Revision 1

Vorlanite, $(CaU^{6+})O_4$, from Jabel Harmun, Palestinian Autonomy, Israel

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ABSTRACT

Vorlanite ($CaU^{6+})O_4$ ($Fm\bar{3}m$, a = 5.3647(9) Å, V = 154.40(4) Å^3, Z = 2) was found in larnite pyrometamorphic rocks of the Hatrurim formation at the Jabel Harmun locality, Judean Desert, Palestinian Autonomy. Black vorlanite crystals from these larnite rocks are dark-grey 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)Å^3, Z = 2) from the type locality Upper Chegem caldera, Northern Caucasus. Heating above 750°C of dark-grey vorlanite from the Jabel Harmun, as well as dark-red vorlanite from Caucasus, led to formation of yellow trigonal uranate $CaUO_4$. 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, $(CaU^{6+})O_4$, 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-grey color with greenish hue in transmitted light (Fig. 1).

Vorlanite, $(CaU^{6+})O_4$, from Caucasus ($Fm\bar{3}m$, a = 5.3813(2) Å) formed out of the trigonal calcium uranate $CaUO_4$ ($R\bar{3}m$, 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” $CaUO_4$ with ordered $[UO_2]^{2+}$ 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-grey 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: U*M*β for Caucasian vorlanite, Ca*K*α for wollastonite and diopside; Fe*K*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 -82ºC. The laser was coupled to the microscope via a single-mode optical fibre with a diameter of 50 µm. A dry Olympus MPLAN (1006/0.90NA) objective was used. The scattered radiation was focused onto a multi-mode fibre (50 µm 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 (Mo*K*αl = 0.71073 Å) 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-GREY VORLANITE AND DISCUSSION

Crystals of dark-grey vorlanite were found in dark-brown larnite pebbles hosted in rock known as pseudoconglomerate. Larnite rocks have been originally formed by pyrogenic metamorphism due to caustobiolith combustion at temperatures above 1000°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 β-Ca_2SiO_4, ye'elimite $Ca_4Al_6O_{12}(SO_4)$, fluorine analogs of the mayenite-kyuygenite series $Ca_{12}Al_{14}O_{32}F_2$–$Ca_{12}Al_{14}O_{32}[F_2(H_2O)_4]$, fluorellestadite $Ca_5(SiO_4)_{1.5}(SO_4)_{1.5}F$, ternesite $Ca_5(SiO_4)_2(SO_4)$, brownmillerite $Ca_2Fe^{3+}AlO_5$–srebrodolskite $Ca_2Fe^{3+}Fe^{3+}O_5$, shulamitite $Ca_3Ti^{4+}Fe^{3+}AlO_8$–Fe^{3+}-analog of shulamitite $Ca_3Ti^{4+}Fe^{3+}Fe^{3+}O_8$ are the main minerals of these pebbles. Kyuygenite with the end-member formula $Ca_{12}Al_{14}O_{32}[Cl_2(H_2O)_4]$ was recently discovered in high-temperature skarns of the Upper Chegem caldera in Caucasus (Galuskin et al. 2013a). Shulamitite detected in pyrometamorphic 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 $KCa_{12}(SiO_4)_4(SO_4)_2O_2F$ (Galuskin et al. 2013b) and harmunite $CaFe_2O_4$ (Galuskina et al. 2013) and also undiagnosed 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-grey vorlanite from Jabel Harmun are analogous to composition and structure of dark-red vorlanite from Caucasus (Table 1-4, Galuskin et al. 2011). The chemical composition of vorlanite corresponds to stoichiometric $CaUO_4$. Site occupancies determined by using 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-grey 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-grey vorlanite from Jabel Harmun with a blue laser (488 nm) above 750°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°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 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 < 2Å characteristic of the uranyl group $(UO_2)^{2+}$ (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-grey 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 $CaUO_4$ 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 CaU_2O_{5+y} (Terra et al. 2008). Takagawa et al. (1977) synthesized nonstoichiometric dark green or dark grey uranate $SrUO_{3.18-3.20}$

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-$SrUO_4$.

Tetravalent uranium may substitute in vorlanite according to the known isomorphic scheme for uraninite: $CaU^{6+} \rightarrow 2U^{4+}$ (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 $CaUO_4$ (Loopstra and Rietveld 1969; Prodan and Boswell 1986; Takachashi 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 larger volume 77.92 Å^3 (half unit cell volume for comparison with the trigonal uranate) and lower density 7.29 g/cm^3 compared to the ordered uranate: $V = 76.26$ Å^3 and $\rho = 7.45$ g/cm^3 of same composition (Galuskin et al. 2011). The cell parameter and the unit volume $V = 2 \times 77.20(2)$ Å^3 of dark-grey vorlanite from Jabel Harmun are significantly lower (increased density of 7.36 g/cm^3) than those of Caucasian vorlanite.

