

ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT

Vorlanite, (CaU⁶⁺)O₄, from Jabel Harmun, Palestinian Autonomy, Israel†

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ABSTRACT

Vorlanite (CaU⁶⁺)O₄ [*Fm* $\bar{3}$ *m*, *a* = 5.3647(9) Å, *V* = 154.40(4) Å³, *Z* = 2] was found in larnite pyrometamorphic rocks of the Hatrurim formation at the Jabel Harmun locality, Judean Desert, Palestinian Autonomy. Vorlanite crystals from these larnite rocks are dark-gray with greenish hue in transmitted light. This color in transmitted light is in contrast to dark-red vorlanite [*Fm* $\bar{3}$ *m*, *a* = 5.3813(2) Å, *V* = 155.834(10) Å³, *Z* = 2] from the type locality Upper Chegem caldera, Northern Caucasus. Heating above 750 °C of dark-gray vorlanite from the Jabel Harmun, as well as dark-red vorlanite from Caucasus, led to formation of yellow trigonal uranate CaUO₄. The unusual color of vorlanite from Jabel Harmun is assumed to be related to small impurities of tetravalent uranium.

Keywords: Vorlanite, structure, Raman spectroscopy, lakargiite, Hatrurim formation, Jabel Harmun, Judean Desert

INTRODUCTION

Vorlanite, (CaU⁶⁺)O₄, a mineral with radiation-induced disordered structure of the fluorite type, was originally discovered in altered xenoliths within ignimbrites of the Upper Chegem caldera, Vorlan Mountain, Northern Caucasus, Kabardino-Balkaria (Galuskin et al. 2009, 2011).

Vorlanite occurs also as rare accessory mineral in larnite and spurrite pyrometamorphic rocks of the Hatrurim formation. Rocks of the Hatrurim formation are widely distributed in the region of the Dead Sea on the territory of Israel, Palestinian Autonomy, and Jordan (Picard 1931; Kolodny and Gross 1974; Burg et al. 1991, 1999). We detected numerous black platy vorlanite crystals in larnite pyrometamorphic rocks from the Jabel Harmun locality, Judean Desert, Palestinian Autonomy, Israel. The remarkable property of vorlanite from the Jabel Harmun in contrast to Caucasian vorlanite is its dark-gray color with greenish hue in transmitted light (Fig. 1).

Vorlanite, (CaU⁶⁺)O₄, from Caucasus [*Fm* $\bar{3}$ *m*, *a* = 5.3813(2) Å] formed out of the trigonal calcium uranate CaUO₄ (*R* $\bar{3}$ *m*, *a* = 3.878 Å, *b* = 17.564 Å) where α -decay events of uranium caused disordering of Ca and U associated with randomly oriented uranyl-bonds (Galuskin et al. 2012). Vorlanite experienced 0.56 displacements per atom (dpa) during α -decay events (Galuskin

et al. 2011). Caucasian vorlanite is black in hand specimens but dark-red in transmitted light, which is highly surprising for minerals containing hexavalent uranium. In addition, the platy crystals inherited the morphology of “protovorlanite”—a trigonal uranate. Above 750 °C dark-red disordered vorlanite transformed irreversibly to bright-yellow, ordered, trigonal uranate (Galuskin et al. 2012).

Most recently vorlanite was also described as tiny inclusions in uranium-bearing opals from Sierra Pieña Blanca, Mexico (Othmane et al. 2013). It was assumed that these nanocrystals formed under oxidizing conditions below 50 °C. However, this finding requires additional investigations because composition and structure of this unusual mineral may also be interpreted as Ca-rich uraninite. In addition, the nanocrystals did not form by radiation-induced transformation from the trigonal precursor “protovorlanite” CaUO₄ with ordered [UO₂]²⁺ groups (Galuskin et al. 2011, 2012).

In this paper we present results of structure, composition and Raman spectroscopy experiments aiming at recovery of the primary structure of dark-gray vorlanite from the Judean Desert.

