

Crystal chemistry of schreibersite, (Fe,Ni)₃P

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ABSTRACT

Schreibersite, (Fe,Ni)₃P, the most abundant cosmic phosphide, is a principal carrier of phosphorus in the natural Fe-Ni-P system and a likely precursor for prebiotic organophosphorus compounds at the early stages of Earth's evolution. The crystal structure of the mineral contains three metal sites allowing for unrestricted substitution of Fe for Ni. The distribution of these elements across the structure could serve as a tracer of crystallization conditions of schreibersite and its parent celestial bodies. However, discrimination between Fe ($Z = 26$) and Ni ($Z = 28$) based on the conventional X-ray structural analysis was for a long time hampered due to the proximity of their atomic scattering factors. We herein show that this problem has been overcome with the implementation of area detectors in the practice of X-ray diffraction. We report on previously unknown site-specific substitution trends in schreibersite structure. The composition of the studied mineral encompasses a Ni content ranging between 0.03 and 1.54 Ni atoms per formula unit (apfu): the entire Fe-dominant side of the join Fe₃P-Ni₃P. Of 23 schreibersite crystals studied, 22 comprise magmatic and non-magmatic iron meteorites and main group pallasites. The near end-member mineral (0.03 Ni apfu) comes from the pyrometamorphic rocks of the Hatrurim Basin, Negev desert, Israel. It was found that Fe/Ni substitution in schreibersite follows the same trends in all studied meteorites. The dependencies are nonlinear and can be described by second-order polynomials. However, the substitution over the *M2* and *M3* sites within the most common range of compositions ($0.6 < \text{Ni} < 1.5$ apfu) is well approximated by a linear regression: $\text{Ni}(M2) = 0.84 \times \text{Ni}(M3) - 0.30$ apfu (standard error 0.04 Ni apfu). The analysis of the obtained results shows a strong divergence between the variation of unit-cell parameters of natural schreibersite and those of synthetic (Fe,Ni)₃P. This indicates that Fe/Ni substitution trends in the mineral and its synthetic surrogates are different. A plausible explanation might be related to the differences in the system equilibration time of meteoritic schreibersite (millions of years) and synthetic (Fe,Ni)₃P (~100 days). However, regardless of the reason for the observed difference, synthetic (Fe,Ni)₃P cannot be considered a structural analog of natural schreibersite, and this has to be taken into account when using synthetic (Fe,Ni)₃P as an imitator of schreibersite in reconstructions of natural processes.

Keywords: Phosphide, schreibersite, Fe₃P, Fe-Ni-P system, meteorite, planetary interiors, crystal structure, solid solution