

1 **Revision 1**

2 **Transjordanite, Ni<sub>2</sub>P, a new terrestrial and meteoritic phosphide, and natural solid solutions**  
3 **barringerite-transjordanite (hexagonal Fe<sub>2</sub>P–Ni<sub>2</sub>P)**

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13  
14 **Abstract**

15 This paper is a first detailed report of natural hexagonal solid solutions along the join Fe<sub>2</sub>P–Ni<sub>2</sub>P.

16 Transjordanite, Ni<sub>2</sub>P, a Ni-dominant counterpart of barringerite (a low-pressure polymorph of Fe<sub>2</sub>P),

17 is a new mineral. It was discovered in the pyrometamorphic phosphide assemblages of the Hatrurim

18 Formation (the Dead Sea area, Southern Levant) and was named for the occurrence on the

19 Transjordan Plateau, West Jordan. Later on, the mineral was confirmed in the Cambria meteorite

20 (iron ungrouped, fine octahedrite) and it likely occurs in CM2 carbonaceous chondrites (Mighei

21 group). In reflected light, transjordanite is white with a beige tint. It is non-pleochroic and weakly

22 anisotropic. Reflectance values for four COM recommended wavelengths are [*R*<sub>max</sub>/*R*<sub>min</sub>, % (*λ*, nm)]:

23 45.1/44.2 (470), 49.9/48.5 (546), 52.1/50.3 (589), 54.3/52.1 (650). Transjordanite is hexagonal,

24 space group  $\bar{P}62m$ ; unit cell parameters for the holotype specimen, (Ni<sub>1.72</sub>Fe<sub>0.27</sub>)<sub>1.99</sub>P<sub>1.02</sub>, are *a*

25 5.8897(3), *c* 3.3547(2) Å, *V* 100.78(1) Å<sup>3</sup>, *Z* = 3. *D*<sub>calc</sub> = 7.30 g/cm<sup>3</sup>. Crystal structure of holotype

26 transjordanite was solved and refined to  $R_1 = 0.013$  based on 190 independent observed [ $I > 2\sigma(I)$ ]  
27 reflections. The crystal structure represents a framework composed of two types of infinite rods  
28 propagated along the  $c$ -axis: (1) edge-sharing tetrahedra  $[M(1)P_4]$  and (2) edge-sharing  $[M(2)P_5]$   
29 square pyramids. Determination of unit-cell parameters for 12 members of the  $Fe_2P$ – $Ni_2P$  solid  
30 solution demonstrates that substitution of Ni for Fe in transjordanite and *vice versa* in barringerite  
31 does not obey Vegard's law, indicative of preferential incorporation of minor substituent into  $M(1)$   
32 position. Terrestrial transjordanite may contain up to 3 wt. % Mo whereas meteoritic mineral bears  
33 up to 0.2 wt. % S.

34  
35 **Keywords:** transjordanite, barringerite, phosphide, Fe-Ni-P system,  $Fe_2P$ ,  $Ni_2P$ , crystal structure,  
36 phase transitions, solid solution, Vegard's law, pyrometamorphism, meteorite, prebiotic  
37 phosphorylation

## 39 **Introduction**

40 Phase relationships in the system Fe-Ni-P play a significant role in crystallization pathways of  
41 metal-rich celestial bodies whose fragments are delivered as the iron and stony-iron meteorites  
42 (Buchwald 1975; Goldstein et al. 2009). Iron-nickel phosphides are considered to be a reservoir for  
43 reduced phosphorus in deep planetary interiors (Dera et al. 2008; Minin et al. 2018; He et al. 2019)  
44 and a source of low-valent phosphorus in the prebiotic phosphorylation processes on early Earth  
45 (Pasek et al. 2017; Gibard et al. 2019). Barringerite,  $(Fe,Ni)_2P$ , was the second phosphide discovered  
46 in nature (Buseck 1969), and is the next typical phosphide mineral following the schreibersite–  
47 nickelposphide series,  $Fe_3P$ – $Ni_3P$  (Buchwald 1975; Britvin et al. 1999). Extraterrestrial barringerite  
48 was described from several meteorite groups, including pallasites (Buseck 1969; Zucchini et al.  
49 2018), irons (Anthony et al. 1995), howardites (Nazarov et al. 1994, Gounelle et al. 2003),  
50 carbonaceous chondrites (Mikouchi et al. 2006; Nazarov et al. 2009), and in Lunar basaltic-

51 anorthositic breccia Yamato 793274 (Brandstätter et al. 1991). The occurrence of barringerite on  
52 Earth is sometimes considered as a signature of extraterrestrial component (indication of impact  
53 event) (Drake et al. 2018), though its finding in garnet peridotite (Yang et al. 2005) has an obvious  
54 terrestrial origin whereas barringerite from burnt coal dumps was formed under anthropogenic  
55 influence (Bariand et al., 1977; Pierrot et al. 1977; Yao 2003). Barringerite grains recovered from  
56 heavy placer concentrates (Eremenko et al. 1974; Chen et al. 1983) are of debatable (probably  
57 meteoritic) origin. Ni-dominant members of  $\text{Ni}_2\text{P}$ – $\text{Fe}_2\text{P}$  series were reported from two Mighei-type  
58 (CM2) carbonaceous chondrites, Boriskino and Allan Hills 83100 (Nazarov et al. 2009).

