Discovery of terrestrial allabogdanite (Fe,Ni)$_2$P, and the effect of Ni and Mo substitution on the barringerite-allabogdanite high-pressure transition

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ABSTRACT

Minerals formed at high pressures are sensitive indicators of extreme pressure-temperature conditions that occur in nature. The discovery of the high-pressure polymorph of (Fe,Ni)$_2$P, allabogdanite in the surficial pyrometamorphic rocks of the Hatrurim Formation (the Mottled Zone) surrounding the Dead Sea basin in Israel is the first terrestrial occurrence of a mineral previously only found in iron meteorites. Stepwise annealing experiments demonstrate that allabogdanite is metastable at ambient pressure and that it irreversibly transforms into its low-pressure polymorph, barringerite, upon heating to 850 ± 50 °C. High-pressure, high-temperature diamond-anvil cell (DAC) experiments confirm the results of annealing experiments. The DAC data indicate that Hatrurim allabogdanite is metastable below 7.4 GPa, and the low- to high-pressure phase transition (barringerite → allabogdanite) occurs at 25 ± 3 GPa and 1400 ± 100 °C. The observed transition pressure of Hatrurim allabogdanite is significantly higher than that of pure synthetic Fe$_2$P (8 GPa) due to partial substitution of Fe for Ni (4 wt%) and Mo (2.5 wt%). Because the influence of substituting impurities on the conditions of phase transitions can be unexpectedly strong, our findings confirm that caution should be exercised when extrapolating data from experiments on synthetic compounds to natural systems. Based on the discovery of terrestrial allabogdanite (Fe,Ni)$_2$P coupled with experiments probing the phase transitions in this natural composition, we contend that terrestrial allabogdanite formed via transformation from barringerite and possess potential scenarios of its formation.

Keywords: Allabogdanite, barringerite, phosphide, Fe$_2$P, high pressure, crystal structure, phase transitions, Fe-Ni-P system

INTRODUCTION

The area of the Eastern Mediterranean in the historical region of the Southern Levant bears the remnants of an enigmatic rock complex known as the Mottled Zone or the Hatrurim Formation (Fig. 1) (Gross 1977; Vapnik et al. 2007). This formation represents the world’s largest area of sedimentary rocks subjected to combustion metamorphism (pyrometamorphism) – the processes of surficial high-temperature calcination and fusion of sediments that produces mineral assemblages resembling cement clinkers or basic igneous rocks (Sokol et al. 2019). Numerous outcrops of the Mottled Zone span an area of 150 × 200 km$^2$ on both sides of the Dead Sea, encompassing the Judean and Negev deserts in Israel, Palestinian Authority, and Transjordan Plateau in West-Central Jordan, with several patches mapped as far north as the Sea of Galilee (Kinneret) (the Maqarin site) (Fig. 1). These exposed outcrops are likely remnants of wider fields deflated by later erosion (Matmon 2017). The largest preserved Mottled Zone massifs are the Daba-Siwaqa complex in West-Central Jordan (>300 km$^2$) and the Hatrurim Basin in Israel (~50 km$^2$) (Fig. 1). Geological dating of the Mottled Zone has produced a range of ages, with the majority falling between 16 and 2.5 Ma (million years) (see a review in Sokol et al. 2019).

The mineralogy of the Mottled Zone rock suite is diverse and contains both highly reduced (e.g., Britvin et al. 2015; Galuskina et al. 2017) and highly oxidized mineral assemblages (Sokol et al. 2011; Juroszek et al. 2020), including those more characteristic of meteorites than terrestrial rocks (Weber and Bischoff 1994; Galuskina et al. 2016). Phosphides are typical accessory minerals in the Mottled Zone and have been identified in several localities at both sides of the Dead Sea, in Israel and West-Central Jordan (Britvin et al. 2015, 2019a, 2019b, 2020a, 2020b, 2020c). Phosphides typically form under highly reducing conditions and contain phosphorus in an oxidation state lower than zero. These minerals are commonly encountered in iron meteorites, whereas phosphorous normally occurs in its oxidized form in minerals from the Earth’s