

1 **Revision 1**

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3 **Nazarovite, Ni₁₂P₅, a new terrestrial and meteoritic mineral structurally related to**
4 **nickelphosphide, Ni₃P**

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22 **Abstract**

23 Nazarovite, Ni₁₂P₅, is a new natural phosphide discovered on Earth and in meteorites. Terrestrial
24 nazarovite originates from phosphide assemblages confined to pyrometamorphic suite of the
25 Hatrurim Formation (the Mottled Zone), the Dead Sea basin, Negev desert, Israel. Meteoritic
26 nazarovite was identified among Ni-rich phosphide precipitates extracted from the Marjalahti
27 meteorite (main group pallasite). Terrestrial mineral occurs as micrometer-sized lamella intergrown
28 with transjordanite (Ni₂P). Meteoritic nazarovite forms chisel-like crystals up to 8 μm long. The
29 mineral is tetragonal, space group *I4/m*. The unit-cell parameters of terrestrial and meteoritic
30 material, respectively: *a* 8.640(1) and 8.6543(3), *c* 5.071(3) and 5.0665(2) Å, *V* 378.5(2) and
31 379.47(3) Å³, *Z* = 2. Crystal structure of terrestrial nazarovite was solved and refined on the basis of
32 X-ray single-crystal data (*R*₁ = 0.0516), whereas the structure of meteoritic mineral was refined by
33 the Rietveld method using an X-ray powder diffraction profile (*R*_B = 0.22 %). The mineral is
34 structurally similar to phosphides of schreibersite–nickelphosphide join, Fe₃P–Ni₃P. Chemical
35 composition of nazarovite (terrestrial/meteoritic, electron microprobe, wt.%): Ni 81.87/78.59, Fe
36 <0.2/4.10; Co <0.2/0.07, P 18.16/17.91, Total 100.03/100.67, leading to the empirical formula
37 Ni_{11.97}P_{5.03} and (Ni_{11.43}Fe_{0.63}Co_{0.01})_{12.07}P_{4.94}, based on 17 atoms per formula unit. Nazarovite
38 formation in nature, both on Earth and in meteorites, is related to the processes of Fe/Ni
39 fractionation in solid state, at temperatures below 1100 °C.

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42 **Keywords:** Ni₁₂P₅, nickelphosphide, Fe–Ni–P system, crystal structure, pyrometamorphism,
43 meteorite, planetary interiors, nanoprecipitates

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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; Sun et al. 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-neighbour transition metals, but their phosphides exhibit substantially different chemistry and crystal chemistry (Table 1). The crystal-chemical misfits result in unexpectedly restricted Fe/Ni substitutions. In fact, the joins Fe₃P–Ni₃P (schreibersite–nickelphosphide) and Fe₂P–Ni₂P (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 melliniite, 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 Ni₁₂P₅ is named nazarovite, in honour 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.

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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 of altered diopside microbreccia collected along the Halamish wadi, Hatrurim basin, Negev desert, Israel (e.g., Britvin et al. 2021b). It was studied in conventional polished thick rock sections.

Nazarovite from the Marjalahti pallasite

An acid-resistant precipitate was obtained from a piece of the metal taken from the same meteorite slice where keplerite, $\text{Ca}_9(\text{Ca}_{0.5}\square_{0.5})\text{Mg}(\text{PO}_4)_7$, was recently described (specimen MM74/2, the Mining Museum) (Britvin et al. 2021d). A ~0.5 cm (Fe,Ni) metal chunk, free of olivine and chromite rims, was preliminarily treated in hot 10 % HCl for 1 minute, in order to clean it up from surface contaminants. The etched piece was rinsed off by distilled water and then immersed into 10 mL of hot 10 % HCl, in 50 mL glass baker on a hot plate. After complete dissolution of acid-soluble α -(Fe,Ni) (kamacite), the liquid with the insoluble residue was mixed with ~30 mL of methanol and allowed to stay for 20 min, followed by gentle removal of the solution with a 20 mL syringe until ~1 cm level of residual liquid remained. This wash-up procedure was repeated 5 times, and after that the remaining liquid with precipitate was transferred onto a watch glass and air-dried. The residue was comprised by a few mm-sized grains of schreibersite, $(\text{Fe,Ni})_3\text{P}$, and taenite, γ -(Fe,Ni). In addition, a tiny film of white color with straw-yellowish tint and metallic luster was observed at the bottom of the glass. It was found that the film is a microgranular phosphide precipitate which was harvested into a drop of epoxy resin. The soft acid treatment of meteoritic iron applied herein follows the method used in the metallurgy for the liberation of phosphide precipitates from the Ni-

95 based alloys (e.g., Lee et al., 1996). It is noteworthy that this procedure does not lead to the
96 appearance of new phosphide phases, therefore nazarovite is not a newly formed phosphide. The
97 obtained phosphide precipitate sample was first subjected to X-ray powder diffraction study and
98 later on, after embedding and polishing procedures, to electron microprobe analysis.

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100 **Electron microprobe analysis (EMPA) and electron backscatter diffraction (EBSD)**

101 EMPA data were obtained using an Oxford Instruments AzTec Energy X-Max 20 EDX
102 spectrometer (20 kV, 1 nA) attached to a Hitachi S-3400N SEM. Cobalt was determined separately
103 using an INCA WAVE 500 WDX spectrometer (20 kV, 15 nA). Pure Ni, Fe and Co metals, along
104 with InP were used as standards. Electron backscatter diffraction (EBSD) mapping was carried out
105 on the section etched for 20 min with an Ar-ion beam generated by an Oxford Instruments IonFab-
106 300 instrument. Diffraction pattern acquisition was carried out with an Oxford Instruments Nordlys-
107 HKL detector operated at 30 kV and 1.5 nA on the sample coated with ~2 nm carbon film and glued
108 onto a 70 ° tilted stage. The EBSD patterns matching and mapping were performed using the
109 structural models of Ni₁₂P₅ (Rundqvist and Larsson 1959) and transjordanite end-member, Ni₂P
110 (Britvin et al. 2020a).

