca₁₂Al₁₄O₃₂F₂, zado-vite BaCa₆[(SiO₄)(PO₄)](PO₄)₂F, aradite BaCa₆[(SiO₄)(PO₄)](VO₄)₂F (Galuskin *et al.*, 2013*b,d,e–g*); shulamitite Ca₃TiFe³⁺AlO₈ (Sharygin *et al.*, 2013).

Type material is deposited in the mineralogical collections of the Museum of Natural History in Bern, Bernastrasse 5, CH-3005 Bern, Switzerland, catalogue number NMBE 42401.

Methods of investigation

Crystal morphology and chemical composition of vapnikite and associated minerals were examined using optical microscopes, analytical electron scanning microscope Philips XL30 ESEM/EDAX (Faculty of Earth Sciences, University of Silesia) and electron microprobe CAMECA SX100 (Institute of Geochemistry, Mineralogy

and Petrology, University of Warsaw). Electron probe microanalyses of vapnikite were performed at 15 kV and 40 nA using the following lines and standards: CaK α , UM β – vorlanite; contents of Na, Mg, Al, Si, K, Ti, Mn, Fe, Zr, Sr, Nb, Ba, Th, Ce, La, etc. are below the detection limit.

The Raman spectra of vapnikite were recorded on a WITec confocal Raman microscope CRM alpha 300 equipped with an air-cooled solid-state laser, emitting at 488 nm and a CCD camera operating at -82°C . The excitation laser radiation was coupled to a microscope through a single-mode optical fibre with a diameter of 50 μm . An air Olympus MPLAN (100 \times /0.90NA) objective was used. Raman-scattered light was focused onto 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 in the range 1–40 mW. Some 15–20 scans with integration time of 10–15 s and a resolution of 3 cm⁻¹ were collected and averaged. The spectrometer monochromator was calibrated using the Raman scattering line of a Si plate (520.7 cm⁻¹).

Single-crystal X-ray diffraction studies of vapnikite from Israel were carried out using a SuperNova Dual diffractometer with a mirror monochromator (CuK $\alpha = 1.54184$ Å) and an Atlas CCD detector (Aligent Technologies) at the Institute of Physics, University of Silesia, Poland. Copper X-radiation was chosen because of the very small crystal size and the stronger intensity of Cu radiation compared to Mo X-radiation. The intensities were corrected for Lorentz and polarization effects and an absorption correction based on the multi-scan method was applied. In spite of the large absorption coefficient of 104.1 mm⁻¹, the small crystal size and data redundancy of ~ 3 led to an adequate absorption correction as indicated by $R_{\text{int}} = 0.0379$ (Table 2).

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). Split positions were refined with common anisotropic atom-displacement parameters.

Occurrence and physical properties of vapnikite

Numerous tiny vapnikite grains <5–10 μm in size were discovered in larnite-rich pyrometamorphic pseudoconglomerates of the Hatrurim Formation from the Jabel Harmun locality, Judean Desert, Palestinian Autonomy, Israel. Rocks of the

Hatnurim Formation are widely distributed in the region surrounding the Dead Sea on the territory of Israel, Palestinian Autonomy and Jordan (Picard, 1931; Kolodny and Gross, 1974; Burg *et al.*, 1991, 1999). Larnite rocks were formed by pyrogenic metamorphism due to caustobololith combustion at temperatures above 800°C (Kolodny and Gross, 1974; Sokol *et al.*, 2007, 2010). Their pebble-like shape can be explained by low-temperature hydrothermal alteration of larnite-rich rocks with subsequent weathering (Gross, 1977). The geological description of the Jabel Harmun locality and existing hypotheses for the genesis of these pyrometamorphic rocks of the Hatnurim Formation are summarized by Galuskina *et al.* (2014) and references therein. The Jabel Harmun is also the locality where

harmunite (IMA2012-045, Galuskina *et al.*, 2013a, 2014), nabimusaite (IMA2012-057, Galuskin *et al.*, 2013e) and fluormayenite (IMA2013-019, Galuskin *et al.*, 2013f) were discovered.

Only one dark-brown larnite pebble of pseudoconglomerate from the western slope of the Jabel Harmun contained xenomorphic grains of vapnikite up to 20–30 µm in size, which were suitable for single-crystal X-ray diffraction (Fig. 1a–c). The dark-brown colour of the pebble is due to abundant grains of brownmillerite $\text{Ca}_2\text{Fe}^{3+}(\text{Al}, \text{Fe}^{3+})\text{O}_5$. In addition to brownmillerite and larnite $\beta\text{-Ca}_2\text{SiO}_4$, rock-forming minerals are ye’elimite $\text{Ca}_4\text{Al}_6\text{O}_{12}(\text{SO}_4)$ and/or minerals of the fluormayenite–fluorkyuygenite series $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{F}_2\text{--Ca}_{12}\text{Al}_{14}\text{O}_{32}[(\text{H}_2\text{O})_4\text{F}_2]$.

