

LETTER: ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT†

Thermally induced transformation of vorlanite to “protovorlanite”: Restoration of cation ordering in self-irradiated CaUO₄

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ABSTRACT

Vorlanite, cubic CaUO₄ heated at temperatures above 750 °C, transforms irreversibly into rhombohedral CaUO₄, proving that the latter crystallized as a precursor of vorlanite in high-temperature skarns. Vorlanite most probably originated due to pseudomorphic transformation of rhombohedral CaUO₄, caused by disordering of cations and uranyl-bonds that resulted from α -decay events of uranium. The ease of the transition from rhombohedral CaUO₄ to vorlanite and the fast reversal transition during heating can be explained by the similarity of both structures. Formation of vorlanite prevents CaUO₄ from undergoing metamictization.

Keywords: Vorlanite, rhombohedral CaUO₄, radiation damage, phase transformation, Raman spectroscopy

INTRODUCTION

The recently described, new mineral vorlanite, CaUO₄ [fluorite-type structure, $Fm\bar{3}m$, $a = 5.3813(2)$ Å], is unique among U⁶⁺ minerals, being isostructural with uraninite (Galuskin et al. 2011). The chemical composition of vorlanite is identical with that of synthetic rhombohedral calcium uranate, CaUO₄ [$R\bar{3}m$, $a = 6.2683$ Å, $\alpha = 36.04^\circ$] (Loopstra and Rietveld 1969). However, while in the ordered structure of rhombohedral CaUO₄, U⁶⁺ and Ca²⁺ occupy two different distorted eightfold-coordinated sites, in vorlanite both cations randomly occupy a single site, eightfold-coordinated by equidistant O²⁻ (see Fig. 6 in Galuskin et al. 2011). The X-ray refinement of vorlanite structure gives the average distance (U,Ca)-O = 2.33 Å, whereas the Raman spectra reveal the existence of disordered uranyl bonds (O-U-O = 2×1.98 Å) not evident in the average structure and demonstrate thereby an important similarity of vorlanite to rhombohedral CaUO₄ with ordered uranyl bonds (O-U-O = 2×1.96 Å) (Loopstra and Rietveld 1969; Galuskin et al. 2011).

In hand specimens, vorlanite resembles hematite. Its black (dark red in thin section), platy crystals reveal $\bar{3}m$ symmetry, in contrast with the space group symmetry, $Fm\bar{3}m$. The discrepancy between the external crystal symmetry of vorlanite and the cubic symmetry of its structure prompted Galuskin et al. (2011) to suggest that vorlanite originated due to pseudomorphic replace-

ment of originally rhombohedral CaUO₄ (“protovorlanite”). To test this hypothesis, we heated a suite of vorlanite crystals in a furnace and by laser, and inspected them with optical microscopes, Raman spectrometer Dilor XY (excitation Ar⁺ laser, $\lambda = 514.5$ nm, spectral resolution 2 cm⁻¹), and high-brilliance X-ray powder diffractometer Rigaku (MoK α radiation, APEX CCD detector) at the Bavarian Geoinstitut. Analysis by SEM/EDS was performed using an environmental analytical scanning electron microscope Philips XL30 at the Faculty of Earth Sciences (University of Silesia).

EXPERIMENTAL RESULTS

A single crystal of vorlanite ($75 \times 50 \times 10$ μm) was heated by an Ar⁺ laser (power 1.2 W) for 30 s. Temperature in the laser ablation crater exceeded 1400 °C, as inferred from melting of adjacent quartz glass, simultaneously heated by the same laser beam (Fig. 1a). After heating, vorlanite changed color from dark red to honey yellow. The Raman spectrum collected from the outer portion of the vorlanite crystal 5 min after heating corresponds to that from rhombohedral CaUO₄ (Fig. 2, spectrum 6). The X-ray diffraction pattern of heated vorlanite corresponds to that from a polycrystalline aggregate of rhombohedral CaUO₄.