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112 **Powder X-ray diffraction (PXRD) and Rietveld refinement**

113 Powder diffraction patterns were obtained by the use of a Rigaku RAXIS Rapid II
114 diffractometer (Table 2). The instrument has a CoK α -radiation source (rotating anode, 40 kV, 15
115 mA), microfocus mirror monochromator and semi-cylindrical imaging plate detector ($r = 127.4$
116 mm). The images were acquired in Debye-Scherrer geometry (Gandolfi-type rotation). A plate-to-
117 profile data conversion was performed with the osc2xrd program (Britvin et al. 2017). Further
118 processing of the pattern of the terrestrial nazarovite-transjordanite grain was carried out with Stoe
119 WinXPOW software (Stoe and Cie GmbH). Rietveld refinement of the powder profile obtained

120 from the meteoritic precipitate (Supplementary Fig. S1) was carried out with Bruker TOPAS v.5.0
121 software (Bruker AXS). The basic refinement details and refined fractional coordinates are given in
122 Supplemental Tables S1 and S2.

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124 **Single-crystal X-ray diffraction (SCXRD)**

125 SCXRD data were obtained only for terrestrial nazarovite; they were collected by means of a
126 Bruker Kappa APEX DUO diffractometer (1024K CCD detector). The crystal used for the study is
127 depicted in Figure 1. Because of the small size of nazarovite lamella, we did not extract them from
128 the surrounding transjordanite matrix. Instead, the whole two-phase grain was subjected to data
129 collection. A single-crystal nazarovite domain (UB-matrix) could be separated from several
130 transjordanite UB-matrices using CrysAlisPro software (Rigaku Oxford Diffraction), followed by a
131 standard set of data reduction procedures. The crystal structure of terrestrial nazarovite was solved
132 and refined to $R_1 = 0.0516$ using the *SHELX*-2018 set of programs (Sheldrick 2015) incorporated
133 into Olex2 GUI (Dolomanov et al. 2006). A summary of data collection and structure refinement
134 details is given in Supplementary Table 3. The detailed information can be retrieved from the CIF
135 file attached to Supplementary Data.

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137 **Results**

138 **Occurrence and general appearance**

139 Microcrystalline diopside constitutes up to 80 % of microbreccia containing phosphide
140 minerals, whereas the interstices are filled with secondary thaumasite, ettringite and unidentified
141 Mg-Fe hydrous silicates. The accessory minerals are comprised by hematite, magnetite, and diverse
142 Fe-Ni phosphides (Britvin et al. 2021c). Nazarovite occurs as single-crystal lamella up to 10 μm
143 long penetrating the grain of transjordanite, Ni_2P (Fig. 1). EBSD mapping reveals that all nazarovite
144 lamella exposed onto the section surface have the same crystallographic orientation, whereas

145 surrounding transjordanite forms a patchy polycrystalline aggregate (Fig. 1d-f). Nazarovite-
146 transjordanite intergrowths have white colour in reflected light; both minerals are indistinguishable
147 from each other under the polarizing microscope. Due to very small size of nazarovite lamella, the
148 microhardness and reflectance values of the mineral could not be measured.

149 Nazarovite of meteoritic origin was identified in microgranular precipitates obtained by
150 dissolution of α -(Fe,Ni) metal (kamacite) of the Marjalahti meteorite (main-group pallasite). The
151 dominant phase of precipitates is acicular to thin-prismatic nickelposphide, $(\text{Ni,Fe})_3\text{P}$, which
152 accounts for 85-90 wt.% of acid-resistant residue (Supplementary Fig. S1). Nazarovite occurs as
153 chisel-like crystals up to 8 μm wide and 3 μm thick disseminated among nickelposphide (Fig. 2).

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155 **Crystal structure**

156 The unit-cell parameters of terrestrial and meteoritic nazarovite are almost identical, in
157 agreement with the composition approaching pure Ni_{12}P_5 (Table 3). The crystal structure of the
158 mineral contains 2 independent Ni positions and 2 P sites (Table 4). The Ni(1) atom is coordinated
159 by 12 atoms – 5Ni(1), 3Ni(2), 3P(1), and 1P(2). Ni(2) has 15-fold coordination – by 6Ni(1), 5Ni(2),
160 and 4P(1). Phosphorus atoms, P(1) and P(2), are surrounded solely by Ni and have coordination
161 numbers 10 and 8, respectively. Due to a relative simplicity of the P-centered polyhedra, the
162 nazarovite structure can be better illustrated in a phosphorus-centered approach (Fig. 3), in contrast
163 to the early descriptions of synthetic Ni_{12}P_5 based on the metal-centered polyhedra (Rundqvist and
164 Larsson 1959; Larson 1965). The nazarovite framework (Fig. 3a,b) is topologically similar to that of
165 the minerals belonging to schreibersite–nickelposphide join, Fe_3P – Ni_3P (Britvin et al. 2021a). Both
166 nazarovite and nickelposphide are tetragonal, have very similar lattice metrics (Table 3), and the
167 relationship between their unit-cell contents can be expressed as $2\times\text{Ni}_{12}\text{P}_5$ ($\text{Ni}_{24}\text{P}_{10}$) \leftrightarrow $8\times\text{Ni}_3\text{P}$
168 (Ni_{24}P_8). It can be seen that the nazarovite cell contains by 2 P atoms more than that of
169 nickelposphide. These additional P(2) atoms are inserted approximately into the positions which

170 are vacant in the structure of nickelposphide (Fig. 3). The P(2) coordination polyhedron of
171 nazarovite represents an almost perfect cube [P_{Ni8}]. The introduction of [P_{Ni8}] cubes into the lattice
172 results in its symmetrization, manifested by the conversion from the space group $I4\bar{3}$ (Ni₃P) to $I4/m$
173 (Ni₁₂P₅). The additional effect of phosphorus incorporation is a relative stretching of the lattice
174 along the *c*-axis that is manifested in the increase of the *c/a* ratio (Table 3).