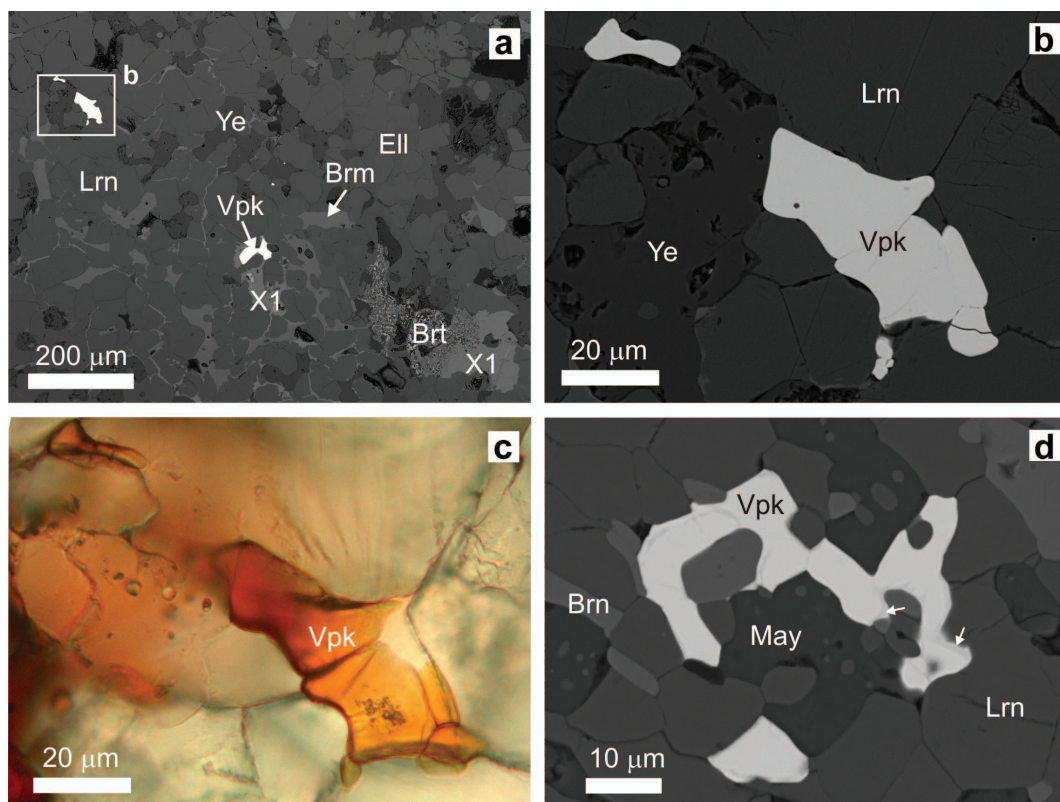


FIG. 1. (a) Fragment of a larnite pebble from a pseudoconglomerate of the Jabel Harmun, Judean desert, where larger grains of vapnikite were found; image produced with backscattered electrons (BSE). The boxed area is magnified in parts (b) (BSE image) and (c) (optical image) is framed; (b) BSE image; (c) optical image; (d) vapnikite in a larnite pebble from the Hatnurim Basin, the Negev desert. $\text{Ca}_2\text{UO}_5 \cdot n\text{H}_2\text{O}$ rims are indicated by arrows, BSE. Vpk = vapnikite, Lrn = larnite, Ye = ye’elimite, Ell = fluorellistadite, Brm = brownmillerite, May = ‘chlormayenite’ $\approx \text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_2$, X1 = potentially new mineral, $\text{BaCa}_6(\text{SiO}_4)_2(\text{SO}_4)_2\text{O}$.

Some rock fragments are enriched in fluorelles-tadite–fluorapatite $\text{Ca}_5(\text{SiO}_4)_{1.5}(\text{SO}_4)_{1.5}\text{F}-\text{Ca}_5(\text{PO}_4)_3\text{F}$, P-bearing ternesite $\text{Ca}_5[(\text{SiO}_4), (\text{PO}_4)]_2[(\text{SO}_4), (\text{PO}_4)]$ (Galuskin *et al.*, 2013a), shulamitite $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{3+}(\text{Al}, \text{Fe}^{3+})\text{O}_8$ (Sharygin *et al.*, 2013), baryte BaSO_4 , periclase MgO , Ba-bearing nabimusaite $(\text{K}, \text{Ba})\text{Ca}_{12}(\text{SiO}_4)_4(\text{SO}_4)_2\text{O}_2(\text{F}, \text{O})$ and the potentially new mineral $\text{BaCa}_6(\text{SiO}_4)_2(\text{SO}_4)_2\text{O}$, probably isostructural with recently discovered zadovite $\text{BaCa}_6[(\text{SiO}_4)(\text{PO}_4)]_2(\text{PO}_4)_2\text{F}$ (IMA2013-031, Galuskin *et al.*, 2013g). These rocks contain rarely oldhamite CaS and the potentially new mineral CaCu_2S_2

(Galuskin *et al.*, 2013c). In pebbles, vapnikite is often associated with vorlanite $(\text{CaU}^{6+})\text{O}_4$, which, in contrast to xenomorphic vapnikite, forms pseudotrigonal flattened poikiloblastic crystals with well developed $\{001\}$ faces (Fig. 2a,b; Galuskin *et al.*, 2013h). Vapnikite and vorlanite are usually enriched in different parts of the larnite-bearing rocks.

Vapnikite is yellow-brown, as is its synthetic analogue $\beta\text{-Ca}_3\text{UO}_6$ (Read *et al.*, 2013). The streak is white with a yellow hue. In association with vapnikite, vorlanite is grey-green (Galuskin *et al.*, 2013h), in contrast to the dark-red colour of