59 It is noteworthy that the compound  $\text{Fe}_2\text{P}$  may crystallize in two polymorphic modifications:  
60 the low-pressure (LP) hexagonal one having barringerite (LP- $\text{Fe}_2\text{P}$ ) structure (Rundquist and  
61 Jellinek 1959), and the high-pressure (HP, > 8 GPa) orthorhombic polymorph which adopts  $\text{Co}_2\text{Si}$   
62 structure type (Sénateur et al. 1976; Dera et al. 2008). Synthetic  $\text{Ni}_2\text{P}$  has a barringerite-type LP  
63 structure to at least 50 GPa (Dera et al. 2009). Natural high-pressure  $(\text{Fe},\text{Ni})_2\text{P}$ , allabogdanite, was  
64 discovered in a small iron meteorite Onello (Britvin et al. 2002) and was recently confirmed in two  
65 other irons belonging to the same Ni-rich ataxite group: Barbianello and Santa Catharina (Britvin et  
66 al. 2019b). The discovery of allabogdanite raises a question of proper (either LP or HP) diagnostic  
67 of natural, in particular meteoritic,  $(\text{Fe},\text{Ni})_2\text{P}$  minerals, as there is only one meteoritic barringerite  
68 (Buseck 1969) whose structural attribution was validated using an X-ray diffraction.

69 Barringerite is the most abundant phosphide mineral among terrestrial phosphide  
70 associations recently reported in a pyrometamorphic suite of the Hatrurim Formation, in the vicinity  
71 of the Dead Sea (in Israel and West Jordan) (Britvin et al. 2015, 2017b). During the ongoing  
72 research of those phosphide assemblages, we found that a complete series of solid solutions between  
73 barringerite-type polymorphs of  $\text{Fe}_2\text{P}$  and  $\text{Ni}_2\text{P}$  does exist in nature. The Ni-dominant member of the  
74 series, a new mineral, was named transjordanite, for the type locality on the Transjordan Plateau in  
75 West Jordan. Both the mineral and its name have been approved by the IMA Commission on New

76 Minerals, Nomenclature and Classification (IMA 2013–106). The holotype specimen of  
77 transjordanite is deposited at the Mineralogical Museum of the Department of Mineralogy, Saint  
78 Petersburg State University, St. Petersburg, Russia, catalogue number 19605. In the course of an  
79 investigation of meteoritic phosphide assemblages from a collection of the Mining Museum, Saint  
80 Petersburg Mining Institute (Britvin 2007), an interesting association of Fe<sub>2</sub>P–Ni<sub>2</sub>P minerals was  
81 revealed in the Cambria iron meteorite (fine octahedrite). Recent re-examination had showed that  
82 this assemblage contains Ni-dominant analogue of barringerite and thus comprises the first  
83 confirmed extraterrestrial occurrence of transjordanite. Whereas synthetic compounds along the join  
84 Fe<sub>2</sub>P–Ni<sub>2</sub>P are well studied owing to their promising magnetic properties (e.g., Zach et al. 2004;  
85 Balli et al. 2007), wear resistance (Sudagar et al. 2013) and catalytic applications (Hitihami-  
86 Mudiyansele et al. 2015; Wexler et al. 2016), the majority of Fe<sub>2</sub>P–Ni<sub>2</sub>P minerals have no  
87 characterization except of electron microprobe data. We herein provide a detailed report on naturally  
88 occurring transjordanite and its solid solutions with barringerite, in comparison with the reported  
89 data on their synthetic analogues.

90

### 91 **Occurrence of transjordanite**

92 The Hatrurim Formation, otherwise known as the Mottled Zone, has attracted significant  
93 mineralogical interest during the past decades. This is the world's largest, geologically juvenile suite  
94 of pyrometamorphic rocks whose outcrops are scattered over the area ~30,000 km<sup>2</sup> across the  
95 territory of Israel, Palestinian Authority and West Jordan. The description of geological setting and  
96 mineral assemblages of the Mottled Zone is given in a series of papers (Gross 1977; Burg et al.  
97 1999; Vapnik et al. 2007; Geller et al. 2012; Novikov et al. 2013; Kolodny et al. 2014; Sokol et al.  
98 2019). Phosphide assemblages of the Mottled Zone represent super-reduced part of its mineralogy  
99 (Britvin et al. 2015). The minerals related to barringerite-transjordanite series are the most abundant  
100 phosphides of the Mottled Zone, found both on Israel and Jordan shoulders of this formation.

101 Transjordanite from Jordan, including the holotype specimen, comes from the small phosphorite  
102 quarry in West Jordan (31° 21' 52" N, 36° 10' 55" E) which crops out the so-called “paralavas” of the  
103 Daba-Siwaqa complex. Paralavas comprise Cretaceous-Tertiary sediments (chalks and marls)  
104 melted at the temperature beyond 1100 °C, yielding different types of remelted basic silicate rocks.  
105 Phosphides, including minerals of transjordanite-barringerite series, are commonly confined to the  
106 interstices between calcined unmelted sediments and paralavas (Britvin et al. 2015). In the Hatrurim  
107 Basin (located a few km west of the southern subbasin of the Dead Sea, Israel), transjordanite was  
108 found in an unusual diopside microbreccia occurred in the midstream of the Nahal Halamish  
109 (Halamish wadi).