METHODS OF INVESTIGATIONS

Crystal morphology and chemical composition of vorlanite and associated minerals were examined using optical microscopes, analytical electron scanning microscope Philips XL30 ESEM/EDAX (Faculty of Earth Sciences, University of Silesia, Poland) and electron microprobe CAMECA SX100 (Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw, Poland). Electron-microprobe analyses of vorlanite were performed at 15 kV and 40–50 nA using the following lines and standards: *UM*β for Caucasian vorlanite, *CaK*α for wollastonite and diopside, and *FeK*α for hematite.

The Raman spectra of vorlanite were recorded using a WITec confocal CRM alpha 300 Raman microscope (Jagiellonian Centre for Experimental Therapeutics, Cracow, Poland) equipped with an air-cooled solid-state laser operating at 488 nm and a CCD detector which was cooled to –82 °C. The laser was coupled to

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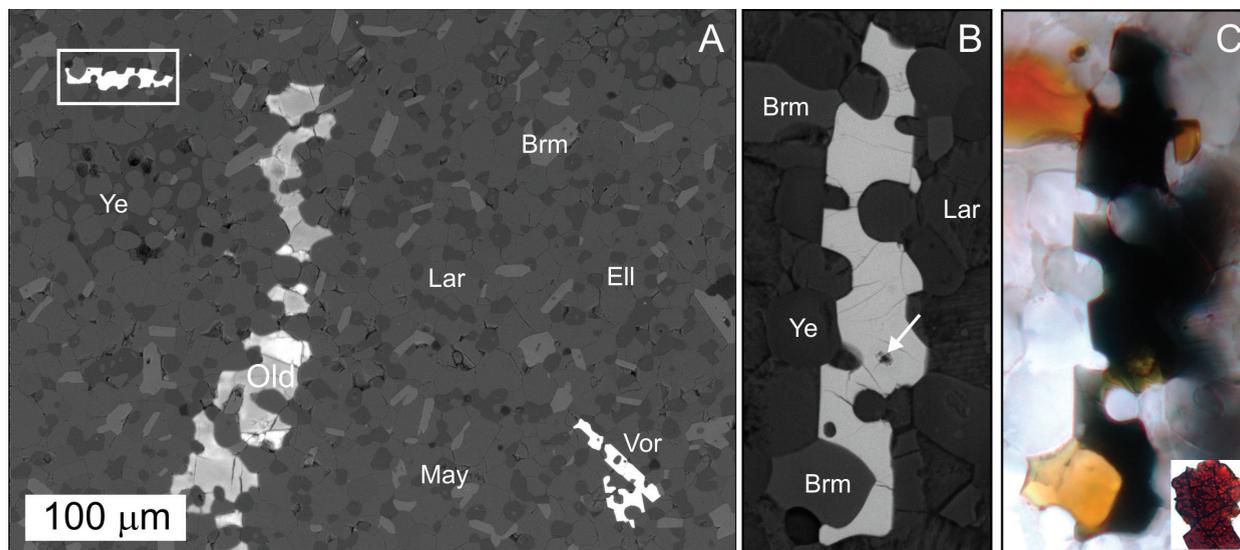


FIGURE 1. (a) Poikilitic crystals of vorlanite in larnite-brownmillerite-ye'elimite-mayenite rock. Magnified crystal in **b** and **c** is framed. Oldhamite, CaS, phosphoresces under the electron beam. Fragments of the second crystal of vorlanite at the bottom on the right of the BSE image were used for single X-ray diffraction study; (**b**, **c**) vorlanite crystal used in Raman spectroscopic experiment: (**b**) BSE image, arrow points to a crater burned by laser, (**c**) transmitted light picture with switched on condenser lens; around the crater vorlanite transformed to yellow rhombohedral uranate; inset at the bottom right: red grain of vorlanite from Caucasus ($30 \times 20 \times 6 \mu\text{m}$), distinguished in color from dark-gray Jabel Harmun vorlanite. Vor = vorlanite, Ye = ye'elimite, Old = oldhamite, Lar = larnite, Ell = fluorellestadite, Brm = brownmillerite.

the microscope via a single-mode optical fiber with a diameter of $50 \mu\text{m}$. A dry Olympus MPLAN (1006/0.90NA) objective was used. The scattered radiation was focused onto a multi-mode fiber ($50 \mu\text{m}$ diameter) and monochromator. The power of the laser at the sample position was 44 mW for measurement and 100–120 mW for heating and crater production. 150 scans with integration times of 0.3–0.5 s and a resolution of 3 cm^{-1} were collected and averaged. The monochromator of spectrometer is calibrated using the Raman scattering line produced by a silicon plate (520.7 cm^{-1}).