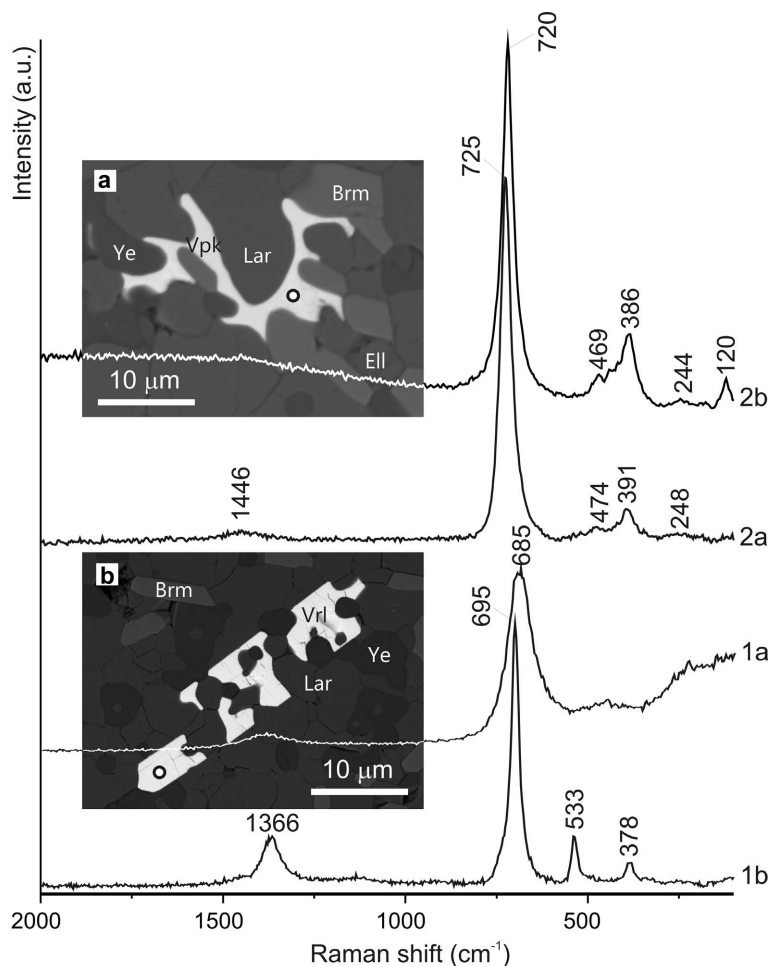


FIG. 2. (a) Typical xenomorphic vapnikite grain; (b) poikiloblastic crystal of vorlanite 9 mm from vapnikite shown in Fig. 3a; Circles in 2a and 2b indicate spots at which single Raman spectra were collected (up to 5 mW) and where later a crater was produced by a 40 mW laser. Raman spectra obtained with low laser power (up to 5 mW) of: 1a – initial vorlanite, 1b – vorlanite altered after thermal laser impact; 2a – initial vapnikite; 2b – vapnikite altered after thermal laser impact.

vorlanite from the type locality of the Upper Chegem caldera, Northern Caucasus (Galuskin *et al.*, 2011).

The flat xenomorphic character of vapnikite grains, wedged between rock-forming minerals, made extraction for single-crystal structure investigation and for optical and hardness measurement a challenge.

Vapnikite is transparent and shows strong vitreous lustre. Vapnikite does not usually fluoresce in ultraviolet light, but sometimes weak-yellowish fluorescence (254 nm and 366 nm) can be observed. Microhardness of vapnikite varies slightly $VHN_{25} = 516\text{--}548$, mean 534 kg mm^{-2} (average of 7 measurements), corresponding to ~ 5 in the Mohs scale. Vapnikite has irregular fracture; cleavage and parting are not observed. Density could not be measured because of the small grain size. The calculated density is 5.322 g cm^{-3} using the empirical formula (Table 1). It was only possible to determine that vapnikite is biaxial with a mean refractive index in a random cross-section of 1.78(3) because of the small size and the rare occurrence of vapnikite crystals with dimensions $>10\text{ }\mu\text{m}$. The mineral is not pleochroic.

Vapnikite does not dissolve in 10% HCl whereas vorlanite dissolves quickly in 10% HCl at room temperature (Galuskin *et al.*, 2011). Synthetic Ca_3UO_6 decomposes within a week in an aqueous environment at 573 K and 0.2 GPa (van Duivenboden and IJdo, 1986).

Micron-sized grains of vapnikite were also detected in different types of larnite-bearing rocks from other localities of the Hatrurim Formation:

Nabi Musa, Judean Desert and Hatrurim Basin, Negev Desert (Fig. 1d).

Composition, structure and Raman spectra of vapnikite

Vapnikite grains are usually chemically homogeneous. All impurities are below the detection limit of microprobe analysis (Table 1, analysis 1). Micron-sized rims with a composition $\text{Ca}_2\text{UO}_5 \cdot n\text{H}_2\text{O}$ and/or $\text{CaUO}_4 \cdot n\text{H}_2\text{O}$, $0 < n < 1$ (Table 1, analyses 2, 3) are characteristic of a few vapnikite grains (Fig. 1d). $\text{CaUO}_4 \cdot n\text{H}_2\text{O}$ also forms rims around vorlanite associated with vapnikite. $\text{Ca}_2\text{UO}_5 \cdot n\text{H}_2\text{O}$ ($n = 1.3\text{--}1.7$) and $\text{CaUO}_4 \cdot n\text{H}_2\text{O}$ ($n = 0\text{--}1$) form in the system $\text{CaO}\text{--}\text{UO}_3\text{--}\text{H}_2\text{O}$ at high alkalinity (Atkins *et al.*, 1988; Moroni and Glasser, 1995; Gorman-Lewis *et al.*, 2008; Cantrell *et al.*, 2011).

Structural data were obtained for one very small vapnikite grain $24\text{ }\mu\text{m} \times 11\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ (Fig. 1b). Experimental data and the results of structure refinement are given in Tables 2–5. The crystal structure of vapnikite (Fig. 3) corresponds to that of its synthetic analogue $\beta\text{-Ca}_3\text{UO}_6$ (Loopstra and Rietveld, 1969; van Duivenboden and IJdo, 1986; Mitchell 2002; Read *et al.*, 2013). The main difference between these structures is a larger degree of U, Ca disorder observed for the mineral.