110 Cambria is a 16 kg iron meteorite found in 1818 nearby Lockport, Niagara County, New  
111 York, U.S.A., 43° 12' N, 78° 49' W. It belongs to a group of fine octahedrites (10.4 wt. % Ni) and is  
112 chemically classified as an ungrouped (anomalous) iron. A detailed description of the meteorite  
113 along with a review of early references is given by Buchwald (1975) who emphasizes that Cambria  
114 is a unique iron which apparently underwent a violent (perhaps shock-induced) event during its  
115 escape from the parent body. A characteristic feature of Cambria is its enrichment in troilite whose  
116 millimeter- to centimeter-sized nodules constitute up to 8 % of a surface of meteorite slices  
117 (Buchwald 1975). At the interface with encasing “kamacite” (Ni-rich variety of  $\alpha$ -iron), troilite  
118 nodules are encrusted with millimeter-thick rims of brecciated schreibersite. A few millimeter-sized  
119 chips of troilite-phosphide assemblages were extracted for the study from the Cambria specimen  
120 M9/1 stored in the Mining Museum, Saint Petersburg Mining Institute (Britvin 2007).

121

## 122 **Appearance and mineral associations**

123 Terrestrial transjordanite from the Hatrurim Formation appears as irregular grains reaching 0.2 mm  
124 in size which are disseminated in a matrix of altered diopside microbreccia (Fig. 1). The mineral is  
125 frequently corroded and replaced by the rims of polycrystalline murashkoite, FeP (Britvin et al.

126 2019c) (Fig. 1A, B). Associated phosphides may also include zuktamurite,  $\text{FeP}_2$ , negevite,  $\text{NiP}_2$ ,  
127 and halamishite,  $\text{Ni}_5\text{P}_4$  (Britvin et al. 2015, 2019a) whereas sulfides comprise pyrrhotite (Fig. 2A, B)  
128 and troilite. Other associated minerals are represented by hematite, magnetite, Cu-bearing trevorite,  
129 merrillite-like phosphate, and an intimate mixture of undefined phosphates and hydrous silicates  
130 (Fig. 1, Table S1). Late hydrothermal (or possibly, supergene) calcite fills up the interstices and  
131 fractures between phosphide-bearing assemblages. Transjordanite grains which compositionally  
132 approach  $\text{Ni}_2\text{P}$  end-member (Fig. 1C, D, Table 1) may contain molybdenite (exsolution?) lamellae  
133 cross-cutting the host transjordanite matrix. Molybdenite, in due course, is commonly replaced by  
134 powdery pseudomorphs of unidentified Ca molybdate (Fig. 1D, Table S1).

135 Mineral association of meteoritic transjordanite is completely different from that of terrestrial  
136 one. The examined sections of the Cambria meteorite are composed of recrystallized microgranular  
137 troilite (10-20  $\mu\text{m}$  grain size) stuffed with fragments of finely brecciated schreibersite (Fig. 2A).  
138 Schreibersite grains are cleaved by numerous shear fractures which are infilled with troilite. Both  
139 minerals show no signs of alteration along their interfaces, besides of partial replacement of troilite  
140 with supergene Fe-oxides. However, the smaller (less than 100  $\mu\text{m}$ ) schreibersite fragments  
141 dispersed in troilite are frequently encrusted with 5-10  $\mu\text{m}$ -thick, onion-like rims composed of  
142 submicrocrystalline transjordanite-barringerite aggregate (Fig. 2B, C) where the grain size could not  
143 be resolved using the SEM employed for imaging purposes (apparently less than 0.5  $\mu\text{m}$ ). It is  
144 noteworthy that the overall structure of phosphide-troilite assemblages found in the Cambria  
145 octahedrite almost entirely replicates the structure of schreibersite-barringerite-troilite interfaces  
146 described in the Ollague pallasite – the type meteorite where barringerite was discovered as a new  
147 mineral (Buseck 1969). Because Cambria and Ollague belong to different meteorite groups, the  
148 obvious similarity of their phosphide-troilite assemblages might provide some insights into post-  
149 formation thermal history of these meteorites which is discussed in concluding chapters.

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151  
152 **Analytical methods**  
153 Examination of the minerals under reflected light was carried out in rock sections embedded into  
154 epoxy resin and polished using conventional preparation techniques. Reflectance values were  
155 measured by means of a MSF-21 spectrophotometer (LOMO Company, St. Petersburg) using WTiC  
156 as a reflectance standard, monochromator slit of 0.4 mm with beam diameter of 0.1 mm. The  
157 Vicker's hardness was measured with PMT-3 microhardness tester (LOMO) under 20 g load.  
158 Energy-dispersive (EDX) compositional screening and elemental mapping was performed on  
159 carbon-coated sections using an Oxford Instruments AzTec Energy X-Max 20 spectrometer attached  
160 to a Hitachi S-3400N scanning electron microscope (SEM) operated at 20 kV accelerating voltage  
161 and 1 nA beam current. Electron microprobe data for selected grains (Tables 1 and 2) were obtained  
162 by means of an INCA WAVE 500 wavelength-dispersive (WDX) spectrometer attached to the same  
163 SEM under 20 kV accelerating voltage and 15 nA beam current, 2  $\mu\text{m}$  beam size, 20 s peak counting  
164 time, 10 s background counting time. The following standards were used: GaP ( $PK\alpha$ ), pyrite ( $FeK\alpha$ ,  
165  $SK\alpha$ ), metallic Cr ( $CrK\alpha$ ), Co ( $CoK\alpha$ ), Ni ( $NiK\alpha$ ), and Mo ( $MoL\alpha$ ). Phosphide grains selected for X-  
166 ray diffraction studies were hand-picked from the polished sections. Powder X-ray diffraction  
167 (PXRD) study was carried out by means of a Rigaku RAXIS Rapid II diffractometer equipped with  
168 a curved (semi-cylindrical) imaging plate (Debye-Scherrer geometry,  $r = 127.4$  mm) and  $CoK\alpha$ -  
169 radiation source (rotating anode, 40 kV, 15 mA), with Rigaku VariMax microfocus mirror optics. In  
170 order to achieve a better measurement accuracy, the imaging plate was calibrated against NIST Si  
171 640e standard. PXRD data aimed at determination of unit-cell parameters were acquired from  
172 undestroyed phosphide grains using a Gandolfi technique implemented in a Rigaku RAXIS Rapid II  
173 diffractometer (see above). PXRD patterns of the holotype specimen and of the mineral from the  
174 Cambria meteorite (Table S2) were obtained on powdered micro-spherical samples. Imaging plate-  
175 to-profile data conversion was performed using *osc2xrd* software (Britvin et al. 2017b). Unit-cell