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176 **Chemical composition**

177 The appearance of an additional P(2) site in nazarovite (relative to nickelposphide) results
178 in the abrupt decrease of the structural tolerance towards Fe substitution. As was already mentioned,
179 Ni₃P (nickelposphide) forms a continuous series of solid solutions with Fe₃P (schreibersite) (Table
180 1). In contrast, both occurrences of nazarovite show the compositions either approaching or exactly
181 matching end-member Ni₁₂P₅ (Table 5). The marked difference in the affinity of respective
182 phosphides towards Fe is illustrated by the comparison of both minerals from the Marjalahti
183 pallasite, where nazarovite has a Ni/Fe ratio of more than 18, whereas the same ratio in
184 nickelposphide is just 2 (Table 5). Such a difference is not an occasional one, but is supported by
185 the studies on synthetic systems: Fe₁₂P₅ does not exist in the Fe–P phase diagram, and Fe does not
186 substitute for Ni in synthetic Ni₁₂P₅ (Drábek 2006). Therefore, the extreme Ni enrichment of natural
187 nazarovite can be considered as its intrinsic property rather than a geochemical curiosity.

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189 **Discussion**

190 Nazarovite is an example of the influence of crystal-chemical factors on the elemental
191 differentiation in the Fe–Ni–P system. In both terrestrial and meteoritic environments, the mineral
192 was evidently formed in the solid state at temperatures below 1100 °C, as it can be deduced from the
193 studies of the Ni–P phase diagram (Schmetterer et al. 2009). The results of EBSD and X-ray single-
194 crystal study suggest that spatially separated nazarovite lamellae shown in Figure 1 represent the

195 subdomains (the remnants?) of the same single crystal. The latter implies that nazarovite may in fact
196 be a primary, earlier phase in the assemblage, whereas surrounding patchy transjordanite is a
197 subsequent one, possibly formed via solid-state substitution of nazarovite.

198 The Marjalahti is one of a few witnessed pallasite falls (see a historical summary in Britvin
199 et al. 2021d). The fragments of this meteorite, harvested immediately after the fall, were not affected
200 by terrestrial weathering; thereby nazarovite in the Marjalahti has a cosmic origin, rather than being
201 a product of surficial alteration of schreibersite ($(\text{Fe},\text{Ni})_3\text{P}$), as it was discussed with respect to
202 barringerite, $(\text{Fe},\text{Ni})_2\text{P}$ (Buseck 1969; Britvin et al. 2020a). The identification of nazarovite in
203 phosphide assemblages is hampered due to its compositional similarity to nickelporphide,
204 $(\text{Ni},\text{Fe})_3\text{P}$, and transjordanite, $(\text{Ni},\text{Fe})_2\text{P}$. However, there is evidence that this phosphide may be
205 more widespread in nature. Armstrong et al. (1987) described mm-sized fremdlinge (sulphide- and
206 metal-rich droplets) within the B-type calcium-aluminium inclusion (CAI) of the Allende meteorite,
207 a CV3 carbonaceous chondrite. Among other opaque phases, Armstrong et al. (1987) reported a Ni
208 phosphide containing 80–81 wt.% Ni and less than 0.5 wt.% Fe. The authors calculated a phosphide
209 formula of Ni_5P_2 , but the assumed ideal Ni/P atomic ratio of 2.5 is quite close to that of 2.4 in
210 nazarovite (Table 1). Garvie (2019) described Ni-rich phosphide nanoprecipitates from the Odessa
211 octahedrite, containing both nickelporphide (the major phase) and the second phosphide that can
212 be attributed to either Ni_{12}P_5 (i.e., nazarovite) or Ni_8P_3 . Taking into account that Odessa belongs to
213 the most common IAB group of iron meteorites whereas Marjalahti is a typical main-group pallasite,
214 we propose that the similar Ni-rich phosphide precipitates can be extracted from acid-resistant
215 residues of many metal-rich meteorites.

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Implications

218 The study of natural Ni and Fe phosphides expands our knowledge of the phase relations
219 within Fe-Ni metal-rich assemblages, which are thought to constitute planetary interiors of celestial

220 bodies. The presence of nazarovite determines the upper thermal limit of 1100 °C for the formation
221 of its assemblages, and opens the opportunities for determination of pressure stability limits. The
222 influence of crystal-chemical factors on the processes of elemental differentiation in reduced
223 systems is a largely obscure field of mineralogy and geochemistry. Here the most prominent is the
224 Fe-Ni system (e.g., Goldstein et al. 2009), where the formation of γ -(Fe,Ni) (taenite) succeeds in
225 further selective enrichment of this phase in Ni relative to coexisting α -(Fe,Ni) (kamacite). The
226 much less studied are Fe-Ni carbide systems, where haxonite, $(\text{Fe,Ni})_{23}\text{C}_6$, is always and
227 considerably enriched in Ni as compared to cohenite, $(\text{Fe,Ni})_3\text{C}$ (Krot et al. 1997; Scott and
228 Goldstein 2012), but the reason for such a behavior is unclear. Among natural phosphides, one can
229 mention the selective affinity of Co towards allabogdanite, the high-pressure modification of
230 $(\text{Fe,Ni})_2\text{P}$ (Britvin et al. 2019b). The present paper contributes to this area of planetary science, at
231 the junction between crystal chemistry and cosmochemistry. From the methodological point of
232 view, this study illustrates how advances in the X-ray instrumentation enhance the quality of crystal-
233 chemical research, in particular in meteoritics and planetary science. The full-scale structural study
234 of μm -sized mineral grains is now achievable using standard in-house instruments – a step toward
235 complementary to the fingerprint techniques like EBSD and the Laue X-ray method.

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Acknowledgments

238 This study was funded by the Russian Science Foundation, grant 18-17-00079. The authors are
239 indebted to the curators of the Mining Museum, St. Petersburg Mining Institute, for the specimen of
240 the Marjalahti pallasite provided for this study. We gratefully acknowledge the referees, Laurence
241 Garvie and Michael Zolensky, for helpful comments and suggestions, and the Technical Editor for
242 the crystallographic data corrections. This paper has benefited from editorial handling by Daniel
243 Hummer. The authors are thankful to the X-ray Diffraction Centre, Centre for Microscopy and

244 Microanalysis, Nanophotonics, Nanotechnology and Geomodel Resource Centres of St. Petersburg
245 State University for the access to instrumental and computational resources.