Powder-diffraction data were collected from a vapnikite single crystal using the pseudo-Gandolfi software of the SuperNova Dual diffractometer ($\text{CuK}\alpha = 1.54184\text{ }\text{\AA}$). However, due to the many overlapping reflections, corresponding intensities

TABLE 1. Chemical composition (wt.%) of vapnikite (1) and its hydrated rims (2, 3).

	1 (mean 14)			2	3
UO_3	63.36	0.37	62.78–63.87	68.68	81.85
SiO_2	n.d.			0.08	0.00
CaO	36.28	0.2	35.94–36.64	27.82	16.87
H_2O^a				3.43	1.28
Sum	99.64			100.00	100.00
Ca	2.980			2.018	1.025
U^{6+}	1.020			0.977	0.975
Si				0.005	
H_2O				0.770	0.484

^a calculated as difference from 100%; formula in column 1 normalized to 4 cations, in column 2 to 3 cations and in column 3 to 2 cations.

TABLE 2. Data collection and structure-refinement details for vapnikite.

Cell dimensions (Å)	$a = 5.739(1)$ $b = 5.951(1)$ $c = 8.312(1)$ $\beta = 90.4(1)$
V (Å ³)	283.82(7)
Space group	$P2_1/n$
Z	2
Temperature	293(2) K
Diffractometer	SuperNova Dual
X-ray radiation	CuK α
Crystal size (mm)	$0.021 \times 0.011 \times 0.010$
Reflections collected	1646
Max. 2θ	150.06
Index range	$-4 \leq h \leq 7$ $-7 \leq k \leq 7$ $-10 \leq l \leq 9$
Unique reflections	579
Reflections $I > 4\sigma(I)$	553
Number of parameters	59
R_{int}	0.0379
$R\sigma$	0.0237
Goof	1.073
$R1, I > 4\sigma(I)$	0.0354
$R1, \text{all data}$	0.0360
$wR2$ (on F^2)	0.0992
LH (e Å ⁻³)	2.0 close to U3
LP (e Å ⁻³)	-2.1 close to O2

could not be determined properly (Fig. 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). A

simulated powder-diffraction pattern calculated from the refined structural parameters is given in supplementary Table S1, (available from www.minersoc.org/pages/e_journals/dep_mat_mm.html).

A Raman spectroscopic local-heating experiment of the same type that caused the restoration of cation order in self-irradiated Ca- and U-disordered vorlanite (Galuskin *et al.*, 2012, 2013*h*) was undertaken. For this purpose, vapnikite and vorlanite (as reference) grains were selected in the same thin section of a larnite rock from Jabel Harmun (Fig. 2*a,b*). First, Raman spectra of both minerals were obtained using low laser power (up to 5 mW). Subsequently, thermally induced craters on the mineral surface were created with increased laser power of 40 mW. After 5 min, Raman spectra with low laser power (up to 5 mW) were collected on the walls of the craters. Raman spectra obtained with low laser power for the initial minerals and after crater burning (from the wall of the crater) are presented in Fig. 2 for vorlanite (labelled 1*a*, 2*a*) and vapnikite (labelled 1*b*, 2*b*), respectively.

The Raman spectrum of initial vapnikite is characterized by the presence of two main bands at 725 and 391 cm⁻¹ which originate from stretching and bending U–O vibrations. The initial spectrum of vorlanite has a single band at 685 cm⁻¹. The Raman spectrum of thermally altered vorlanite is characterized by three sharp bands at 695, 533 and 378 cm⁻¹. Such changes indicate a phase transition from cubic vorlanite to trigonal Ca-uranate (Galuskin *et al.*, 2012, 2013*h*). On the other hand, the bands observed in the Raman spectrum of thermally altered

TABLE 3. Atom coordinates, U_{eq} values (Å²) and site occupancies for natural vapnikite.

Site	Atom	x/a	y/b	z/c	U_{eq}	Occupancy
Ca1	Ca	0.5138(3)	0.5507(6)	0.2409(6)	0.0140(7)	0.978(3)
U1'	U	0.495(2)	0.569(3)	0.294(3)	0.0140(7)	0.022(3)
Ca2	Ca	0.5	0	0	0.0062(12)	0.920(8)
U2	U					0.080(8)
U3	U	0	0.5	0	0.0039(3)	0.832(16)
Ca3	Ca					0.168(16)
O1	O	0.1776(8)	0.2117(8)	0.9211(5)	0.0258(13)	1.0
O2	O	0.2958(8)	0.6800(8)	0.9428(5)	0.0279(14)	1.0
O3	O	0.3729(7)	0.9288(9)	0.2658(5)	0.0129(15)	0.93(2)
O3A	O	0.53(3)	0.005(7)	0.273(17)	0.0129(15)	0.07(2)

Refined formula Ca_{3.05}U_{0.95}O₆

TABLE 4. Anisotropic displacement parameters for vapnikite (\AA^2).

Site	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca1/U1'	0.0144(8)	0.0085(10)	0.0192(18)	-0.0020(11)	0.0023(8)	0.0041(6)
Ca2/U2	0.0076(17)	0.0059(17)	0.0052(16)	0.0007(2)	-0.0005(9)	-0.0012(3)
U3/Ca3	0.0048(4)	0.0030(4)	0.0039(4)	-0.00009(6)	0.0009(2)	-0.00027(6)
O1	0.021(2)	0.025(2)	0.031(2)	-0.013(2)	-0.0072(17)	0.006(2)
O2	0.025(3)	0.025(3)	0.034(3)	-0.014(2)	0.014(2)	-0.011(2)
O3/O3A	0.018(2)	0.006(3)	0.014(2)	0.0014(17)	0.0016(15)	0.0036(16)

vapnikite are only slightly (5 cm^{-1}) shifted toward larger wavenumbers. After laser treatment, a new band at 120 cm^{-1} appeared. This behaviour suggests that the laser heating experiment had a lesser effect on the structure of vapnikite than on vorlanite.