176 refinements were carried out by Pawley full pattern decomposition (Pawley 1981) implemented in a  
177 Bruker Topas v. 5.0 software (Bruker 2014). The deviations of parameters determination was  
178 estimated by comparison of several testing duplicate datasets and was found to be  $\pm 0.0002$  Å for *a*  
179 parameter and  $\pm 0.0001$  Å for *c* parameter. Calculation of PXRD pattern for a holotype transjordanite  
180 (Table S2) was performed by means of a Stoe WinXPOW v. 2.08 software (Stoe 2003), taking  
181 atomic coordinates determined by the structure refinement from a single crystal and unit-cell  
182 parameters refined from powder diffraction data. X-ray single-crystal data collection for the  
183 holotype crystal of transjordanite was carried out by means of a Bruker Kappa APEX DUO  
184 diffractometer equipped with a microfocus MoK $\alpha$ -radiation source. A hemisphere of reciprocal  
185 space was collected using  $\phi$ - and  $\omega$ -scans at the frame width of 1°. Data collection and integration  
186 procedures (Table 3) were completed with Bruker APEX2 and SAINT software (Bruker 2003).  
187 Crystal structure was solved by a dual space method and refined to  $R_1 = 0.013$  by means of a  
188 *SHELX*-2014 software (Sheldrick 2015) incorporated into Olex2 program environment (Dolomanov  
189 et al. 2009). Full structural data on holotype transjordanite can be retrieved from the  
190 Crystallographic Information File (CIF) deposited in the Supplemental Data.

191

## 192 **Physical properties**

193 Terrestrial transjordanite from the Hatrurim Formation possesses grayish-white color under  
194 binocular and has a bright metallic luster. Transjordanite-barringerite aggregates from the Cambria  
195 meteorite exhibit gray color. In powdery state, the mineral is gray. In reflected light, transjordanite is  
196 white with beige tint. It is weakly bireflectant ( $\Delta R = 1.8$  % at 589 nm), non-pleochroic and weakly  
197 anisotropic. Reflectance values for the holotype specimen (analysis T03 in Table 1) are given in  
198 Table S3. Microhardness measured for a grain from the Hatrurim Basin (analysis H04 in Table 1) is  
199  $658 \text{ kg/mm}^2$  (average of 3 indentations). Transjordanite containing up to ~95 mol. % Ni<sub>2</sub>P is brittle.



200 However, upon further approaching Ni<sub>2</sub>P end-member (Fig. 1C,D; Table 1), the mineral becomes  
201 ductile. The ductility of synthetic Ni<sub>2</sub>P end-member was mentioned by Rundqvist (1962).

202 The densities calculated for nine Mo-free members of barringerite-transjordanite series  
203 exhibit quasi-linear dependence on Fe/Ni ratio (Fig. 3) which is consistent with the oppositely  
204 directed change of their *a* and *c* unit-cell parameters (Table S4). The obtained density values well  
205 coincide with the reference data reported for synthetic Fe<sub>2</sub>P, Ni<sub>2</sub>P and (Fe<sub>1.00</sub>Ni<sub>1.00</sub>)<sub>Σ=2.00</sub>P (Fruchart  
206 et al. 1969). Four terrestrial Mo-bearing barringerite-transjordanite members (Table 1) demonstrate  
207 an expected systematic increase of calculated density relative to Mo-free Fe<sub>2</sub>P–Ni<sub>2</sub>P solid solutions  
208 (Table S4, Fig. 3). In spite of a decreased accuracy of unit-cell parameters reported for barringerite  
209 from the Ollague pallasite (Buseck 1969), its density also well fits to a general compositional trend.

210 Qualitative testing of magnetic properties of barringerite-transjordanite grains under ambient  
211 conditions showed that they are non-ferromagnetic. This observation is consistent with the  
212 previously reported results for synthetic Fe<sub>2</sub>P–Ni<sub>2</sub>P solid solutions which exhibit the maximum  
213 value of the Curie point at 342 K (69 °C) and 0.16 Ni *apfu*, with an abrupt decrease of ferro- to  
214 paramagnetic transition temperature upon departure from this point (Fruchart et al. 1969; Fujii et al.  
215 1978).