Single-crystal X-ray studies of vorlanite from Israel were carried out using a SuperNova Dual diffractometer with a mirror monochromator ($\text{MoK}\alpha_1 = 0.71073 \text{ \AA}$) and Atlas CCD detector (Agilent Technologies) at the Institute of Physics, University of Silesia, Poland. Experimental details are summarized in Table 2. The structure was solved by direct methods, with subsequent analyses of difference-Fourier maps, and refined with neutral atom scattering factors using SHELX97 (Sheldrick 2008).

RESULTS OF INVESTIGATIONS OF DARK-GRAY VORLANITE AND DISCUSSION

Crystals of dark-gray vorlanite were found in dark-brown larnite pebbles hosted in rocks known as pseudoconglomerate. Larnite rocks have been originally formed by pyrogenic metamorphism due to caustobololith combustion at temperatures above $1000 \text{ }^\circ\text{C}$ (Kolodny and Gross 1974; Sokol et al. 2007, 2010). Their pebble-like shape can be explained by low-temperature hydrothermal processes with subsequent weathering of larnite rocks (Gross 1977). Larnite $\beta\text{-Ca}_2\text{SiO}_4$, ye'elimite $\text{Ca}_4\text{Al}_6\text{O}_{12}(\text{SO}_4)$, fluorine analogs of the mayenite-kyuygenite series $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{F}_2\text{-Ca}_{12}\text{Al}_{14}\text{O}_{32}[\text{F}_2(\text{H}_2\text{O})_4]$, fluorellestadite $\text{Ca}_5(\text{SiO}_4)_{1.5}(\text{SO}_4)_{1.5}\text{F}$, ternesite $\text{Ca}_5(\text{SiO}_4)_2(\text{SO}_4)$, brownmillerite $\text{Ca}_2\text{Fe}^{3+}\text{AlO}_5$ -srebrodolskite $\text{Ca}_2\text{Fe}^{3+}\text{Fe}^{3+}\text{O}_5$, and shulamitite $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{3+}\text{AlO}_8\text{-Fe}^{3+}$ -analog of shulamitite $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{3+}\text{Fe}^{3+}\text{O}_8$ are the main minerals of these pebbles. Kyuygenite with the end-member formula $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}[\text{Cl}_2(\text{H}_2\text{O})_4]$ was recently discovered in high-temperature skarns of the Upper Chegem caldera in Caucasus (Galuskin et al. 2013a). Shulamitite detected in pyrometa-

morphic rocks of the Hatrurim Basin, Negev Desert (the Hatrurim formation), was recently approved by IMA-CNMNC (Sharygin et al. 2013). Rare oldhamite CaS, periclase MgO, magnesioferrite MgFe_2O_4 , baryte BaSO_4 , and the recently discovered minerals nabimusaite $\text{KC}_{12}(\text{SiO}_4)_4(\text{SO}_4)_2\text{O}_2\text{F}$ (Galuskin et al. 2013b) and harmunite CaFe_2O_4 (Galuskina et al. 2013) and also unidentified K-sulfides and potentially new minerals Ca_3UO_6 and CaCu_2S_2 are noted. Vorlanite forms typical poikilitic crystals (Fig. 1), related to its crystallization after larnite, mayenite, and ye'elimite.

Composition and structure of dark-gray vorlanite from Jabel Harmun are analogous to composition and structure of dark-red vorlanite from Caucasus (Tables 1–4; Galuskin et al. 2011). The chemical composition of vorlanite corresponds to stoichiometric CaUO_4 . Site occupancies determined by single-crystal X-ray diffraction data are consistent with a fully occupied O site, with a Ca/U ratio = 1 confirming that practically all uranium has valence 6+ (Table 3). This conclusion was proven for vorlanite from Caucasus by XPS investigations (Galuskin et al. 2011).