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 (Fig. 3A, B). In larnite rocks vorlanite is usually presented by individual crystals (Fig. 1A). In spurrite rocks micron-sized vorlanite crystals form spot-like aggregates (Fig. 3A, B) 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-fluorellestadite, Fe^{3+}- analog of dorrite, 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 dorrite-like minerals and also previous investigations of melt inclusions suggest that these paralavas formed above 1100-1200°C (Sharygin et al. 2006a, b).

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 larnite 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 U^{4+}, which may be responsible for its dark-gray color with greenish hue in transmitted light.

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Figures

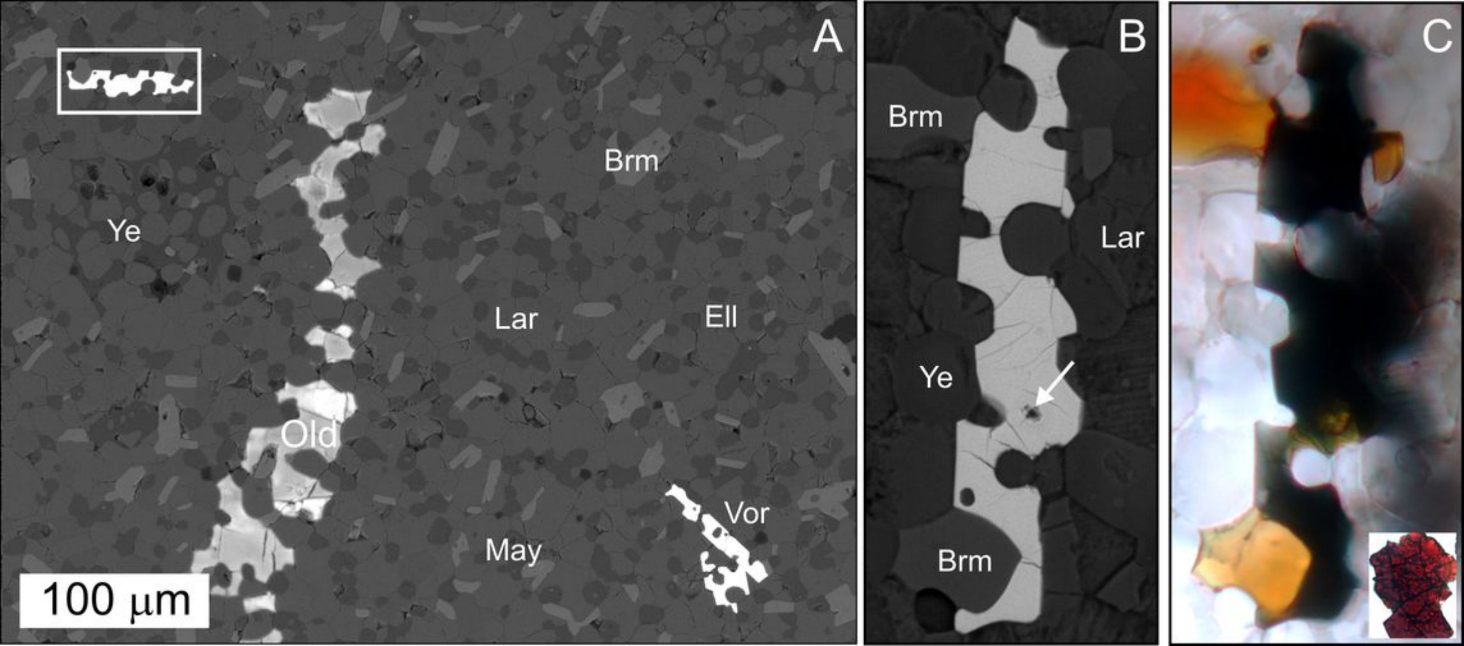
Fig. 1. A – Poikilitic crystals of vorlanite in larnite-brownmillerite-ye'elimite-mayenite rock. Magnified crystal in Fig. 1B and C is framed. Oldhamite, CaS, phosphoresces under the electron beam. Fragments of the second crystal of vorlanite at the bottom on the right of the BSE image were used for 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 (30×20×6 μm), distinguished in color from dark-grey Jabel Harmun vorlanite.

