Nazarovite, Ni$_{12}$P$_5$, a new terrestrial and meteoritic mineral structurally related to nickelphospide, Ni$_3$P

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ABSTRACT

Nazarovite, Ni$_{12}$P$_5$, is a new natural phosphide discovered on Earth and in meteorites. Terrestrial nazarovite originates from phosphide assemblages confined to pyrometamorphic suite of the Hatrurim Formation (the Mottled Zone), the Dead Sea basin, Negev desert, Israel. Meteoritic nazarovite was identified among Ni-rich phosphide precipitates extracted from the Marjalahi meteorite (main group pallasite). Terrestrial mineral occurs as micrometer-sized lamella intergrown with transjordanite (Ni$_3$P). Meteoritic nazarovite forms chisel-like crystals up to 8 μm long. The mineral is tetragonal, space group $I4/m$. The unit-cell parameters of terrestrial and meteoritic material, respectively: $a = 8.640(1)$ and $8.6543(3)$ Å, $c = 5.07(1)$ and $5.0665(2)$ Å, $Z = 2$. The crystal structure of terrestrial nazarovite was solved and refined on the basis of X-ray single-crystal data ($R_w = 0.0516$), whereas the structure of meteoritic mineral was refined by the Rietveld method using an X-ray powder diffraction profile ($R_w = 0.22\%$). The mineral is structurally similar to phosphides of schreibersite–nickelphosphide join, Fe$_3$P$_2$–Ni$_3$P$_2$. Chemical composition of nazarovite (terrestrial/meteoritic, electron microprobe, wt%): Ni 81.87/78.59, Fe <0.2/4.10; Co <0.2/0.07, P 18.16/17.91, total 100.03/100.67, leading to the empirical formula Ni$_{11.97}$P$_{5.03}$ and (Ni$_{1.4}$Fe$_{0.5}$(Co$_{0.0}$)$_{0.94}$)$_{12.0}$P$_{14.0}$ based on 17 atoms per formula unit. Nazarovite formation in nature, both on Earth and in meteorites, is related to the processes of Fe/Ni fractionation in solid state, at temperatures below 1100°C.

Keywords: Ni$_{12}$P$_5$, nickelphospide, Fe-Ni-P system, crystal structure, pyrometamorphism, meteorite, planetary interiors, nanoprecipitates

INTRODUCTION

Natural phosphides belonging to the ternary system Fe-Ni-P serve as a reservoir of reduced (i.e., non-phosphate) phosphorus in the solar system (Goldstein et al. 2009; Britvin et al. 2015; Litasov and Shatskiy 2016). In material science, the crystal chemistry of Fe-Ni phosphides is the foundation for the development of advanced photocatalysts and electrocatalysts (Sun et al. 2016, 2019). In spite of a seemingly compositional simplicity, Fe-Ni-P is a quite complex multiphase field, which can be divided into Fe-P and Ni-P subsystems (Table 1). Iron (Z = 26) and nickel (Z = 28) are near-neighbor transition metals, but their phosphides exhibit substantially different chemistry and crystal structure (Table 1). The crystal-chemical misfits result in unexpectedly restricted Fe/Ni substitutions. In fact, the joins Fe$_3$P–Ni$_3$P (schreibersite-nickelphosphide) and Fe$_3$P–Ni$_3$P (barringerite-transjordanite) are the only examples of continuous Fe-Ni solid solutions (Britvin et al. 2020a, 2021a). A limited Fe-Ni miscibility was reported in murashkoite (Vereshchagin et al. 2021), zuktamrurite, allabogdanite (Britvin et al. 2019b), and mellinite, whereas other phosphides do not show traceable Fe/Ni substitutions. The phenomenon of limited miscibility opens a way to crystal-chemical Fe/Ni fractionation within reduced systems. We herein report a new natural phosphide, an extreme example of such fractionation. The mineral Ni$_{12}$P$_5$, named nazarovite, in honor of Michail Alexandrovich Nazarov (1949–2016), Russian mineralogist and petrologist, for his contributions to the research of reduced meteoritic assemblages (e.g., Anand et al. 2004; Nazarov et al. 2009). Both the mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2019-013). The holotype specimen of nazarovite from the Hatrurim basin is deposited in the collection of the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia, with the registration number 5381/1.

SAMPLES AND METHODS

Terrestrial nazarovite (the holotype material)

The mineral was discovered among phosphide assemblages confined to the rocks of the Hatrurim Formation (the Mottled Zone)—a huge pyrometamorphic complex spanning the Middle East in Israel, West Jordan and West Bank (Gross 1977; Vapnik et al. 2007; Novikov et al. 2013). Nazarovite occurs in the specimens