Discussion

The structure of vapnikite is analogous to that of synthetic $\beta\text{-Ca}_3\text{UO}_6$, which has the structure type of ordered U-bearing double perovskites with the crystal-chemical formula $A_2^{2+}B^{2+}\text{UO}_6$ ($A = \text{Sr, Ba, Pb, Ca}$; $B = \text{Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb}$; van Duivenboden and IJdo, 1986; Knyazev *et al.*, 2011; Read *et al.*, 2013; Fig. 3). Vorlanite, CaUO_4 , associated with vapnikite, crystallized originally as an ordered trigonal

Ca-uranate which transformed as a result of radioactive U decay to disordered cubic vorlanite with a fluorite structure-type. Vorlanite recovers the original rhombohedral structure after heating above 750°C (Galuskin *et al.*, 2012, 2013*h*). Calculated cumulative doses for vapnikite and associated vorlanite are similar and correspond to 0.6 displacements per atom, (dpa) for an expected rock age of 3 Ma (Gur *et al.*, 1995). The analogous heating experiment on vapnikite showed that the Raman spectrum only changed slightly (Fig. 2), suggesting only minor structural changes in its primary structure. This is also supported by single-crystal X-ray diffraction showing that radioactive damage caused only slight disorder in the vapnikite structure. A larger degree of Ca, U disorder was refined compared to the model proposed for synthetic $\beta\text{-Ca}_3\text{UO}_6$:

TABLE 5. Selected interatomic distances (\AA) for vapnikite.

Atom—Atom	Dist.	Atom—Atom	Dist.
Ca1—O2	2.331(7)	U1'—O1	2.236(15)
Ca1—O3	2.335(5)	U1'—O3	2.262(17)
Ca1—O1	2.354(5)	U1'—O3	2.320(15)
Ca1—O3	2.400(6)	U1'—O2	2.59(2)
Ca1—O1	2.643(6)	U1'—O1	2.71(3)
Ca1—O2	2.821(7)	U1'—O2	2.75(3)
Ca1—O2	2.872(7)	U1'—O1	2.911(19)
Ca1—O3A	2.61(14)	U1'—O3A	2.61(5)
Ca1—O3A	2.71(5)	U1'—O3A	2.79(14)
Mean O3	2.54	Mean	2.54
Mean O3A	2.62	Mean	2.65
Ca2—O2 $\times 2$	2.284(4)	U3—O2 $\times 2$	2.066(4)
Ca2—O1 $\times 2$	2.328(4)	U3—O1 $\times 2$	2.103(4)
Ca2—O3 $\times 2$	2.370(4)	U3—O3 $\times 2$	2.117(4)
Mean	2.336	Mean	2.095
Ca2—O3A $\times 2$	2.27(14)	U3—O3A $\times 2$	1.90(14)
Ca1—U1	0.47(2)	O3—O3A	1.04(0.14)

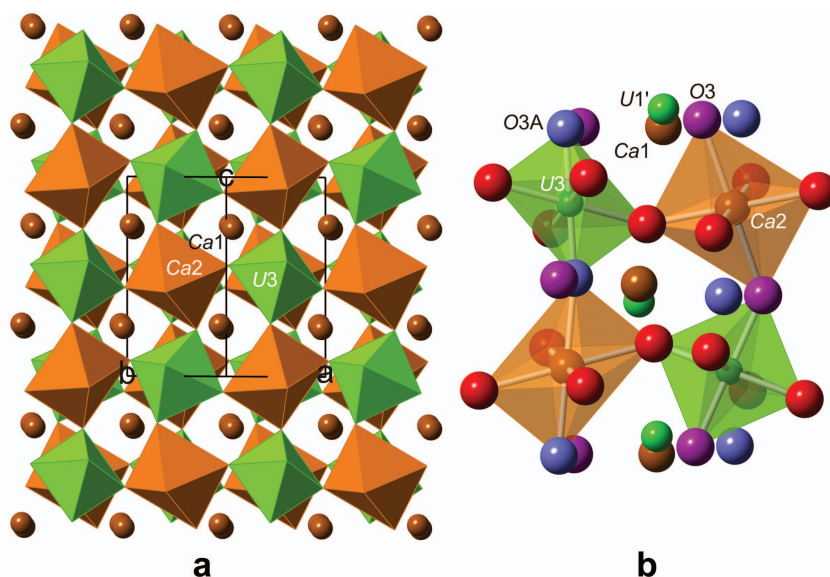


FIG. 3. (a) Structure of vapnikite corresponding to monoclinic ordered double perovskite ($P2_1/n$) with common crystal-chemical formula $A_2BB'O_6$, where $A = \text{Ca1}$ site – brown spheres; $B = \text{Ca2}$ octahedral site in dark-orange; $B' = \text{U3}$ at small octahedral site in green. (b) Magnified portion of the vapnikite structure; additional low-occupied sites are shown: $\text{U1}'$ – green spheres; O3A – blue spheres (for explanation see text).