Vor -vorlanite, Ye - ye'elimite, Old - oldhamite, Lar - larnite, Ell - fluorellestadite, Brm - brownmillerite.

Fig. 2. Raman spectra of vorlanite: 1 – Jabel Harmun locality, 2 – Caucasus type locality and 1*, 2* - products of its thermal transformation, respectively.

Fig. 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 Fig. 3E; E – transmitted light with switched on condenser lens.

Vor - vorlanite, Rnk - rankinite, Wol - wollastonite, Mel - melilite, Prv - perovskite, Ell - fluorellestadite-fluorapatite series, Dor - Fe^{3+}-analog of dorrite.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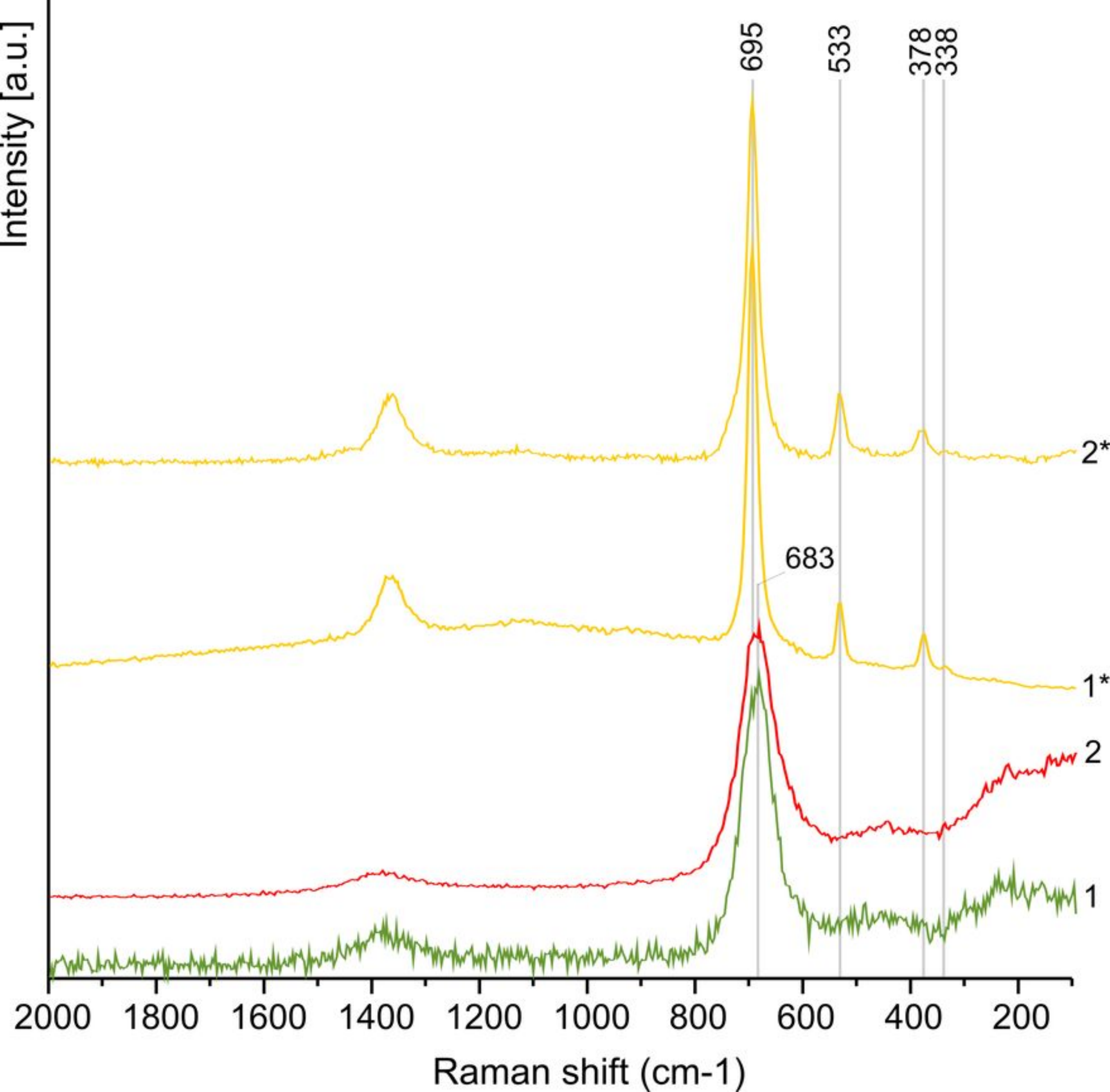