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References cited

248 Anand, M., Taylor, L.A., Nazarov, M.A., Shu, J., Mao, H.-K., and Hemley, R.J. (2004) Space
249 weathering on airless planetary bodies: Clues from the lunar mineral hapkeite. Proceedings of
250 the National Academy of Sciences of the United States of America, 101, 6847–6851.

251 Armstrong, T., Hutcheon, I.D., and Wasserburg, G.J. (1987) Zelda and company: petrogenesis of
252 sulfide-rich Fremdlinge and constraints on solar nebula processes. *Geochimica et*
253 *Cosmochimica Acta*, 51, 3155–3173.

254 Britvin, S.N., Kolomensky, V.D., Boldyreva, M.M., Bogdanova, A.N., Kretser, Yu.L., Boldyreva,
255 O.N., and Rudashevskii, N.S. (1999) Nickelphosphide, $(\text{Ni,Fe})_3\text{P}$, the nickel analog of
256 schreibersite. *Proceedings of Russian Mineralogical Society*, 128, 64–72 (in Russian).

257 Britvin, S.N., Murashko, M.N., Vapnik, Ye., Polekhovskiy, Yu.S., and Krivovichev, S.V. (2015)
258 Earth's phosphides in Levant and insights into the source of Archaean prebiotic phosphorus.
259 *Scientific Reports*, 5, 8355.

260 Britvin, S.N., Dolivo-Dobrovolsky, D.V., Krzhizhanovskaya, M.G. (2017) Software for processing
261 the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku
262 RAXIS Rapid II diffractometer. *Zapiski Rossiyskogo Mineralogicheskogo Obshchestva*,
263 146, 104–107 (in Russian).

264 Britvin, S.N., Murashko, M.N., Vapnik, Ye., Polekhovskiy, Yu.S., Krivovichev, S.V., Vereshchagin,
265 O.S., Vlasenko, N.S., Shilovskikh, V.V., and Zaitsev, A.N. (2019a) Zuktamrurite, FeP_2 , a new
266 mineral, the phosphide analogue of löllingite, FeAs_2 . *Physics and Chemistry of Minerals*, 46,
267 361–369.

- 268 Britvin, S.N., Shilovskikh, V.V., Pagano, R., Vlasenko, N.S., Zaitsev, A.N., Krzhizhanovskaya,
269 M.G., Lozhkin, M.S., Zolotarev, A.A., and Gurzhiy, V.V. (2019b) Allabogdanite, the high-
270 pressure polymorph of (Fe,Ni)₂P, a stishovite-grade indicator of impact processes in the Fe-
271 Ni-P system. *Scientific Reports*, 9, 1047.
- 272 Britvin, S.N., Vapnik, Ye., Polekhovskiy, Yu.S. and Krivovichev, S.V., Krzhizhanovskaya M.G.,
273 Gorelova L.A., Vereshchagin, O.S., Shilovskikh, V.V., and Zaitsev, A.N. (2019c)
274 Murashkoite, FeP, a new terrestrial phosphide from pyrometamorphic rocks of the Hatrurim
275 Formation, Southern Levant. *Mineralogy and Petrology*, 113, 237–248.
- 276 Britvin, S.N., Murashko, M.N., Vapnik, Ye., Polekhovskiy, Yu.S., Krivovichev, S.V.,
277 Krzhizhanovskaya, M.G., Vereshchagin, O.S., Shilovskikh, V.V., and Vlasenko, N.S. (2020a)
278 Transjordanite, Ni₂P, a new terrestrial and meteoritic phosphide, and natural solid solutions
279 barringerite–transjordanite (hexagonal Fe₂P–Ni₂P). *American Mineralogist*, 105, 428–436.
- 280 Britvin, S.N., Murashko, M.N., Vapnik, Ye., Polekhovskiy, Yu.S., Krivovichev, S.V., Vereshchagin,
281 O.S., Shilovskikh, V.V., Vlasenko, N.S., and Krzhizhanovskaya, M.G. (2020b) Halamishite,
282 Ni₅P₄, a new terrestrial phosphide in the Ni–P system. *Physics and Chemistry of Minerals*,
283 2020, 3.
- 284 Britvin, S.N., Murashko, M.N., Vapnik, Ye., Polekhovskiy, Yu.S., Krivovichev, S.V., Vereshchagin,
285 O.S., Shilovskikh, V.V., and Krzhizhanovskaya, M.G. (2020c) Negevite, the pyrite-type NiP₂,
286 a new terrestrial phosphide. *American Mineralogist*, 105, 422–427.
- 287 Britvin, S.N., Krzhizhanovskaya, M.G., Zolotarev, A.A., Gorelova, L.A., Obolonskaya, E.V.,
288 Vlasenko, N.S., Shilovskikh, V.V., and Murashko, M.N. (2021a) Crystal chemistry of
289 schreibersite, (Fe,Ni)₃P. *American Mineralogist*, 106, 10.2138/am-2021-7766
- 290 Britvin, S.N., Murashko, M.N., Vapnik, Ye., Vlasenko, N.S., Krzhizhanovskaya, M.G.,
291 Vereshchagin, O.S., Bocharov, V.N., and Lozhkin, M.S. (2021b) Cyclophosphates, a new