216

## 217 **Chemical composition**

218 *Hatrurim Formation*. EDX screening of more than 200 phosphide-bearing assemblages from both  
219 Israel and West Jordan showed that there exists a complete series of natural solid solutions between  
220 Fe<sub>2</sub>P (barringerite) and Ni<sub>2</sub>P (transjordanite) end-members (Fig. 4). An important characteristic of  
221 these minerals is their intragrain compositional homogeneity – we did never observe chemical  
222 zoning across the dozens of studied grains. At the same time, several neighboring grains within an  
223 area of 5×5 mm<sup>2</sup> may differ in grain-to-grain composition from 0.07 to 1.97 Ni *apfu* (atoms per  
224 formula unit). A peculiar feature of terrestrial barringerite-transjordanite minerals is that they

225 frequently contain noticeable amounts of Mo (up to 3 wt. %) (Fig. 4, Table 1). Chromium and  
226 vanadium which were sporadically detected in barringerite (Britvin et al. 2017b) have never been  
227 encountered in transjordanite. The Co content in transjordanite is generally insignificant and  
228 sometimes falls beyond detection limit of WDX analysis (less than ~0.05 wt. %) (Table 1). The  
229 maximum Co content of ~0.7 wt. % was so far encountered in transjordanite grain with a  
230 composition approaching Ni<sub>2</sub>P end-member (Table 1, Fig. 1). For a crystal chemical study, an array  
231 of 12 grains was selected with the compositions having sufficiently uniform distribution along the  
232 join Fe<sub>2</sub>P–Ni<sub>2</sub>P (Table 1). The holotype specimen of transjordanite from West Jordan corresponding  
233 to (Ni<sub>1.72</sub>Fe<sub>0.27</sub>)<sub>Σ=1.99</sub>P<sub>1.02</sub> (analysis T03 in Table 1) was also included in this selection.

234 *The Cambria meteorite.* Barringerite-transjordanite aggregates replacing schreibersite in the  
235 Cambria octahedrite exhibit strong compositional zoning. The outer zones of contact with troilite are  
236 composed of transjordanite (max. Ni = 1.52 *apfu*) whereas inner shells adjoining schreibersite are  
237 represented by barringerite (max. Fe = 1.58 *apfu*), with a steep compositional gradient in between  
238 (Fig. 2D, 3, Table 2). The average rim composition determined from several areas corresponds to  
239 (Fe<sub>1.18</sub>Ni<sub>0.81</sub>Co<sub>0.01</sub>)<sub>Σ=2.00</sub>(P<sub>0.99</sub>S<sub>0.01</sub>)<sub>Σ=1.00</sub> – the formula which is remarkably close to  
240 (Fe<sub>1.14</sub>Ni<sub>0.83</sub>Co<sub>0.01</sub>)<sub>Σ=1.98</sub>P<sub>Σ=1.02</sub> of holotype barringerite from the Ollague pallasite (Buseck 1969).  
241 Meanwhile, the composition of schreibersite, (Fe,Ni)<sub>3</sub>P, which is a primary mineral relative to  
242 transjordanite-barringerite in Cambria (Fig. 2), is rather uniform from grain to grain. Schreibersite  
243 from Cambria has the atomic ratio Ni/(ΣFeNiCo) = 0.27 (Table 2) which is substantially different  
244 from that of schreibersite from Ollague having Ni/(ΣFeNiCo) = 0.36 (Buseck 1969). Almost all  
245 analyses of transjordanite-barringerite aggregates from Cambria show some content of sulfur (Fig.  
246 2D, 4; Table 2). In this respect, they resemble sulfur-bearing Fe<sub>2</sub>P–Ni<sub>2</sub>P minerals from CM2  
247 carbonaceous chondrites (Nazarov et al. 2009).

248

249 **Powder X-ray diffraction (PXRD) and crystal structure**

250 PXRD analysis aimed at determining the unit-cell parameters (Table S4) was carried out on 12  
251 grains of terrestrial transjordanite-barringerite whose chemical compositions are given in Table 1.  
252 Full PXRD data for a powdered sample of holotype transjordanite (analysis T03 in Table 1) and the  
253 Gandolfi data for transjordanite having the maximum Ni content (analysis H01) are given in Table  
254 S2. PXRD pattern of the mineral from the Cambria meteorite (Table S2) was obtained from an  
255 averaged powder sample comprising a continuous series of Fe<sub>2</sub>P–Ni<sub>2</sub>P solid solutions (*cf.* Fig. 4). In  
256 spite that it thus represents averaged values of *d*-spacings, it is unambiguously indexed in hexagonal  
257 (barringerite) setting, confirming its relation to barringerite structure type. Figure 5 shows the plots  
258 describing the dependence between unit-cell parameters of terrestrial transjordanite-barringerite  
259 minerals and their Ni content. Both *a* and *c* parameter curves exhibit complex, S-shaped  
260 dependencies which strongly violate Vegard's law (Zen 1956; Denton and Ashcroft 1991). At the  
261 same time, these profiles are consistent with the data by Fruchart et al. (1969) for the synthetic  
262 Ni<sub>2</sub>P–Fe<sub>2</sub>P compounds compositionally equilibrated at 850–900 °C (the blue plots on Fig. 5). The  
263 comparison of both datasets shows that the unit-cell parameters of the minerals are equal or larger  
264 than the corresponding values of their synthetic analogues. The latter evidences for a perfect *M*<sub>2</sub>P  
265 stoichiometry of examined minerals because deviations from the ideal *M*<sub>2</sub>P composition (caused by  
266 vacancies on the metal sites) would result in a significant (up to 0.1 Å) decrease of unit-cell  
267 parameters (Carlsson et al. 1973).