In another experiment, different grains of vorlanite were annealed in a thermostatically controlled furnace for 10 min each at 500, 700, 750, 800, and 1000 °C in air. After heating, each grain was examined by Raman spectroscopy. Below 750 °C, vorlanite remained black and preserved a semi-metallic luster, and its Raman spectrum (Fig. 2, spectrum 2) was identical with the untreated sample (Fig. 2, spectrum 1, and Galuskin et al. 2011). After heating two crystals of different size ($120 \times 100 \times 15$ and $55 \times 40 \times 7$ μm) at 750 °C, additional weak bands at 533, 378, and 338 cm⁻¹ appeared in the Raman spectrum of the smallest crystal, together with a shift of the major vorlanite band from 683 to 690 cm⁻¹ (Fig. 2, spectrum 3b). The appearance of the three new bands and shift of the main band are indicative of rhombohedral CaUO₄. The Raman spectrum of synthetic rhombohedral CaUO₄ is distinct from that of vorlanite with two strong bands, at 696 and 534 cm⁻¹, and two medium bands, at 379 and 340 cm⁻¹ (Liegeois-Duyckaerts 1977; Allen and Griffiths 1979). No shift of the major vorlanite band at 683 cm⁻¹ occurred, and bands at 534, 379, and 340 cm⁻¹ were absent in the spectrum of largest crystal (Fig. 2, spectrum 3a). Both crystals, however, changed their color: the largest one, from black to dark yellow; the smallest, one from black to pale yellow. After heating at 800 and 1000 °C, the dark-red vorlanite crystals of different sizes turned into honey-yellow phases with strong adamantine luster (Fig. 3). The crystals preserved their original

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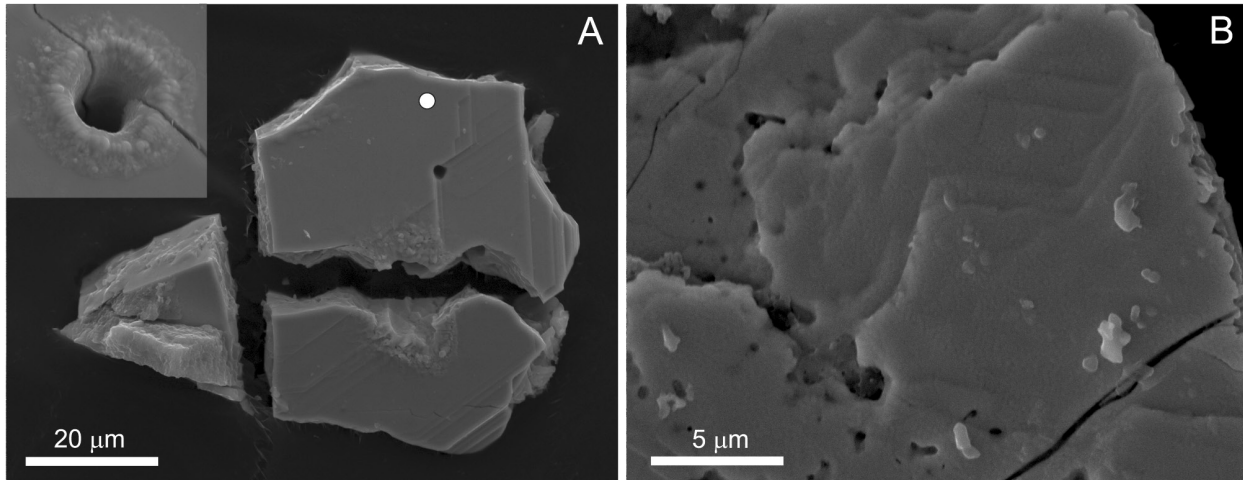


FIGURE 1. (a) SEM image of a vorlanite single crystal, thermally transformed (heated by Ar^+ laser, ablation crater is in the center of crystal) into rhombohedral CaUO_4 (the crystal was broken into three pieces after μXRD studies). The laser beam ablation crater $5\ \mu\text{m}$ across is shown in the inset. The Raman spectrum was collected from a spot marked by a white dot. (b) SEM image of vorlanite crystal surface microtopography after heating at $1000\ \text{°C}$ for 10 min.