Raman spectra of dark-red vorlanite from Caucasus and dark-gray vorlanite from Israel are similar, the one strong broad band centered near 683 cm^{-1} is present in both spectra (Fig. 2, spectra 1 and 2). A Raman spectroscopic local heating experiment on dark-gray vorlanite from Jabel Harmun with a blue laser (488 nm) above $750 \text{ }^\circ\text{C}$ produced in close vicinity to the crater trigonal uranate CaUO_4 . This newly produced phase is indicated by appearance of a yellow ring around the crater (Fig. 1c). Heating of vorlanite from both localities above $750 \text{ }^\circ\text{C}$ led to the same result—ordered trigonal calcium uranate forms after vorlanite. The Raman spectra of the heat produced phases correspond exactly to the Raman spectrum of the known synthetic phase (Liegeois-Duyckaerts 1977; Fig. 2, spectra 1* and 2*).

The accepted structural model for vorlanite suggests that U

TABLE 1. Chemical composition of vorlanite from Jabel Harmun locality

wt%	mean 13	S.D.	Range
UO ₃	83.79	0.37	83.17–84.40
CaO	16.77	0.04	16.68–16.81
Fe ₂ O ₃	0.04	0.04	0–0.14
Total	100.56		
Calculated on two cations			
U ⁶⁺	0.989		
Ca	1.009		
Fe ³⁺	0.002		

TABLE 2. Data collection and structure refinement details for vorlanite

Temperature	296(2) K
Theta range for data collection	6.59 for 41.48°
Index ranges	−10 ≤ h ≤ 9, −9 ≤ k ≤ 9, −10 ≤ l ≤ 9
Reflections collected	1631
Independent reflections	46 (R _{int} = 0.0575; R _σ = 0.0114)
Crystal size	0.008 × 0.010 × 0.020 mm
Crystal system	cubic
Space group	Fm $\bar{3}$ m
Unit-cell dimensions	a = 5.3647(9) Å, α = 90°
V	154.40(4) Å ³
Z	2
D _{calc}	7.359 g/cm ³
Goodness-of-fit on F ²	1.212
Final R indices	46 data; I > 4σ(I), R1 = 0.0088 all data R1 = 0.0088, wR2 = 0.0174
Largest diff. peak and hole	0.260 and −0.358 eÅ ^{−3}

TABLE 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for vorlanite

Atom	x/a	y/b	z/c	sof	U _{eq}
U	0	0.5	0	0.5	0.01848(9)
Ca	0	0.5	0	0.5	0.01848(9)
O	0.25	0.25	0.25	1	0.0614(15)

Note: Isotropic displacement parameters for all sites because $U_{11} = U_{22} = U_{33}$ and $U_{12} = U_{13} = U_{23} = 0$.

TABLE 4. Bond lengths (Å) and angles (°) for vorlanite

Atoms	Bond length (Å)	mult.
U1/Ca1-O1	2.3230(4)	×8
U1/Ca1-U1/Ca1	3.7934(6)	×4
Angle (°)		
O1-U1/Ca1-O1	180.0	×4
O1-U1/Ca1-O1	109.47	×12
O1-U1/Ca1-O1	70.53	×12

and Ca randomly occupy a single eightfold-coordinated site with mean metal (M) to oxygen (O) distances M-O of 8×2.33 Å. However, Raman investigations on vorlanite indicate that there are also short U-O bonds <2 Å characteristic of the uranyl group (UO₂)²⁺ (Galuskin et al. 2011), i.e., the true local U-coordination is 6+2. It was assumed that in the real structure of vorlanite not only the positions of the cations Ca and U are disordered over a single site, but there is also “uranyl disorder,” i.e., O-U-O uranyl bonds are randomly aligned parallel to one of the four symmetry-equivalent cube diagonals (Galuskin et al. 2011).