$\text{Ca}_2(\text{Ca}_{0.96}\text{U}_{0.04})(\text{U}_{0.96}\text{Ca}_{0.04})\text{O}_6$ (Read *et al.*, 2013). Refinement of site occupancies in vapnikite resulted in a slightly non-stoichiometric Ca/U ratio, which is within 3 estimated standard deviations of the refined occupancies and may be an artifact due to correlations among site occupancies and the scale factor: $(\text{Ca}_{1.96}\text{U}_{1'.04})(\text{Ca}_{2.02}\text{U}_{2.08})(\text{U}_{3.83}\text{Ca}_{3.17})\text{O}_{12}\text{O}_{2.03}\text{O}_{3.15}\text{O}_{3\text{A}0.15} = \text{Ca}_{3.05}\text{U}_{0.95}\text{O}_6$. Thus, disorder is not only observed at the octahedrally coordinated Ca2 and U3 sites with an average value of 12% anti-site mixing, but also at the [7]-coordinate Ca1 site, at which U substituting for Ca is displaced by 0.47 Å from the Ca1 position. Incorporation of U^{6+} at the octahedrally coordinated Ca2 site, combined with Ca incorporation at the U3 site, leads to splitting of O3 into the subsites O3 and O3A , separated by ~1 Å (Table 5). Structural parameters of vapnikite and its chemical composition are close to the corresponding parameters and composition of the synthetic double perovskite $\beta\text{-Ca}_3\text{UO}_6$ (Read *et al.*, 2013). In summary, the endmember crystal-chemical formula of vapnikite is Ca_3UO_6 .

Vapnikite is one of the few minerals in which U^{6+} does not show a well expressed coordination of the type 2+4, i.e. the two shortest [$d(\text{U}=\text{O}) \approx$

1.7–1.9 Å] of the six bonds form the linear uranyl group UO_2^{2+} whereas the remaining U longer bonds have $d(\text{U}-\text{O}) \approx 2.1\text{--}2.6$ Å (Burns *et al.*, 1997; Burns 1999, 2005). In the case of vapnikite, the U-octahedron is close to ideal with bond distances: $\text{U3}-\text{O1} = 2.103(4)$ Å, $\text{U3}-\text{O2} = 2.066(4)$ Å, $\text{U3}-\text{O3} = 2.117(5)$ Å.

The wedged position of vapnikite grains and vorlanite poikiloblastic crystals between primary minerals (Figs 1, 2a,b) suggests their crystallization from a high-temperature residual fluid/melt at the retrograde stage of alteration of the pyrometamorphic larnite rocks of the Hatrurim Formation. Interestingly, most investigators studying the genesis of the Hatrurim rocks accept the hypothesis of dry conditions related to the combustion processes for larnite formation (Matthews and Gross, 1980; Sokol *et al.*, 2007, 2008, 2010). However, during the last few years, a series of new rock-forming minerals has been described, suggesting more complex high-temperature mineralization with the participation of a liquid phase. The latter minerals comprise the ternesite–‘silicocarnotite’ and fluormayenite–fluorkyuygenite series, nabimu-saite, jasmundite, vorlanite and others (Galuskin *et al.*, 2013a,d–f,h).

Acknowledgements

Investigations were partially supported by the National Sciences Center (NCN) of Poland by decision no. DEC-2012/05/B/ST10/00514 (E.G. and I.G.). The authors thank Frank Hawthorne, Peter Leverett and an anonymous reviewer for their careful reviews which helped to improve a previous version of the manuscript.