- 292 class of native phosphorus compounds, and some insights into prebiotic phosphorylation on
293 early Earth. *Geology*, 49, 382–386.
- 294 Britvin, S.N., Vereshchagin, O.S., Shilovskikh, V.V., Krzhizhanovskaya, M.G., Gorelova, L.A.,
295 Vlasenko, N.S., Pakhomova, A.S., Zaitsev, A.N., Zolotarev, A.A., Bykov, M., Lozhkin, M.S.,
296 and Nestola, F. (2021c) Discovery of terrestrial allabogdanite (Fe,Ni)₂P, and the effect of Ni
297 and Mo substitution on the barringerite-allabogdanite high-pressure transition. *American*
298 *Mineralogist*, 106, 944–952.
- 299 Britvin, S.N., Galuskina, I.O., Vlasenko, N.S., Vereshchagin, O.S., Bocharov, V.N.,
300 Krzhizhanovskaya, M.G., Shilovskikh, V.V., Galuskin, E.V., Vapnik, Ye., and Obolonskaya,
301 E.V (2021d) Keplerite, Ca₉(Ca_{0.5}□_{0.5})Mg(PO₄)₇, a new meteoritic and terrestrial phosphate
302 isomorphous with merrillite, Ca₉NaMg(PO₄)₇. *American Mineralogist*, 106, 10.2138/am-2021-
303 7834
- 304 Buseck, P.R. (1969) Phosphide from meteorites: Barringerite, a new iron-nickel mineral. *Science*,
305 165, 169–171.
- 306 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A., and Puschmann, H. (2009) OLEX2: a
307 complete structure solution, refinement and analysis program. *Journal of Applied*
308 *Crystallography*, 42, 339–341.
- 309 Dowty, E. (2006). ATOMS for Windows. Shape Software, Kingsport, Tennessee, USA.
- 310 Drábek, M. (2006) Phosphide solid-solutions within the metal-rich portion of the quaternary system
311 Co–Fe–Ni–P AT 800°C, and mineralogical implications. *Canadian Mineralogist*, 44, 399–408.
- 312 Garvie, L.A.J. Germanium- and gallium-rich nickel phosphide “Ni₃P” nanoprecipitates from the
313 Odessa (IAB-MG) iron meteorite. 50th Lunar and Planetary Science Conference, Abstract
314 #2639.
- 315 Goldstein, J.I., Scott, E.R.D., and Chabot, N.L. (2009) Iron meteorites: Crystallization, thermal
316 history, parent bodies, and origin. *Chemie der Erde*, 69, 293–325.

- 317 Gross, S. (1977) The mineralogy of the Hatrurim Formation, Israel. Geological Survey of Israel
318 Bulletin, 70, 1–80.
- 319 Initskaya, O.N., Akselrud, L.G., Mikhalenko, S.I., and Kuzma, Yu.B. (1987) Crystal structure of
320 alpha-Ni₈P₃. Kristallografiya, 32, 50–54 (in Russian).
- 321 Jeitschko, W., and Braun, D.J. (1978) Synthesis and crystal structure of the iron polyphosphide
322 FeP₄. Acta Crystallographica, B34, 3196–3201.
- 323 Krot, A.N., Zolensky, M.E., Wasson, J.T., Scott, E.R.D., Keil, K., and Ohsumi, K. (1997) Carbide
324 magnetite assemblages in type 3 ordinary chondrites. Geochimica et Cosmochimica Acta, 61,
325 219–237.
- 326 Larsson, E. (1965) An X-ray investigation of the Ni-P system and the crystal structures of NiP and
327 NiP₂. Arkiv för Kemi, 23, 335–365.
- 328 Lee, H.-J., Akiyama, E., Habazaki, H., Kawashima, A., Asami, K., and Hashimoto, K. (1996) The
329 effect of phosphorus addition on the corrosion behavior of arc-melted Ni-10Ta-P alloys in 12
330 M HCl. Corrosion Science, 38, 469–485.
- 331 Litasov, K., and Shatskiy, A. (2016) Composition of the Earth's core: a review. Russian Geology
332 and Geophysics, 57, 22–46.
- 333 Nazarov, M.A., Kurat, G., Brandstaetter, F., Ntaflos, T., Chaussidon, M., and Hoppe, P. (2009)
334 Phosphorus-bearing sulfides and their associations in CM chondrites. Petrology, 17, 101–123.
- 335 Novikov, I., Vapnik, Ye., and Safonova, I. (2013) Mud volcano origin of the Mottled Zone,
336 Southern Levant. Geoscience Frontiers, 4, 597–619.
- 337 Oryshchyn, S., Babizhetskii, V.S., Chikhrii, S.I., Akselrud, L.G., Stojko, S., Bauer, D., Guerin, P.,
338 and Kuzma, Yu.B. (2004) Crystal structure of Ni₅P₂. Neorganicheskie Materialy, 40, 450–456
339 (in Russian).

- 340 Pratesi, G., Bindi, L., and Moggi-Cecchi, V. (2006) Icosahedral coordination of phosphorus in the
341 crystal structure of melliniite, a new phosphide mineral from the Northwest Africa 1054
342 acapulcoite. *American Mineralogist*, 91, 451–454.
- 343 Rundqvist, S., and Ersson, N.O. (1969) Structure and bonding in skutterudite-type phosphides.
344 *Arkiv för Kemi*, 30, 103–115.
- 345 Rundqvist, S., and Larsson, E. (1959) The crystal structure of Ni₁₂P₅. *Acta Chemica Scandinavica*,
346 13, 551–560.
- 347 Schmetterer, C., Vizdal, J., and Ipsier, H. (2009) A new investigation of the system Ni–P.
348 *Intermetallics*, 17, 826–834.
- 349 Scott, E.R.D., and Goldstein, J.I. (2012) Occurrence of carbides and graphite in iron meteorites and
350 origin of C-rich irons. *Lunar Planetary Science*, 43, #2671 (abstract).
- 351 Sheldrick, G.M. (2015) Crystal structure refinement with *SHELXL*. *Acta Crystallographica*, C71, 3–
352 8.
- 353 Skála, R., and Drábek, M. (2003) Nickelphosphide from the Vicenice octahedrite: Rietveld crystal
354 structure refinement of a synthetic analogue. *Mineralogical Magazine*, 67, 783–792.
- 355 Sugitani, M., Kinomura, N., Koizumi, M., and Kume, S. (1978) Preparation and properties of a new
356 iron phosphide FeP₄. *Journal of Solid State Chemistry*, 26, 195–201.
- 357 Sun, M., Liu, H., Qu, J., and Li, J. (2016) Earth-Rich Transition Metal Phosphide for Energy
358 Conversion and Storage. *Advanced Energy Materials*, 6, 1600087.
- 359 Sun, Z., Zhu, M., Lv, X., Liu, Y., Shi, C., Dai, Y., Wang, A., and Majima, T. (2019) Insight into Iron
360 Group Transition Metal Phosphides (Fe₂P, Co₂P, Ni₂P) for Improving Photocatalytic
361 Hydrogen Generation. *Applied Catalysis B: Environmental*, 246, 330–336.
- 362 Vapnik, Ye., Sharygin, V.V., Sokol, E.V., and Shagam, R. (2007) Paralavas in a combustion
363 metamorphic complex: Hatrurim Basin, Israel. *The Geological Society of America, Reviews in*
364 *Engineering Geology*, 18, 133–153.