A basic difference between vorlanite from Jabel Harmun and Caucasian vorlanite is the dark-gray color with greenish hue in transmitted light of the former vorlanite. This color could indicate that not all uranium is hexavalent. Color change of synthetic trigonal uranate CaUO₄ from yellow to dark-green was observed on heating above 1100 °C, when the disordered phase with fluorite-type structure formed and the composition corresponded to CaU₂O_{5+y} (Terra et al. 2007). Tagawa et al. (1997) synthesized nonstoichiometric dark green or dark gray uranate SrUO_{3.18–3.20}

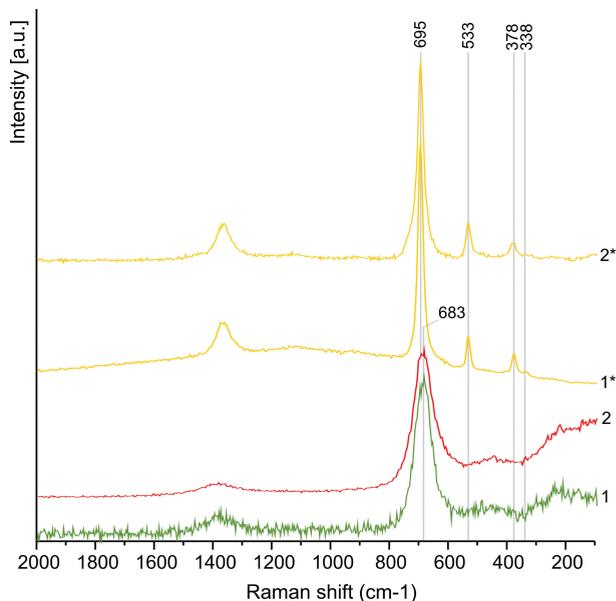


FIGURE 2. Raman spectra of vorlanite: 1 = Jabel Harmun locality; 2 = Caucasian type locality; and 1*, 2* = products of its thermal transformation, respectively.

at 1000 °C in hydrogen atmosphere. The color of these uranates changed to red when exposed to air after three months and the corresponding X-ray diffraction pattern indicated that structure and cell parameters of the red phase were in agreement with rhombohedral α-SrUO₄.

Tetravalent uranium may substitute in vorlanite according to the known isomorphous scheme for uraninite: CaU⁶⁺ → 2U⁴⁺ (Janeczek and Ewing 1992). In addition, precursor of vorlanite corresponds to the O-deficient synthetic phase CaUO_{4-x} with x < 0.5, in which uranium can be tetra- or pentavalent and corresponding cell parameters are greater than those of stoichiometric CaUO₄ (Loopstra and Rietveld 1969; Prodan and Boswell 1986; Takahashi et al. 1993). However, presence of significant oxygen vacancies in vorlanite can be excluded based on site occupation refinements performed by us. Test refinements (not shown) converged at an O population of 0.98(4). Thus, in subsequent refinements the value was fixed at 1 (Tables 2–4). If the structures of trigonal uranate and vorlanite are compared, it becomes obvious that disordered cubic vorlanite has a larger volume 77.92 Å³ (half unit-cell volume for comparison with the trigonal uranate) and a lower density 7.29 g/cm³ compared to the ordered uranate: V = 76.26 Å³ and ρ = 7.45 g/cm³ of the same composition (Galuskin et al. 2011). The cell parameter and the unit volume V = 2 × 77.20(2) Å³ of dark-gray vorlanite from Jabel Harmun are significantly lower (increased density of 7.36 g/cm³) than those of Caucasian vorlanite.

A systematic survey of the color of vorlanite from different rocks of the Hatrurin formation from the Jabel Harmun (the Judean Desert) and the Hatrurim Basin (the Negev Desert) showed that in larnite and spurrite rock all vorlanite crystals are dark-gray in transmitted light (Figs. 3a and 3b). In larnite rocks vorlanite is usually present as individual crystals (Fig. 1a). In spurrite rocks micrometer-sized vorlanite crystals form spot-like