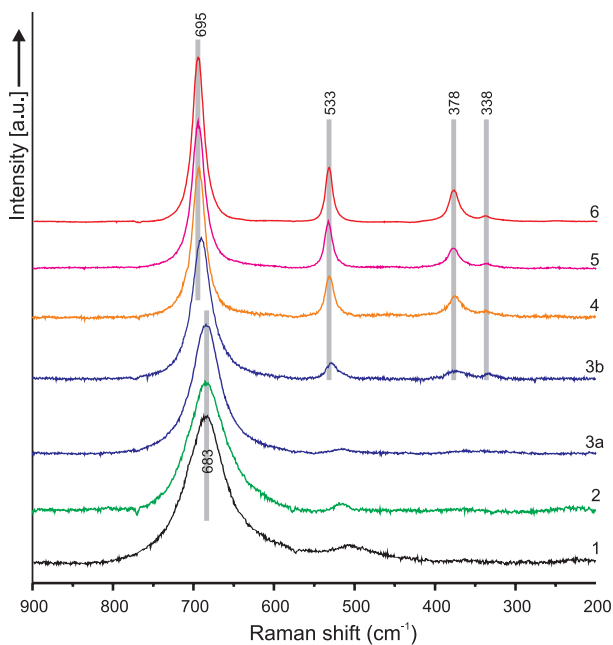


FIGURE 2. Raman spectra of vorlanite as a function of temperature. Line 1 = unheated vorlanite. Line 2 = vorlanite heated at $500\ \text{°C}$. Lines 3a and 3b = spectra of vorlanite heated at $750\ \text{°C}$. Line 3a = Crystal of the size $120 \times 100 \times 15\ \mu\text{m}$. Line 3b = Crystal of the size $55 \times 40 \times 7\ \mu\text{m}$. Line 4 = vorlanite heated at $800\ \text{°C}$. Line 5 = vorlanite heated at $1000\ \text{°C}$. Line 6 = vorlanite heated by green laser above $1000\ \text{°C}$.

morphologies. Only subtle blurring of primary growth layers was observed (Fig. 1B). Both Raman spectra (Fig. 2, spectra 4 and 5) and X-ray microdiffraction (μXRD) patterns (Fig. 3) correspond to those of rhombohedral CaUO_4 .

DISCUSSION

Vorlanite crystals undergo a phase transition above $750\ \text{°C}$ and transform irreversibly into a rhombohedral phase. This observation confirms our earlier suggestion (Galuskin et al.

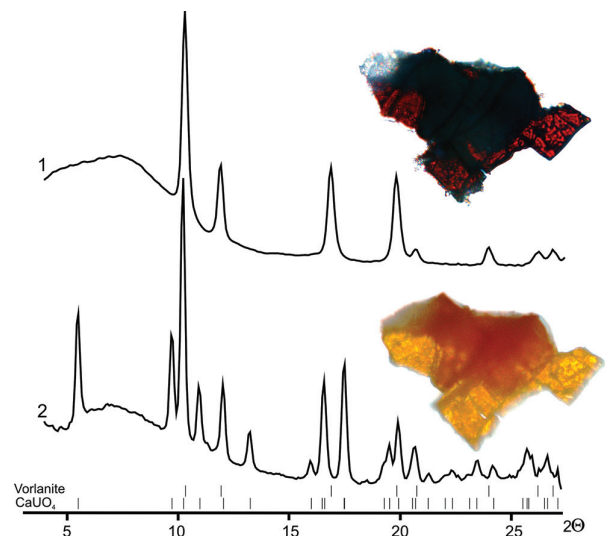


FIGURE 3. X-ray diffraction patterns of vorlanite (crystal size $80 \times 60 \times 10\ \mu\text{m}$) before (line 1) and after (line 2) heating for 10 min at $1000\ \text{°C}$. Note the change in color of vorlanite seen under the optical microscope (plane polarizers) from dark red in untreated sample to yellow after heating.