- 365 Vereshchagin, O.S., Pankin, D.V., Smirnov, M.B., Vlasenko, N.S., Shilovskikh, V.V., and Britvin,
366 S.N. (2021) Raman spectroscopy: A promising tool for the characterization of transition metal
367 phosphides. *Journal of Alloys and Compounds*, 853, 156468.

368 **List of figure captions**

369

370 **Figure 1.** Nazarovite in the phosphide assemblage of the Hatrurim Basin. (a) Polished section in
371 reflected light. Phosphide grain within the weathered silicate paralaava. (b) The same grain, BSE
372 image with enhanced contrast. A series of tiny nazarovite lamellae (light) penetrate transjordanite
373 matrix. The biggest lamella was used for the structure solution and refinement. (c) EBSD phase map
374 of the same grain (nazarovite is yellow, transjordanite is green). (d) EBSD map in inverse pole
375 figure (IPF) colouring. Note that all nazarovite lamellae (blue) are represented by single crystals,
376 whereas encasing transjordanite forms a polycrystalline aggregate (patchy areas). (e) EBSD pole
377 figure of nazarovite in the area depicted in (d), projection onto $\{001\}$. Note that all nazarovite
378 lamellae have coincident crystallographic orientation, with the *c*-axis approximately parallel to the
379 image plane. (f) EBSD pole figure of transjordanite in the same area – a polycrystal consisting of at
380 least 3 randomly oriented domains. Abbreviations: Nz – nazarovite, Tj – transjordanite (Ni_2P), Mgt
381 – magnetite.

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383 **Figure 2.** Nazarovite crystal (Nz) among an aggregate of nickelposphide crystals. Polished section
384 of acid-resistant precipitate encapsulated into epoxy resin. SEM BSE image. The Marjalahti
385 pallasite.

386

387 **Figure 3.** Crystal structures of nazarovite, Ni_{12}P_5 , and nickelposphide, Ni_3P , in a phosphorus-
388 centered representation. (a) Nazarovite, a slice on (001). Framework of edge-sharing P(1)-centered
389 polyhedra $[\text{PNi}_{10}]$ (yellow) and perfect P(2)-centered cubes $[\text{PNi}_8]$ (green). (b) A cut of the
390 nazarovite framework illustrating the alternation of $[\text{PNi}_8]$ and empty $[\square\text{Ni}_8]$ cubes interleaved along
391 the *c*-axis. (c) Nickelposphide, a slice on (001) in the same orientation as of nazarovite. A

392 framework of edge-sharing polyhedra $[P(Ni_7P_2)]$, with the narrow open channels propagating along
393 the *c*-axis. Drawn in ATOMS v.6 (Dowty 2006).

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395 **Tables**

396 Table 1. Juxtaposition of natural and synthetic phosphides in the system Fe–Ni–P ^a.

M:P atomic ratio	Fe–P join		Ni–P join		Struct. type	Ref. ^b
	Mineral	Ideal formula	Mineral	Ideal formula		
4		Ni ₄ P	Melliniite		Al ₄ Au	[1]
3	Schreibersite	Fe ₃ P	Ni ₃ P	Nickelphosphide	Ni ₃ P	[2]
2.67			Ni ₈ P ₃		Ni ₈ P ₃	[3]
2.5			Ni ₅ P ₂		Ni ₅ As ₂	[4]
2.4			Ni ₁₂ P ₅	Nazarovite	Ni ₁₂ P ₅	[5]
2	Barringerite	Fe ₂ P	Ni ₂ P	Transjordanite	Fe ₂ P	[6]
2	Allabogdanite	Fe ₂ P	Ni ₂ P	Orishchinite	Co ₂ Si	[7]
1.25			Ni ₅ P ₄	Halamishite	Ni ₅ P ₄	[8]
1	Murashkoite	FeP			MnP	[9]
1			NiP		NiP	[10]
0.5	Zuktamrurite	FeP ₂			Marcasite	[11]
0.5			NiP ₂	Negevite	Pyrite	[12]
0.33			NiP ₃		Skutterudite	[13]
0.25		FeP ₄			FeP ₄	[14]
0.25		FeP ₄			CrP ₄	[15]

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398 ^a The phases which can exist under ambient conditions (either in stable or in quenched state).

399 ^bReferences: [1] Pratesi et al. 2006; [2] Britvin et al. 1999, 2021a; [3] Il'nitskaya et al. 1987; [4]
 400 Oryshchyn et al. 2004; [5] This work; [6] Britvin et al. 2020a; [7] Britvin et al. 2021c; [8] Britvin et
 401 al. 2020b; [9] Britvin et al. 2019c; [10] Larsson 1965; [11] Britvin et al. 2019a; [12] Britvin et al.
 402 2020c; [13] Rundqvist and Ersson 1969; [14] Jeitschko and Braun 1978; [15] Sugitani et al. 1978.

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Table 2. Powder X-ray diffraction data for nazarovite (d in Å)

Hatrurim basin				Marjalahti pallasite				
I_{obs}	d_{obs}	I_{calc}	d_{calc}	I_{obs}	d_{obs}	I_{calc}	d_{calc}	hkl
5	4.374	3	4.374	3	4.370	2	4.372	101
		3	4.320					200
		2	3.073	3	3.080	4	3.076	211
		2	3.054	5	3.062	4	3.060	220
		11	2.732	15	2.736	13	2.737	310
5	2.503	9	2.504	8	2.508	6	2.507	301
54	2.341	39	2.342	43	2.339	40	2.341	112
		16	2.187	<i>b</i>		18	2.186	202
		17	2.167	<i>b</i>		14	2.169	321
13	2.160	23	2.160	<i>b</i>		21	2.164	400
15 ^a	2.040	19	2.036	27	2.038	22	2.040	330
		7	1.937			4	1.939	411
40 ^a	1.931	59	1.932	69	1.934	62	1.935	420
100	1.860	100	1.859	100	1.858	100	1.859	312
		7	1.694	10	1.696	8	1.697	510
		3	1.644	5	1.643	3	1.645	402
				5	1.637	6	1.638	501
		8	1.636					431
		3	1.588					332
		5	1.537			8	1.538	422
		2	1.409	5	1.410	4	1.410	512
		3	1.381			3	1.381	323
		5	1.366	6	1.368	5	1.368	620
		9	1.279	<i>b</i>		11	1.281	532
		9	1.268	<i>b</i>		10	1.267	004
		6	1.222	<i>b</i>		9	1.224	710
		3	1.208			2	1.209	433
		13	1.203	14	1.204	18	1.204	622

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^a The line partially overlaps with the reflection from transjordanite. ^b Line completely overlaps with the reflection from nickelporphide, (Ni,Fe)₃P.