268 Vegard's law (Zen 1956; Denton and Ashcroft 1991) postulates a linear change of unit-cell  
269 parameters across a given series of solid solutions, provided that the substituting elements randomly  
270 occupy the permitted positions in the structure. Strong deviations from Vegard's law indicate a  
271 selective incorporation of substituting element into preferred structural positions, as it can be  
272 exemplified by the schreibersite–nickelphosphide series, Fe<sub>3</sub>P–Ni<sub>3</sub>P (Skála and Císařová 2005). The  
273 crystal structure of transjordanite (Fe<sub>2</sub>P structure type, Table 4) bears two independent metal sites.  
274 The metal atom at *M*(1) position is coordinated by four P atoms forming a distorted tetrahedron

275 [MP<sub>4</sub>] (Fig. 6). The metal occupying *M*(2) site is bonded to five P atoms in [MP<sub>5</sub>] square-pyramidal  
276 coordination (Table 3). The whole structure can be expressed as an interleaved sequence of two  
277 types of infinite rods propagating along the *c* axis (Fig. 6). The first rod type is composed of corner-  
278 sharing [M(1)P<sub>4</sub>] tetrahedra alternating with the empty square pyramids [□P<sub>5</sub>]. The next type of rods  
279 is built up of edge-sharing [M(2)P<sub>5</sub>] square pyramids alternating with the empty tetrahedra [□P<sub>4</sub>].  
280 The rods are arranged into a framework *via* common P–P edges of adjacent metal-phosphorus  
281 polyhedra. The combination of two metal-centered and two empty polyhedra can be expressed as a  
282 rhombohedral supercell highlighted on Fig. 6B (Fruchart et al. 1969). A study of Fe/Ni distribution  
283 between *M*(1) and *M*(2) sites by means of Mössbauer spectroscopy (Maeda and Takashima 1973)  
284 revealed rather unusual behavior of substituting metal: the substituent (either Fe into Ni<sub>2</sub>P or Ni into  
285 Fe<sub>2</sub>P) begins to incorporate exclusively into *M*(1) (tetrahedral) site until reaching a limit of about 30  
286 mol. % (0.6 *apfu*). Then the substitution continues almost randomly into *M*(1) and *M*(2) sites. Such a  
287 behavior readily explains the observed S-shaped profile of cell parameters *vs.* composition  
288 dependence plot (Sénateur et al. 1977). The knowledge of Fe/Ni substitution behavior allowed  
289 selection of a proper approach to refinement of site occupancies in the crystal structure of natural  
290 transjordanite. Upon testing of a free refinement of *M*(1) and *M*(2) site occupancies, the crystal  
291 structure of holotype transjordanite was finally refined with Fe being entirely incorporated into  
292 *M*(1) position (Table 4). The refined *M*(1) site occupancy was found to be (Ni<sub>0.86</sub>Fe<sub>0.14</sub>), in an  
293 excellent agreement with the formula (Ni<sub>1.72</sub>Fe<sub>0.27</sub>)<sub>Σ=1.99</sub>P<sub>1.02</sub> derived from electron microprobe data.

## 295 **Origin of the barringerite-transjordanite series minerals**

296 *Hatrurim Formation.* The intragrain homogeneity of terrestrial barringerite-transjordanite, their  
297 perfect *M*<sub>2</sub>P stoichiometry and Fe/Ni ordering suggest that these minerals were annealed in the solid  
298 state at the temperature permitting Fe/Ni diffusion processes. Based on the experiments on synthetic  
299 Fe<sub>2</sub>P–Ni<sub>2</sub>P system, one can suggest that the annealing temperature was not lower than 850–900 °C

300 (Fruchart et al. 1969).  $\text{Fe}_2\text{P}$  and  $\text{Ni}_2\text{P}$  melt congruently at 1370 and 1105 °C, respectively  
301 (Schmetterer et al. 2009; Okamoto 1990), hence phosphide crystallization and metal ordering could  
302 occur in the range between 850 and 1370 °C, i.e., either in the melted or solidified paralava (Vapnik  
303 et al. 2007). Phosphides could be equally formed by reduction of merrillite-type phosphates found in  
304 the same assemblages (Fig. 1, Table S1) or by gas-phase transport reactions involving phosphine  
305 and volatile metal-carbonyl complexes (Britvin et al. 2015). The latter mechanism can also be  
306 applied for explanation of high Ni and Mo content confined to phosphide minerals (Table 1, Fig. 4).

307 *Meteoritic occurrences.* Contrary to terrestrial mineral series, barringerite-transjordanite  
308 assemblages in Cambria exhibit strong chemical heterogeneity. At the same time, the adjacent relict  
309 schreibersite grains have rather uniform composition (Table 2, Fig. 2C, D). The various scenarios  
310 can be proposed for explanation of the emergence of the observed assemblages. The most  
311 straightforward one relies upon post-formational thermal history of both Ollague and Cambria  
312 meteorites. The Ollague pallasite was shown to be an artificially reheated fragment of the Imilac  
313 meteorite. It was suggested that barringerite in Ollague might represent a product of reaction  
314 between schreibersite and troilite during the annealing process (Buchwald 1976). Although Cambria  
315 did not undergo artificial treatment, it was severely ablated during penetration of the Earth's  
316 atmosphere (Buchwald 1975). Troilite nodules in Cambria are confined to a peripheral zone of the  
317 meteorite, and they were heavily annealed during ablation process (Buchwald 1975). In that case,  
318 the emergence of barringerite-transjordanite rims in Cambria could be explained by natural thermal  
319 annealing. However, the replacement of  $M_3\text{P}$  phosphide (schreibersite) by  $M_2\text{P}$  one (barringerite-  
320 transjordanite) would require an infusion of phosphorus into the system or removal of the metal  
321 from there. Therefore, taking into account short annealing time, the question persists concerning a  
322 chemical balance budget in the closed system.

