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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, Fm̅̅̅̅₃m, 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 [R₃m, a = 6.2683 Å, α = 36.04°] (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 equivalent 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 3m symmetry, in contrast with the space group symmetry, Fm̅̅̅₃m. 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 replacement 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, λ = 514.5 nm, spectral resolution 2 cm⁻¹), and high-brilliance X-ray powder diffractometer Rigaku (MoKα 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 × 50 × 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, 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 × 100 × 15 and 55 × 40 × 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...