2011) that the rhombohedral CaUO_4 is a high-temperature precursor of vorlanite. Rhombohedral CaUO_4 is stable up to $1100\ \text{°C}$ (Pialoux and Touzelin 1998). The vorlanite-bearing skarn xenoliths formed between 800 and $1000\ \text{°C}$ for $P < 1\text{--}2$ kbar (Iarnite-mervinite facies; Zharikov et al. 1998; Galuskin et al. 2011 and literature therein), i.e., within the stability field of rhombohedral CaUO_4 . This explains the external $\bar{3}m$ symmetry of vorlanite: it is inherited from its high-temperature precursor. The stability field of rhombohedral CaUO_4 extends from high temperatures to room temperature; therefore, spontaneous phase transformation upon cooling is not expected, and that poses a question: why does the ordered structure of "protovorlanite" turn

into the disordered, cubic fluorite-type structure of vorlanite? Disorder of U and Ca in CaUO_4 at lower temperatures is in contrast with the usual behavior of minerals, which tend to more disordered states at higher temperatures. The molar volume of vorlanite ($46.92 \text{ cm}^3/\text{mol}$) is higher than that of rhombohedral CaUO_4 ($45.285 \text{ cm}^3/\text{mol}$), a feature that may be explained by the disordered state of the former (Galuskin et al. 2011), but is not expected in a lower temperature polymorph. There must have been another factor that caused the transition from "protovorlanite" to vorlanite. We suggest that the phase transformation in CaUO_4 was caused by a rearrangement of atoms that resulted from the α -decay events of U.

Vorlanite experienced 0.56 displacements per atom (dpa) during α -decay events of U (Galuskin et al. 2011). Less than half of that dose (0.25 dpa) caused full metamictization of uranian garnet, elbrusite-(Zr), associated with the vorlanite (Galuskina et al. 2010). The rhombohedral CaUO_4 did not lose periodicity; instead, increasing cumulative dose of α -decay events of U may have destabilized the structure of "protovorlanite" transforming it into the more radiation-resistant, fluorite-type structure of vorlanite. Experimental investigations of radiation stability of complex oxides like pyrochlore and murataite show that metamictization competes with the process of formation of the defect fluorite-type structure (Wang et al. 1999; Sickafus et al. 2000, 2001; Lian et al. 2005; Ewing 2005; Lumpkin et al. 2007). Resistance to amorphization of complex oxides is governed by the competition between the short-range covalent and long-range ionic forces (Trachenko et al. 2005, 2006). According to Trachenko et al. (2005), complex materials are amorphized by radiation damage if their chemical composition favors formation of covalent bonds. In uranyl minerals, bonding in the linear UO_2^{2+} ion, with average U^{6+} -O bond lengths $\sim 1.8 \text{ \AA}$, is strongly covalent (Burns 1999). Rhombohedral CaUO_4 is more covalent than vorlanite due to ordering of linear uranyl groups in distorted UO_8 polyhedra. The change of chemical bonding (electronic configuration) during transformation of rhombohedral CaUO_4 to vorlanite is manifested by change of both color and luster from honey yellow and adamantine to dark red and semi-metallic, respectively. The change of electronic configuration in vorlanite was recorded by XPS spectra in the range of $\text{U}4f$ bonding energy. In vorlanite, significant shortening was observed of the distance between the main peaks $\text{U}4f_{5/2}$, $\text{U}4f_{7/2}$, and neighboring satellites in comparison to that seen in the spectra of rhombohedral CaUO_4 (Galuskin et al. 2011).

The transition from "protovorlanite" to vorlanite does not require overcoming a high-energy barrier, because of the similarities between their structures (Fig. 1). This is confirmed by the reverse transition at temperatures above $750 \text{ }^\circ\text{C}$. The full recovery (ordering) of the rhombohedral structure occurs fast, perhaps even instantaneously. The transition from "protovorlanite" to vorlanite does not change the coordination of cations. We conclude that vorlanite is thermodynamically a metastable phase formed in response to α -decay events of U in thermodynamically stable, rhombohedral CaUO_4 . In other words, crystallization of CaUO_4 always results in the ordered rhombohedral structure, which, however, becomes unstable with increasing cumulative dose of α -decay events and transforms into the radiation-

resistant, fluorite-type structure of vorlanite, preventing it from undergoing metamictization. Certainly, irradiation experiments accompanied by molecular dynamics simulations are needed to substantiate our conclusion. On the basis of analysis of available literature data it is arguable that vorlanite is the first mineral with radiation-induced structure.