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Table 3. Crystal parameters of nazarovite and synthetic end-member nickelposphide.

Mineral	Nazarovite			Nickelposphide
Locality	Hatrurim	Hatrurim	Marjalahti	Synthetic
Method	SCXRD	PXRD	Rietveld	Rietveld
Formula	Ni ₁₂ P ₅	Ni ₁₂ P ₅	(Ni _{11.43} Fe _{0.67}) ₁₂ P ₅	Ni ₃ P
Space group	<i>I4/m</i>	<i>I4/m</i>	<i>I4/m</i>	<i>I4</i> ⁻
<i>a</i> (Å)	8.640(1)	8.639(5)	8.6543(3)	8.9546(1)
<i>c</i> (Å)	5.071(3)	5.072(3)	5.0665(2)	4.3871(1)
<i>c/a</i> × 10	5.869	5.871	5.853	4.899
<i>V</i> (Å ³)	378.5(2)	378.6(6)	379.47(3)	351.78(2)
<i>Z</i>	2	2	2	8
<i>D_x</i> (g cm ⁻¹)	7.54	7.54	7.55	7.82
Reference	This work	This work	This work	Skála and Drábek 2003

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Table 4. Selected interatomic bond distances (Å) for nazarovite.

Bond	Distance	
	Hatrurim	Marjalahti
Ni1–Ni1	2.522(3)	2.53(2)
Ni1–Ni1	2.549(3)	2.54(2)
Ni1–Ni1	2.587(3)	2.605(10)
Ni1–Ni1	2.639(2) ×2	2.647(7) ×2
Ni1–Ni2	2.540(2)	2.531(10)
Ni1–Ni2	2.574(2)	2.556(10)
Ni1–Ni2	2.705(2)	2.716(10)
Ni1–P1	2.222(3)	2.340(14)
Ni1–P1	2.424(3)	2.350(15)
Ni1–P1	2.455(3)	2.556(15)
Ni1–P2	2.252(1)	2.262(7)
Ni2–Ni2	2.544(4)	2.574(16)
Ni2–P1	2.240(4)	2.083(17)
Ni2–P1	2.242(4)	2.206(19)
Ni2–P1	2.600(2) ×2	2.571(3) ×2

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424 Table 5. Chemical composition (wt. %) of nazarovite and associated phosphides.
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	Hatrurim basin		Marjalahti pallasite	
	Nazarovite	Transjordanite	Nazarovite	Nickelphosphide
	<i>n</i> = 7 (range)	<i>n</i> = 6 (range)	<i>n</i> = 4 (range)	<i>n</i> = 5 (range)
Ni	81.87 (81.39–82.29)	79.04 (78.26–79.73)	78.59 (78.01–79.42)	59.35 (52.90–63.92)
Fe	< 0.2	< 0.2	4.10 (3.46–5.13)	25.81 (21.22–31.37)
Co	< 0.2	< 0.2	0.07 (0.00–0.29)	0.23 (0.20–0.27)
P	18.16 (18.01–18.35)	21.01 (20.85–21.12)	17.91 (17.52–18.23)	15.01 (14.89–15.21)
Total	100.03	100.05	100.67	100.40
Formula amounts				
	$\Sigma = 17$ apfu	$\Sigma = 3$ apfu	$\Sigma = 17$ apfu	$\Sigma = 4$ apfu
Ni	11.97	1.99	11.43	2.06
Fe			0.63	0.94
Co			0.01	0.01
Σ	11.97	1.99	12.07	3.01
P	5.03	1.01	4.94	0.99

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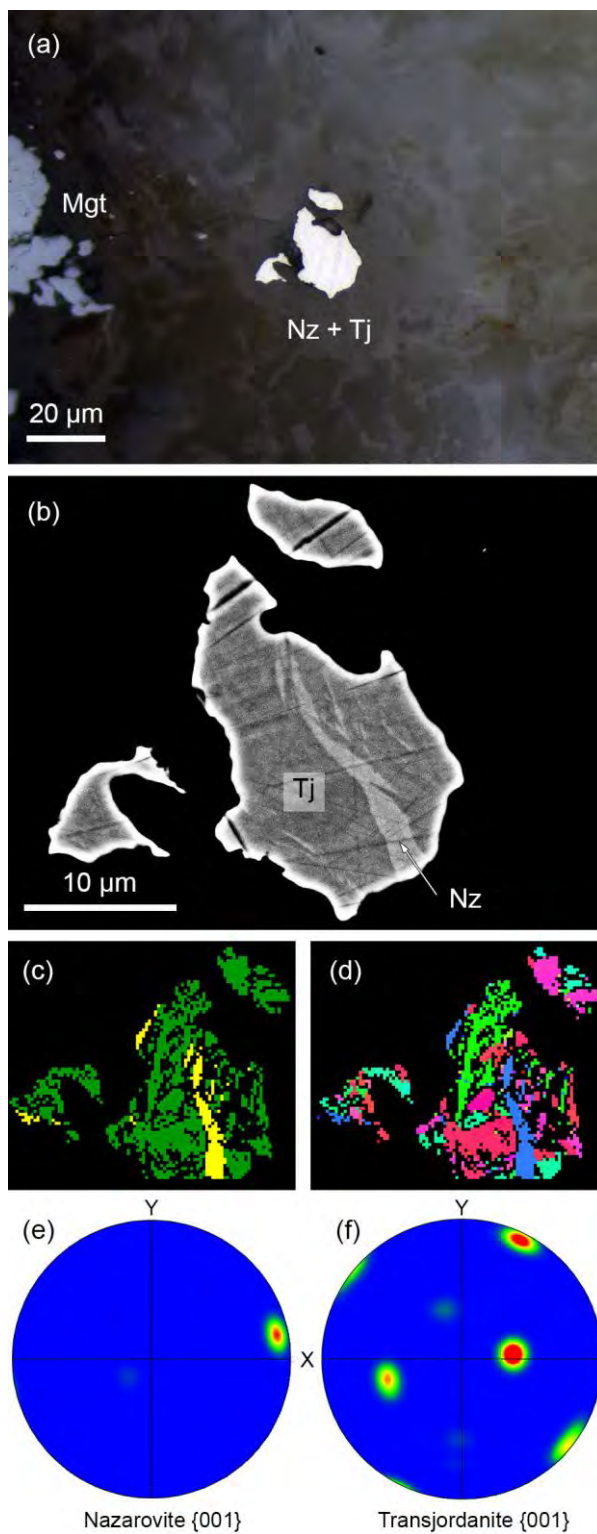
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435 **Figures**