References

- Atkins, M., Beckley, A.N. and Glasser, F.P. (1988) Influence of cement on the near-field environment and its specific interaction with uranium and iodine. *Radiochimica Acta*, **44-45**, 255–261.
- Bentor, Y.K. (editor) (1960) Israel. In: *Lexique Stratigraphique International, Asie, Vol. III, Sec. 10.2*. Centre national de la recherche scientifique, Paris.
- Britvin, S.N., Murashko, M., Vapnik, Y., Polekhovsky, Y.S. and Krivovichev, S.V. (2013a) Halamishite, IMA 2013-105. CNMNC Newsletter No. 19, February 2014, page 167; *Mineralogical Magazine*, **78**, 165–170.
- Britvin, S.N., Murashko, M., Vapnik, Y., Polekhovsky, Y.S. and Krivovichev, S.V. (2013b) Negevite, IMA 2013-104. CNMNC Newsletter No. 19, February 2014, page 166; *Mineralogical Magazine*, **78**, 165–170.
- Britvin, S.N., Murashko, M., Vapnik, Y., Polekhovsky, Y.S. and Krivovichev, S.V. (2013c) Transjordanite, IMA 2013-106. CNMNC Newsletter No. 19, February 2014, page 167; *Mineralogical Magazine*, **78**, 165–170.
- Britvin, S.N., Murashko, M., Vapnik, Y., Polekhovsky, Y.S. and Krivovichev, S.V. (2013d) Zuktamrurite, IMA 2013-107. CNMNC Newsletter No. 19, February 2014, page 167; *Mineralogical Magazine*, **78**, 165–170.
- Britvin, S.N., Vapnik, Y., Polekhovsky, Y.S. and Krivovichev, S.V. (2013e) Murashkoite, IMA 2012-071. CNMNC Newsletter No. 15, February 2013, page 8; *Mineralogical Magazine*, **77**, 1–12.
- Burg, A., Starinsky, A., Bartov, Y. and Kolodny, Y. (1991) Geology of the Hatrurim Formation (“Mottled Zone”) in the Hatrurim basin. *Israel Journal of Earth Sciences*, **40**, 107–124.
- Burg, A., Kolodny, Y. and Lyakhovsky, V. (1999) Hatrurim-2000: The “Mottled Zone” revisited, forty years later. *Israel Journal of Earth Sciences*, **48**, 209–223.
- Burns, P.C. (1999) The crystal chemistry of uranium. Pp. 23–90 in: *Uranium: Mineralogy, Geochemistry and the Environment* (P.C. Burns and R. Finch, editors). Reviews in Mineralogy, **38**. Mineralogical Society of America, Washington, DC.
- Burns, P.C. (2005) U^{6+} minerals and inorganic compounds: insights into an expanded structural hierarchy of crystal structures. *The Canadian Mineralogist*, **43**, 1839–1894.
- Burns, P.C., Ewing, R.C. and Hawthorne, F.C. (1997) The crystal chemistry of hexavalent uranium: Polyhedral geometries, bond-valence parameters, and polymerization of polyhedra. *The Canadian Mineralogist*, **35**, 1551–1570.
- Cantrell, K.J., Heald, S.M., Arey, B.W. and Lindberg, M.J. (2011) Inhibited release of mobile contaminants from Hanford tank residual waste. Paper No. 11447 in: *Waste Management 2011: Global Achievements and Challenges in Waste Management*, February 27–March 3, 2011, Phoenix, Arizona. Waste Management Symposia Inc., Tucson, Arizona, USA.
- Cooper, M.A. and Hawthorne, F.C. (1995) Diaboleite, $Pb_2Cu(OH)_4Cl_2$, a defect perovskite structure with stereoactive lone-pair behaviour of Pb^{2+} . *The Canadian Mineralogist*, **33**, 1125–1129.
- Galuskin, E.V., Armbruster, T., Galuskina, I.O., Lazic, B., Winiarski, A., Gazeev, V.M., Dzierżanowski, P., Zadov, A.E., Pertsev, N.N., Wrzalik, R., Gurbanov, A.G. and Janeczek, J. (2011) Vorlanite (CaU^{6+}) O_4 – a new mineral from the Upper Chegem caldera, Kabardino-Balkaria, Northern Caucasus, Russia. *American Mineralogist*, **96**, 188–196.
- Galuskin, E.V., Galuskina, I.O., Dubrovinsky, L.S. and Janeczek, J. (2012) Thermally induced transformation of vorlanite to “protovorlanite”: restoration of cation ordering in self-irradiated $CaUO_4$. *American Mineralogist*, **97**, 1002–1004.
- Galuskin, E., Galuskina, I., Lazic, B. and Vapnik, Ye. (2013a) Rock-forming P-bearing ternesite from pyrometamorphic rocks of the hatrurim formation, Israel. *Mineralogia - Special papers*, **41**, 40.
- Galuskin, E.V., Galuskina, I.O., Pakhomova, A., Armbruster, T., Vapnik, Ye., Dzierżanowski, P. and Murashko, M. (2013b) Aradite, IMA 2013-047. CNMNC Newsletter No. 17, October 2013, page 3001; *Mineralogical Magazine*, **77**, 2997–3005.
- Galuskin, E., Galuskina, I., Vapnik, Ye., Murashko, M., Prusik, K. and Dzierżanowski, P. (2013c) Oldhamite CaS and potentially new mineral $CaCu_2S_2$ from pyrometamorphic rock of the Hatrurim formation. Goldschmidt 2013, Conference Abstracts, *Mineralogical Magazine*, **77**, 1134.
- Galuskin, E.V., Gfeller, F., Armbruster, T., Sharygin, V.V., Galuskina, I.O., Krivovichev, S.V., Vapnik, Ye., Murashko, M., Dzierżanowski, P. and Wirth, R. (2013d) Fluorkyuygenite, IMA 2013-043. CNMNC Newsletter No. 17, October 2013, page 3000; *Mineralogical Magazine*, **77**, 2997–3005.
- Galuskin, E.V., Gfeller, F., Armbruster, T., Galuskina, I.O., Vapnik, Ye., Murashko, M., Włodyka, R. and