323 The second possible scenario implies the formation of barringerite-transjordanite rims by  
324 replacement (or overgrowth) of schreibersite at a temperature below “freezing” of diffusion

325 processes in the Fe–Ni–P system, i.e., below 300 °C (Romig and Goldstein 1980). This could be  
326 accomplished after the completion of nebular condensation of schreibersite (Lodders 2003), but  
327 prior to accretion of troilite nodules, according to a scheme:  $2(\text{Fe,Ni})_3\text{P (solid)} + \text{P (vapor)} \rightarrow$   
328  $3(\text{Fe,Ni})_2\text{P (solid)}$ . This hypothesis places phosphide assemblages of Cambria and pallasites (Buseck  
329 1969; Zucchini et al. 2018) inline with the phosphides of carbonaceous chondrites (Gounelle et al.  
330 2003; Nazarov et al. 2009). A substantial argument supporting this point of view is noticeable sulfur  
331 content encountered in  $M_2\text{P}$  phosphides from Cambria (Table 2, Fig. 4) and CM2 chondrites  
332 (Nazarov et al. 2009).

333 One more hypothesis which is amongst those introduced by Buseck (1969) implies that  
334 barringerite in the Ollague pallasite (and thus in Cambria as well) can be a product of terrestrial  
335 weathering of schreibersite. This assumption is supported by the widespread industrial use of  
336 electroless Ni phosphides deposition in aquatic environment (Sudagar et al. 2013) and by finding of  
337 natural schreibersite formed at the deep-sea conditions (Borodaev et al. 1982). This interesting point  
338 of view readily explains the enrichment of barringerite-transjordanite in Ni, relative to schreibersite.  
339 In the meteorites, the  $M_3\text{P} \rightarrow M_2\text{P}$  replacement process would be accompanied by partial oxidation  
340 of phosphidic Fe to  $\text{Fe}^{3+}$ . The latter would precipitate in the form of iron hydroxides along the  
341 troilite-phosphide interfaces (Fig. 2). Such a process would be of great importance for elucidation of  
342 prebiotic phosphorylation pathways (Pasek et al. 2017; Kitadai and Maruyama 2018). It is not clear,  
343 however, why such a replacement has never been encountered among weathered troilite-  
344 schreibersite assemblages which are ubiquitous in iron and stony-iron meteorites (Buchwald 1975).

345

## 346 **Implications**

347 The importance of study of natural  $\text{Fe}_2\text{P}$ – $\text{Ni}_2\text{P}$  solid solutions relies upon their relation to the Fe-Ni-  
348 P system which is, along with the Fe-Ni-S and Fe-Ni-C ternaries, belongs to the most significant  
349 reduced cosmochemical systems. The knowledge of phase relationships and compositional

350 variations of Fe-Ni phosphide minerals has a broad range of implications, including the origin of  
351 Solar System, composition of deep planetary interiors, meteoritics, terrestrial processes in super-  
352 reduced environments, and processes of prebiotic phosphorylation occurred on early Earth.

353

354

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- 536

537 **List of figure captions**

538 **Figure 1.** Transjordanite assemblages in the Hatrurim Formation, Southern Levant. (A)  
539 Transjordanite in a matrix of altered paralava. Transjordan Plateau, West Jordan (the type locality).  
540 Photomicrograph in reflected light. (B) The same grain, SEM BSE image. Transjordanite is  
541 corroded by rims of murashkoite, FeP. (C) Transjordanite (Ni<sub>2</sub>P end-member) in phosphate-oxide  
542 assemblage. SEM BSE image. (D) Grain of transjordanite (H01 in Table 1) cross-cutted by altered  
543 molybdenite lamellae that are replaced by unknown hydrous Ca molybdate (Ca-Mo-O). (C) and (D):  
544 Nahal Halamish, Hatrurim basin, Israel. Abbreviations: Tj, transjordanite; Cal, calcite; Di, diopside;  
545 Mgt, magnetite; Mr, murashkoite; Po, pyrrhotite; Trv, trevorite, NiFe<sub>2</sub>O<sub>4</sub>; UN1 to UN6 – unknown  
546 phosphates and silicates (compositions are given in Table S1 in Supplementary Data).

547

548 **Figure 2.** Phosphide-troilite assemblages of the Cambria meteorite. (A) Fractured schreibersite  
549 grains (white with beige tint) in the matrix of microgranular troilite (tan-brown). Dark-gray:  
550 secondary iron hydroxides. Photomicrograph in reflected light. (B) Concentric phosphide  
551 assemblage in troilite matrix. The assemblage is composed of a pair of isometric grains of relict  
552 schreibersite (cores) replaced by a 5-10 µm onion-like barringerite-transjordanite shell.  
553 Photomicrograph in reflected light. (C) The same assemblage, false color BSE phase map. (D)  
554 Element concentrations across the profile depicted on (C). Note the steep Fe/Ni gradient across  
555 barringerite-transjordanite rim. Abbreviations: Tj, transjordanite; Br, barringerite; Schr,  
556 schreibersite; Tr, troilite; Fe-OH, secondary Fe hydroxides.

557

558 **Figure 3.** Calculated density plot for the minerals related to barringerite-transjordanite series. Black  
559 circles correspond to analyses of terrestrial Mo-free phosphides from the Hatrurim Formation. Red  
560 circles denote Mo-bearing compositions (Tables 1 and 6). Blue circles indicate (1) reference values  
561 for synthetic Fe<sub>2</sub>P, Ni<sub>2</sub>P and FeNiP (Fruchart et al. 1969), average density of the mineral from the

562 Cambria octahedrite (this work), and density of holotype barringerite from the Ollague pallasite  
563 (Buseck 1969).