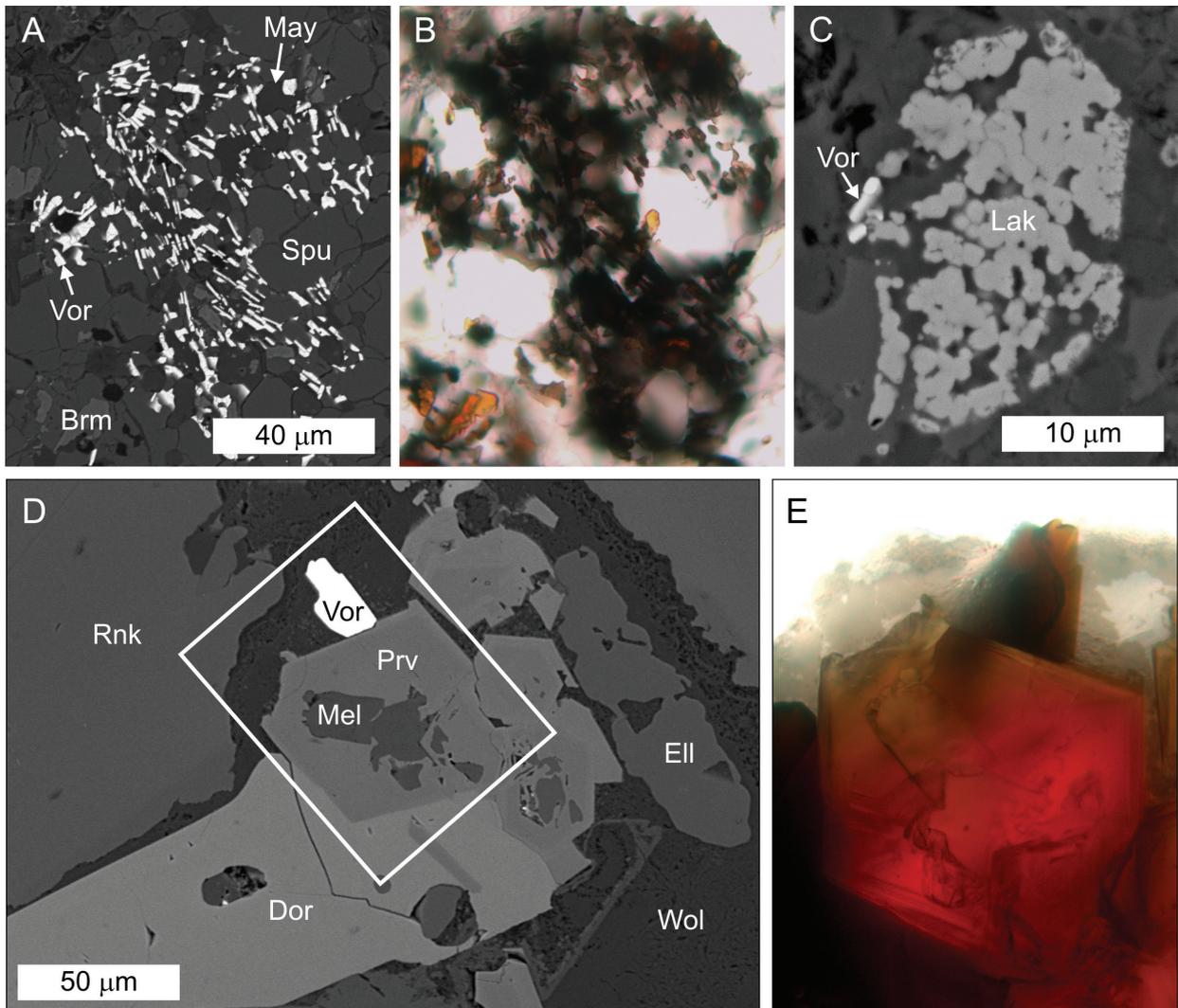


FIGURE 3. (a, b) vorlanite in spurrite rock (a = BSE, b = transmitted light with switched on condenser lens); (c) vorlanite crystals on U-bearing lakargiite pseudomorphs after zircon; (d) crystal of red-brown vorlanite overgrowing perovskite, sample from paralava of the Gurim anticline, the Hatrurim Basin, the Negev Desert. (a) BSE, framed area is magnified in e; (e) transmitted light with switched on condenser lens. Vor = vorlanite, Rnk = rankinite, Wol = wollastonite, Mel = melilite, Prv = perovskite, Eil = fluorellistadite-fluorapatite series, Dor = Fe^{3+} -analog of dorrte.

aggregates (Figs. 3a and 3b) often overgrowing pseudomorphs of uranium-bearing lakargiite after zircon (Fig. 3c). Lakargiite with UO_3 content up to 20 wt% was detected in rocks of the Hatrurim formation for the first time. Lakargiite CaZrO_3 , first discovered in altered xenoliths of the Upper Chegem caldera, was also associated with vorlanite (Galuskin et al. 2008, 2009, 2011).