- Dzierżanowski, P. (2013e) Nabimusaite, IMA 2012-057. CNMNC Newsletter No. 15, February 2013, page 5; *Mineralogical Magazine*, **77**, 1–12.
- Galuskin, E.V., Gfeller, F., Armbruster, T., Galuskina, I.O., Vapnik, Ye., Murashko, M. and Dzierżanowski, P. (2013f) Fluormayenite, IMA 2013-019. CNMNC Newsletter No. 16, August 2013, page 2705; *Mineralogical Magazine*, **77**, 2695–2709.
- Galuskin, E.V., Gfeller, F., Galuskina, I.O., Armbruster, T., Vapnik, Ye., Włodyka, R., Dzierżanowski, P. and Murashko, M. (2013g) Zadovite, IMA 2013-031. CNMNC Newsletter No. 16, August 2013, page 2708; *Mineralogical Magazine*, **77**, 2695–2709.
- Galuskin, E.V., Kusz, J., Armbruster, T., Galuskina, I.O., Marzec, K., Vapnik, Ye. and Murashko, M. (2013h) Vorlanite, $(\text{CaU}^{6+})\text{O}_4$, from Jabel Harmun, Palestinian Autonomy, Israel. *American Mineralogist*, **98**, 1938–1942.
- Galuskina, I.O., Vapnik, Ye., Lazic, B., Armbruster, T., Murashko, M. and Galuskin, E.V. (2013a) Harmunite, IMA 2012-045. CNMNC Newsletter No. 15, February 2013, page 2; *Mineralogical Magazine*, **77**, 1–12.
- Galuskina, I.O., Vapnik, Y., Prusik, K., Dzierżanowski, P., Murashko, M. and Galuskin, E.V. (2013b) Gurimite, IMA 2013-032. CNMNC Newsletter No. 16, August 2013, page 2708; *Mineralogical Magazine*, **77**, 2695–2709.
- Galuskina, I.O., Vapnik, Ye., Lazic, B., Armbruster, T., Murashko, M. and Galuskin, E.V. (2014) Harmunite CaFe_2O_4 – a new mineral from the Jabel Harmun, West Bank, Palestinian Autonomy, Israel. *American Mineralogist*, **99**, 965–975.
- Gorman-Lewis, D., Burns, P.C. and Fein, J.B. (2008) Review of uranyl mineral solubility measurements. *Journal Chemical Thermodynamics*, **40**, 335–352.
- Gross, S. (1977) The mineralogy of the Hatrurim Formation, Israel. *Geological Survey of Israel Bulletin*, **70**, 1–80.
- Gur, D., Steinitz, G., Kolodny, Y., Starinsky, A. and McWilliams, M. (1995) $^{40}\text{Ar}/^{39}\text{Ar}$ dating of combustion metamorphism (“Mottled Zone”, Israel). *Chemical Geology*, **122**, 171–184.
- Hawthorne, F.C. and Ferguson, R.B. (1975) Refinement of the crystal structure of cryolite. *The Canadian Mineralogist*, **13**, 377–382.
- Holc, J. and Goli, L. (1983) The synthesis and crystal structure of $\alpha\text{-Ca}_3\text{UO}_6$. *Journal of Solid State Chemistry*, **48**, 396–400.
- Knyazev, A.V., Chernorukov, N.G., Dashkina, Z.S., Bulanov, E.N. and Ladenkov, I.V. (2011) Synthesis, structures, physicochemical properties, and crystal-chemical systematics of $\text{M}_2^{\text{II}}\text{A}^{\text{II}}\text{UO}_6$ ($\text{M}^{\text{II}} = \text{Pb, Ba, Sr}$; $\text{A}^{\text{II}} = \text{Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb}$) compounds. *Russian Journal of Inorganic Chemistry*, **56**, 888–898.
- Kolodny, Y. and Gross, S. (1974) Thermal metamorphism by combustion of organic matter: isotopic and petrological evidence. *Journal Geology*, **82**, 489–506.
- Loopstra, B.O. and Rietveld, H.M. (1969) The structure of some alkaline-earth metal uranates. *Acta Crystallographica*, **B25**, 787–791.
- Matthews, A. and Gross, S. (1980) Petrologic evolution of the Mottled Zone (Hatrurim) metamorphic complex of Israel. *Israel Journal of Earth Sciences*, **29**, 93–106.
- Mitchell, R.H. (2002) *Perovskites. Modern and Ancient*. Almaz Press, Thunder Bay, Ontario, Canada, 317 pp.
- Moroni, L.P. and Glasser, E.P. (1995) Reactions between cement components and U(VI) oxide. *Waste Management*, **15**, 243–254.
- Murashko, M.N., Chukanov, N.V., Mukhanova, A.A., Vapnik, E., Britvin, S.N., Krivovichev, S.V., Polekhovsky, Yu.S. and Ivakin, Yu.D. (2010) Barioferrite $\text{BaFe}_{12}^{3+}\text{O}_{19}$ – a new magnetoplumbite-group mineral from Hatrurim Formation, Israel. *Zapiski Rossiyskogo Mineralogicheskogo Obshchestva*, **139**, 22–31 [in Russian].
- Novikov, I., Vapnik, Ye. and Safonova, I. (2013) Mud volcano origin of the Mottled Zone, South Levant. *Geoscience Frontiers*, **4**, 597–619.
- Picard, L. (1931) *Geological research in the Judean Desert*. Goldberg Press, Jerusalem, 108 pp.
- Read, C.M., Bugaris, D.E. and zur Loye, H.-C. (2013) Single crystal growth and structural characterization of four complex uranium oxides: CaUO_4 , $\beta\text{-Ca}_3\text{UO}_6$, $\text{K}_4\text{CaU}_3\text{O}_{12}$, and $\text{K}_4\text{SrU}_3\text{O}_{12}$. *Solid State Sciences*, **17**, 40–45.
- Rouse, R.C. (1971) The crystal chemistry of diabolite. *Zeitschrift für Kristallographie*, **134**, 69–80.
- Sharygin, V.V., Lazic, B., Armbruster, T.M., Murashko, M.N., Wirth, R., Galuskina, I.O., Galuskin, E.V., Vapnik, Ye., Britvin, S.N. and Logvinova, A.M. (2013) Shulamitite $\text{Ca}_3\text{TiFe}^{3+}\text{AlO}_8$ – a new perovskite-related mineral from Hatrurim Basin, Israel. *European Journal of Mineralogy*, **25**, 97–111.
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica A*, **64**, 112–122.
- Sokol, E.V., Novikov, I.S., Vapnik, Ye. and Sharygin, V.V. (2007) Gas fire from mud volcanoes as a trigger for the appearance of high-temperature pyrometamorphic rocks of the Hatrurim Formation (Dead Sea area). *Doklady Earth Sciences*, **413A**, 474–480.
- Sokol, E.V., Novikov, I.S., Zateeva, S.N., Sharygin, V.V. and Vapnik Ye. (2008) Pyrometamorphic rocks of the spurrite–merwinite facies as indicators of hydrocarbon discharge zones (the Hatrurim Formation, Israel). *Doklady Earth Sciences*, **420**, 608–614.
- Sokol, E., Novikov, I., Zateeva, S., Vapnik, Ye.,

VAPNIKITE, A NEW DOUBLE-PEROVSKITE MINERAL FROM ISRAEL

- Shagam, R. and Kozmenko, O. (2010) Combustion metamorphism in the Nabi Musa dome: new implications for a mud volcanic origin of the Mottled Zone, Dead Sea area. *Basin Research*, **22**, 414–438.
- Spencer, L.J. and Mountain, E.D. (1923) New lead-copper minerals from the Mendip Hills (Somerset). *Mineralogical Magazine*, **20**, 67–92.
- Van Duivenboden, H.C. and IJdo, D.J.W. (1986) Redetermination of tricalcium uranate(VI). A Rietveld refinement of neutron powder diffraction data. *Acta Crystallographica*, **C42**, 523–525.
- Vapnik, Ye., Sharygin, V.V., Sokol, E.V. and Shagam R. (2007) Paralavas in a combustion metamorphic complex: Hatrurim Basin, Israel. *Reviews in Engineering Geology*, **18**, 1–21.