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REFERENCES CITED

- Allen, G.C. and Griffiths, A.J. (1979) Vibrational spectroscopy of alkaline-earth metal uranate compounds. *Journal of the Chemical Society, Dalton Transactions*, 315–319.
- Burns, P.C. (1999) The crystal chemistry of uranium. In P.C. Burns and R. Finch, Eds., *Uranium: Mineralogy, Geochemistry and the Environment*, 38, p. 23–90. *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America, Chantilly, Virginia.
- Ewing, R.C. (2005) Plutonium and "minor" actinides: safe sequestration. *Earth and Planetary Science Letters*, 229, 165–181.
- 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 ($\text{CaU}^{6+}\text{O}_4$)—A new mineral from the Upper Chegem caldera, Kabardino-Balkaria, Northern Caucasus, Russia. *American Mineralogist*, 96, 188–196.
- Galuskina, I.O., Galuskin, E.V., Armbruster, T., Lazic, B., Kusz, J., Dzierzanowski, P., Gazeev, V.M., Pertsev, N.N., Prusik, K., Zadov, A.E., Winiarski, A., Wrzalik, R., and Gurbanov, A.E. (2010) Elbrusite-(Zr)—A new uranian garnet from the Upper Chegem caldera, Kabardino-Balkaria, Northern Caucasus, Russia. *American Mineralogist*, 95, 1172–1181.
- Lian, J., Wang, L.M., Ewing, R.C., Yudin, S.V., and Stefanovsky, S.V. (2005) Thermally induced phase decomposition and nanocrystal formation in murataite ceramics. *Journal of Materials Chemistry*, 15, 709–714.
- Liegeois-Duyckaerts, M. (1977) Infrared and Raman spectrum of CaUO_4 : 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.
- Lumpkin, G.R., Pruneda, J.M., Rios, S., Smith, K.L., Trachenko, K., Whittle, K.R., and Zaluzec, N.J. (2007) Nature of the chemical bond and prediction of radiation tolerance in pyrochlore and defect fluorite compounds. *Journal of Solid State Chemistry*, 180, 1512–1518.
- 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.
- Sickafus, K.E., Minervini, L., Grimes, R.W., Valdez, J.A., Ishimaru, M., Li, F., McClellan, K.J., and Hartmann, T. (2000) Radiation tolerance of complex oxides. *Science*, 289, 748–751.
- Sickafus, K.E., Minervini, L., Grimes, R.W., Valdez, J.A., and Hartmann, T. (2001) A comparison between radiation damage accumulation in oxides with pyrochlore and fluorite structures. *Radiation Effects and Defects in Solids*, 155, 133–137.
- Trachenko, K., Pruneda, J.M., Artacho, E., and Dove, M.T. (2005) How the nature of the chemical bond governs resistance to amorphization by radiation damage. *Physical Review B*, 71, 184104.
- Trachenko, K., Dove, M.T., and Artacho, E. (2006) Atomistic simulations of resistance to amorphization by radiation damage. *Physical Review B*, 73, 174207.
- Wang, S.X., Begg, B.D., Wang, L.M., Ewing, R.C., Weber, W.J., and Kutty, K.V.G. (1999) Radiation stability of gadolinium zirconate: a waste form for plutonium disposition. *Journal of Materials Research*, 14, 4470–4473.
- Zharikov, V.A., Rusinov, V.L., Marakushev, A.A., Zaraysky, G.P., Omel'yanchenko, B.I., Pertsev, N.N., Rass, I.T., Andreeva, O.V., Abramov, C.C., and Podlesski, K.V. (1998) *Metasomatism and Metasomatic Rocks*, 489 p. Nauka, Moscow (in Russian).