Intensity [a.u.]
695
533
378
338
683
2*
1*
2
1
2000
1800
1600
1400
1200
1000
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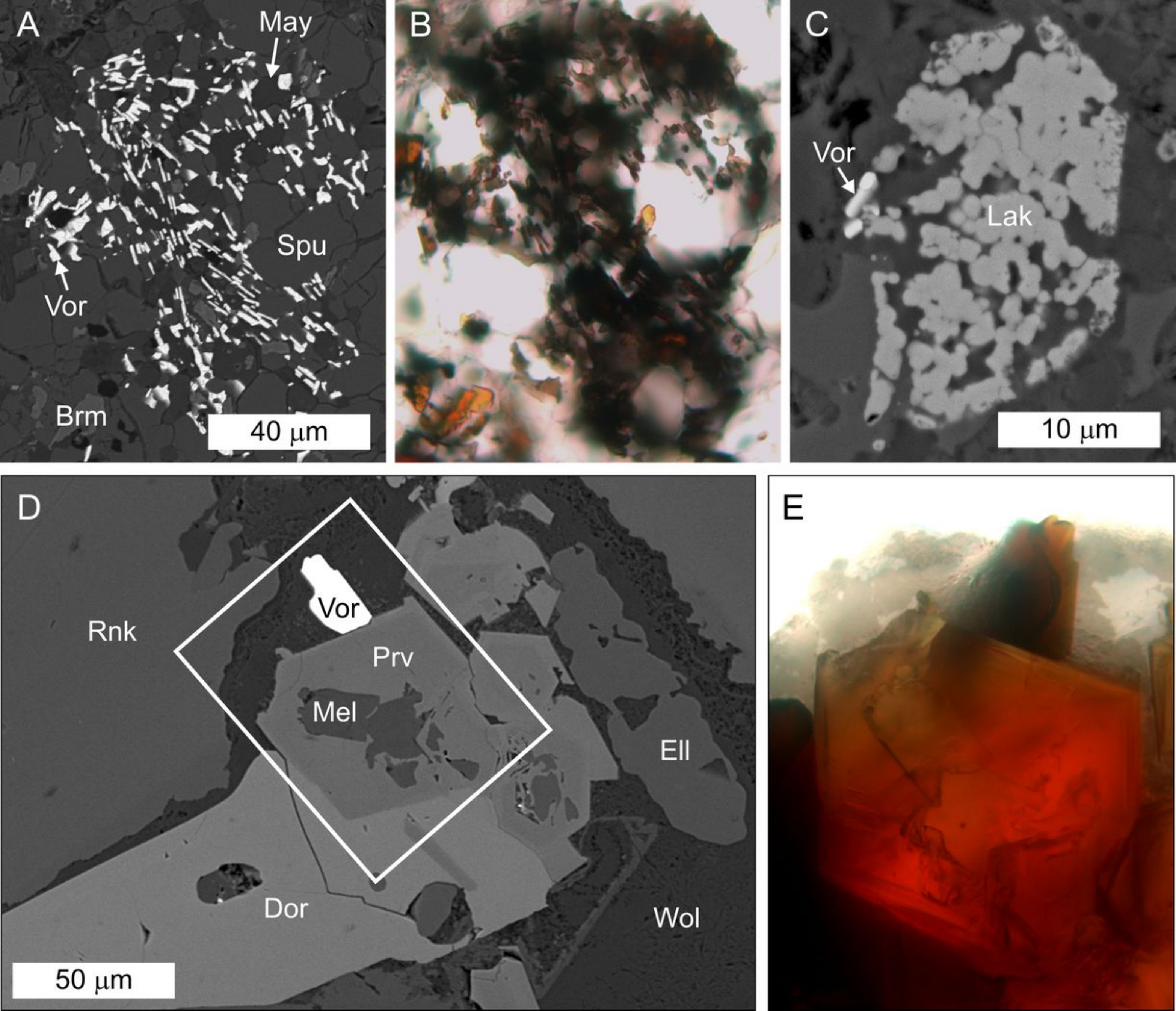
400
200
Raman shift (cm-1)



A
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40 μm
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D
Vor
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Prv
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Dor
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50 μm
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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_2O_3	0.04	0.04	0-0.14
Total	100.56		
calculated on 2 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	$-10 \leq h \leq 9$, $-9 \leq k \leq 9$, $-10 \leq l \leq 9$
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; $I > 4\sigma(I)$, $R1$ = 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 (Å^2) 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)

isotropic displacement parameters for all sites because $U11=U22=U33$ and $U12=U13=U23= 0$

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

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