In only one case, in small veins of paralavas of the Gurim anticline (the Negev Desert) rare vorlanite crystals were found (Fig. 3), which appear red-brown in transmitted light. The main minerals of Gurim paralavas are coarse-grained schorlomite, rankinite, melilite, parawollastonite, kalsilite, fluorapatite-fluorellistadite, Fe^{3+} -analog of dorrte, barioferrite, and ferric spinel represented by the solid solution magnesioferrite-trevorite-franklinite-cuprospinel. Divalent iron is essentially absent in the composition of ferrites and garnets of paralavas indicating strongly oxidizing conditions. The presence of dorrte-like miner-

als and also previous investigations of melt inclusions suggest that these paralavas formed above 1100–1200 °C (Sharygin et al. 2006a, 2006b).

Temperature and pressure, at which “protovorlanite” formed in the different pyrometamorphic rocks, were similar and correspond to conditions of the sanidinite facies. “Protovorlanite,” an orthorhombic uranate CaUO_4 , is stable below 1100 °C (Pialoux and Touzelin 1998). In small xenoliths of the Caucasus rocks and paralava bodies of the Gurim anticline “protovorlanite” formed in open systems characterized by high oxygen fugacity, i.e., all uranium was hexavalent 6+. In pyrometamorphic rocks of the Hatrurim formation, characterized by a dense fine-grained lanite and spurrite matrix, crystallization of “protovorlanite” proceeded under the conditions of limited oxygen fugacity, i.e., U^{4+} may enter the structure of “protovorlanite.” In the course of polymorphic transformation “protovorlanite–vorlanite” as a

result of radioactive decay, vorlanite inherited insignificant U⁴⁺, which may be responsible for its dark-gray color with greenish hue in transmitted light.

