Discovery of terrestrial andreyivanovite, FeCrP, and the effect of Cr and V substitution on the low-pressure barringerite-allabogdanite transition

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Abstract

Iron phosphides with significant variations of Cr (up to 18 wt%) and V (up to 8.6 wt%) contents were detected in gehlenite-bearing breccia at the Hatrurim Complex, Negev desert, Israel. Investigations of the composition and structure of the Fe₂P phosphides showed that when the V+Cr content is higher than 0.26 apfu (atoms per formula unit), a transition from the hexagonal barringerite (P6m2) to orthorhombic allabogdanite (Pnma) takes place. According to the experimental data, allabogdanite is a high-pressure (>8 GPa) polymorph of barringerite. Pseudowollastonite associated with Cr-V-bearing allabogdanite is an indicator of phosphate crystallization at high temperature (>1200 °C) and low pressure. Thus, at the low pressure close to ambient, when more than 13 at% Fe in Fe₂P is substituted by Cr and V, the orthorhombic polymorph is stable. The orthorhombic phosphate with the highest Cr and V contents belongs to the andreyivanovite species with the FeCrP end-member formula. This is the first finding on Earth of that very rare mineral described from the Kaidun meteorite. Some Cr-V-bearing phosphides have an unusual morphology, which cannot be explained by crystallization from a melt. More probably, these phosphides can form in the process of replacing fish bone remains. We believe that sedimentary protolith was not thermally altered and contained a significant amount of bituminous organic matter and phosphorite inclusions. Injecting paralava into the sedimentary rocks determines the conditions for phosphate formation on the boundary of these rocks as a result of the high-temperature carbothermal reduction process.

Keywords: Terrestrial natural phosphides, barringerite, allabogdanite, andreyivanovite, phase transition, Hatrurim Complex

Introduction

A vanadium-bearing andreyivanovite, FeCrP, in association with Cr-V-bearing Fe₂P polymorphs—barringerite and allabogdanite—was found in pseudowollastonite-bearing gehlenite paralava of the Hatrurim Complex, Negev Desert, Israel. Andreyivanovite is a rare mineral that was discovered in the Kaidun meteorite (Zolensky et al. 2008) and later was noted in Rumuruti chondrite (Greshake 2014).

The Hatrurim Complex has recently been known as a source of terrestrial phosphides (Britvin et al. 2015). Here, besides the phosphides typical of meteorites: schreibersite, Fe₃P (Britvin et al. 2021a), barringerite, Fe₄P₂ (Britvin et al. 2017) and its high-pressure analog—allabogdanite (Britvin et al. 2021b), nine new phosphides: halamishite, Ni₃P₂ (Britvin et al. 2020a); negevite, Ni₃P₂ (Britvin et al. 2020b); nazarovite, Ni₅P₆ (Britvin et al. 2022a); zukatamritite, Fe₅P₆ (Britvin et al. 2019a); transjordanite, Ni₅P₆ (Britvin et al. 2020c); polekhovskyite, MoNi₅P₆ (Britvin et al. 2022b); murashkoite, FeP (Britvin et al. 2019b); nickolayite, FeMoP (Murashko et al. 2019); orishchinite, Ni₃P₂ (Britvin et al. 2019c) were discovered. This detection of phosphides in the rocks of the Hatrurim Complex is unexpected. This is true both for the Hatrurim Complex, whose mineral association mainly formed under oxidizing conditions (Galuskina et al. 2017), and for the rocks of the terrestrial genesis on the whole. Phosphides were detected in samples of diopside paralava collected in a small quarry in the Daba Siwaqa pyrometamorphic rock field in Jordan (Britvin et al. 2015) and in the two rock samples found ex situ in dry wadies Halamish (diopside paralava) and Zohar (gehlenite paralava), the Hatrurim Basin, Negev Desert, Israel (Britvin et al. 2015; Galuskin et al. 2020). In 2019, we found a bedrock of gehlenite paralava in the Zohar wadi, and its study led to the discovery of V-bearing andreyivanovite and Cr-V-bearing allabogdanite, aggregations of which resemble fossilized organic fragments.

Allabogdanite is a high-pressure polymorph of barringerite. A synthetic orthorhombic Fe₂P is stable at the pressure range of 8–40 GPa and a temperature of about 1100 °C (Dera et al. 2008). Natural barringerite with low-Ni (up to 0.1 apfu) and low-Mo (up to 0.04 apfu) impurities transfers to allabogdanite at 25 ± 3 GPa and at 1400 ± 100 °C (Britvin et al. 2021b). On the other hand, Litasov et al. (2020) concluded on the basis of theoretical calculations and experimental data that allabogdanite is a lower-temperature phase compared to barringerite, which is stable at the ambient pressure and temperature lower than 500 °C. Unlike isostructural high-pressure and high-temperature allabogdanite, a synthetic analog of andreyivanovite crystallizes from a high-temperature melt at ambient pressure (Kumar et al. 2004).

In this paper, we present the results of an investigation of the