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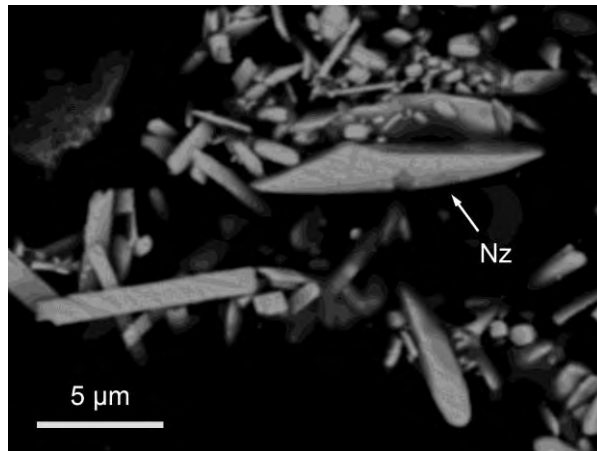
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Figure 1

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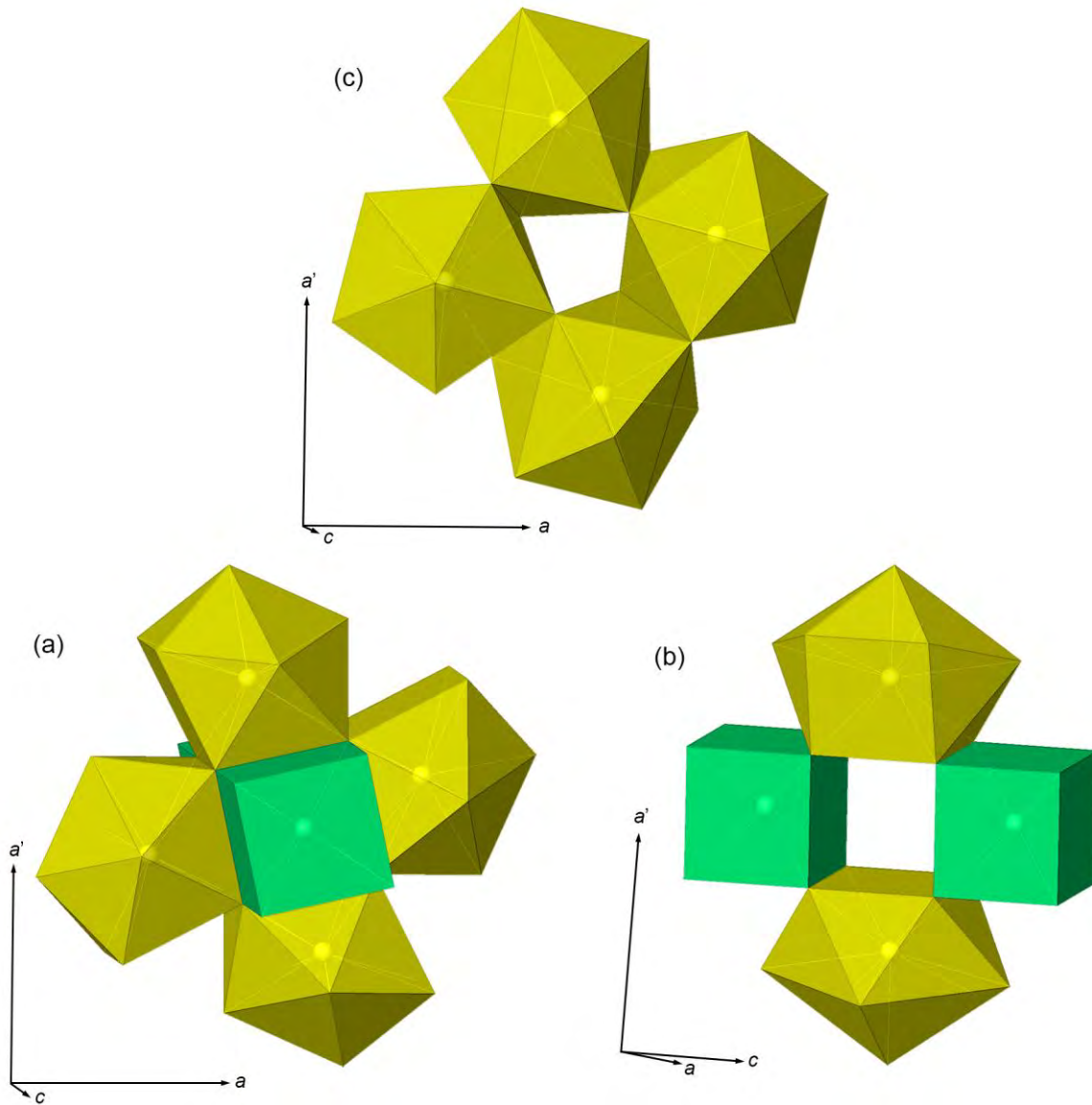
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Figure 2

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Figure 3