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REFERENCES CITED

- 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, 225–234.
- Burg, A., Kolodny, Y., and Lyakhovskiy, V. (1999) Hatrurim-2000: The "Mottled Zone" revisited, forty years later. *Israel Journal of Earth Sciences*, 48, 209–223.
- Galuskin, E.V., Gazeev, V.M., Armbruster, T., Zadov, A.E., Galuskina, I.O., Pertsev, N.N., Dzierzanowski, P., Kadiyski, M., Gurbanov, A.G., Wrzalik, R., and Winiarski, A. (2008) Lakargiite, CaZrO₃: A new mineral of the perovskite group from the North Caucasus, Kabardino-Balkaria, Russia. *American Mineralogist*, 93, 1903–1910.
- Galuskin, E.V., Gazeev, V.M., Lazic, B., Armbruster, T., Galuskina, I.O., Zadov, A.E., Pertsev, N.N., Wrzalik, R., Dzierzanowski, P., Gurbanov, A.G., and Bzowska, G. (2009) Chegemite, Ca₇(SiO₄)₃(OH)₂—A new calcium mineral of the humite-group from the Northern Caucasus, Kabardino-Balkaria, Russia. *European Journal of Mineralogy*, 21, 1045–1059.
- Galuskin, E.V., Armbruster, T., Galuskina, I.O., Lazic, B., Winiarski, A., Gazeev, V.M., Dzierzanowski, P., Zadov, A.E., Pertsev, N.N., Wrzalik, R., Gurbanov, A.G., and Janeczek, J. (2011) Vorlanite (CaU⁶⁺)O₄: 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 CaUO₄. *American Mineralogist*, 97, 1002–1004.
- Galuskin, E.V., Galuskina, I.O., Kusz, J., Armbruster, T., Bailau, R., Dulski, M., Gazeev, V.M., Pertsev, N.N., Zadov, A.E., and Dzierzanowski, P. (2013a) Kyuygenite, IMA 2012-046. *CNMNC Newsletter No. 15*, February 2013, p. 2; *Mineralogical Magazine*, 77, 1–12.
- Galuskin, E.V., Gfeller, F., Armbruster, T., Galuskina, I.O., Vapnik, Y., Murashko, M., Wlodyka, R., and Dzierzanowski, P. (2013b) Nabimusite, IMA 2012-057. *CNMNC Newsletter No. 15*, February 2013, p. 5; *Mineralogical Magazine*, 77, 1–12.
- Galuskina, I.O., Vapnik, Ye., Lazic, B., Armbruster, T., Murashko, M., and Galuskin, E.V. (2013) Harmunite, IMA2011-112. *CNMNC Newsletter No. 15*, February 2013, page 2; *Mineralogical Magazine*, 77, 1–12.
- Gross, S. (1977) The mineralogy of the Hatrurim Formation, Israel. *Geological Survey of Israel Bulletin*, 70, 1–80.
- Janeczek, J., and Ewing, R.C. (1992) Structural formula of uraninite. *Journal of Nuclear Materials*, 190, 128–132.
- Kolodny, Y., and Gross, S. (1974) Thermal metamorphism by combustion of organic matter: Isotopic and petrological evidence. *Journal of Geology*, 82, 489–506.
- Liegeois-Duyckaerts, M. (1977) Infrared and Raman spectrum of CaUO₄: New data and interpretation. *Spectrochimica Acta Part A; Molecular Spectroscopy*, 6–7, 709–713.
- Loopstra, B.O., and Rietveld, H.M. (1969) The structure of some alkaline-earth metal uranates. *Acta Crystallographica*, B25, 787–791.
- Othmane, G., Allard, T., Menguy, N., Morin, G., Esteve, I., Fayek, M., and Calas, G. (2013) Evidence for nanocrystals of vorlanite, a rare uranate mineral, in the Nopal I low-temperature uranium deposit (Sierra Peña Blanca, Mexico). *American Mineralogist*, 98, 518–521.
- Pialoux, A., and Touzelin, B. (1998) Étude du système U–Ca–O par diffractométrie de rayons X à haute température. *Journal of Nuclear Materials*, 255, 14–25.
- Picard, L. (1931) *Geological Research in the Judean Desert*, 108 p. Goldberg Press, Jerusalem.
- Prodan, A., and Boswell, F.W. (1986) The defect structure of reduced CaUO₄. *Acta Crystallographica*, B42, 141–146.
- Sharygin, V.V., Vapnik, Ye., Sokol, E.V., Kamenetsky, V.S., and Shagam, R. (2006a) Melt inclusions in minerals of schorlomite-rich veins of the Hatrurim Basin, Israel: Composition and homogenization temperatures. In N. Pei and L. Zhao, Eds., *ACROFI I, Program with Abstracts*, pp. 189–192. Nanjing, China, 26–28 May 2006.
- Sharygin, V.V., Vapnik, Ye., Sokol, E.V., and Shagam, R. (2006b) Kalsilite-schorlomite-melilite rocks of Hatrurim Formation—Products of pyrogenic alkaline melt crystallization: data on mineralogy and melt inclusions. Abstracts of All Russian seminar "Geochemistry of magmatic rocks" [school "Alkaline magmatism of Earth"], <http://geo.web.ru/conf/alkaline/2006/index22.html> (in Russian).
- 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 Ca₃TiFe³⁺AlO₈—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*, A64, 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 (in Russian).
- Sokol, E., Novikov, I., Zateeva, S., Vapnik, Ye., 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.
- Tagawa, H., Fujino, T., and Tateno, J. (1997) Formation of strontium uranates. *Bulletin Chemical Society of Japan*, 50, 2940–2944.
- Takahashi, K., Fujino, T., and Morsse, L.R. (1993) Crystal chemical and thermodynamic study on CaUO_{4-x}, (Ca_{0.5}Sr_{0.5})UO_{4-x}, and α-SrUO_{4-x} (x = 0 ~ 0.5). *Journal of Solid State Chemistry*, 105, 234–246.
- Terra, O., Audubert, F., Dacheux, N., Guy, C., and Podor, R. (2007) Synthesis and characterization of uranium-bearing britholites. *Journal Nuclear Materials*, 366, 70–86.

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