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565 **Figure 4.** Ternary plots illustrating notable subordinate substitutions in the minerals related to the  
566 barringerite-transjordanite series, in atoms per  $M_2P$  formula unit (*apfu*). (A) Fe-Ni plot for terrestrial  
567 minerals with a statistics on Mo substitution. (B) Fe-Ni plot of phosphide rims in the Cambria  
568 meteorite showing subordinate S content which substitutes for P.

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570 **Figure 5.** Change of unit-cell parameters of terrestrial barringerite-transjordanite minerals along the  
571 join  $Fe_2P-Ni_2P$ . The circles correspond to  $a$  parameter, the squares denote  $c$  parameter. The black  
572 symbols relate to Mo-free minerals, the red ones mark Mo-bearing compositions. The blue graphs  
573 trace the reference data for the synthetic  $Fe_2P-Ni_2P$  solid solutions (Fruchart et al. 1969). The input  
574 analytical data are given in Tables 1 and 6.

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576 **Figure 6.** Crystal structure of transjordanite (structure type  $Fe_2P$ ). (A) Projection onto (0001). (B)  
577 Projection close to  $(1\bar{1}21)$ . A framework built up of two types of infinite rods propagating along  $c$   
578 axis. The type 1 rods are composed of corner-sharing  $[M(1)P_4]$  tetrahedra (green), the type 2 rods are  
579 represented by edge-sharing square pyramids  $[M(2)P_5]$  (yellow).

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583 **Tables**

584 **Table 1. Chemical composition of transjordanite-barringerite series minerals from the**  
 585 **localities of the Hatrurim Formation**  
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	Constituent (wt. %) <sup>a</sup>						Atoms per formula unit				
	Ni	Fe	Co	Mo	P	Total	Ni	Fe	Co	Mo	P
<b>H01</b> <sup>b</sup>	78.10	1.30	0.66	-	20.39	100.45	1.97	0.03	0.02		0.98
<b>H02</b>	73.34	6.05	0.34	-	20.65	100.38	1.84	0.16	0.01		0.98
<b>T03</b> <sup>c</sup>	67.80	10.20	-	-	21.50	99.50	1.72	0.27			1.02
<b>H04</b>	61.23	15.66	0.24	2.09	20.82	100.04	1.55	0.42		0.03	1.00
<b>H05</b>	52.16	25.28	0.10	1.47	20.66	99.67	1.32	0.67		0.03	0.99
<b>H06</b>	47.07	28.33	0.16	3.09	20.77	99.42	1.19	0.76		0.04	1.00
<b>T07</b>	29.23	49.97	-	-	21.34	100.54	0.72	1.28			0.99
<b>H08</b>	18.15	59.93	0.27	-	21.75	100.10	0.45	1.54			1.01
<b>H09</b>	12.66	64.61	0.09	1.86	21.15	100.37	0.32	1.67		0.03	0.98
<b>H10</b>	12.30	65.54	0.12	-	21.72	99.68	0.30	1.68			1.01
<b>H11</b>	9.46	69.39	0.13	-	21.60	100.58	0.23	1.77			1.00
<b>T12</b>	1.82	76.39	0.11	-	21.46	99.78	0.04	1.97			0.99

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588 <sup>a</sup> The bar '-' denotes values below detection limit (~0.05 wt. %). The first letter in sample  
 589 abbreviations: H, Halamish wadi, Israel; T, Transjordan Plateau, Jordan (the type locality).

590 <sup>b</sup>Corresponds to a grain depicted on Fig. 1D. <sup>c</sup>The holotype specimen.

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**Table 2. Chemical composition of transjordanite, barringerite and associated minerals from the Cambria meteorite <sup>a</sup>**

	<b>Tj</b>	<b>Br</b>	<b>Tj-Br</b>	<b>Schr</b>	<b>Tro</b>	<b>Km</b>
	<b>Wt. %</b>					
<b>Ni</b>	60.55	17.62	32.93	23.37 (1.08)	-	4.21
<b>Fe</b>	18.16	60.02	45.51	61.09 (1.19)	62.28 (0.19)	95.70
<b>Co</b>	0.26	0.28	0.27 (0.06)	0.23 (0.05)	0.27 (0.09)	0.48
<b>Cr</b>	-	-	-	-	0.36 (0.05)	-
<b>P</b>	20.53	21.49	21.05 (0.25)	15.45 (0.16)	-	-
<b>S</b>	0.27	0.22 (0.19)	0.31 (0.19)	-	36.97 (0.18)	-
<b>Total</b>	99.77	99.63	100.07	100.14	99.88	100.39
	<b>Atoms per formula unit (<i>apfu</i>)</b>					
<b>Σ <i>apfu</i></b>	3	3	3	4	2	1
<b>Ni</b>	1.52	0.43	0.81	0.80	-	0.040
<b>Fe</b>	0.48	1.58	1.18	2.19	0.978	0.955
<b>Co</b>	0.01	0.01	0.01	0.01	0.004	0.005
<b>Cr</b>	-	-	-	-	0.006	-
<b>Σ</b>	2.01	2.02	2.00	3.00	0.988	1.000
<b>P</b>	0.98	0.99	0.99	1.00	-	-
<b>S</b>	0.01	-	0.01	-	1.012	-
<b>Σ</b>	0.99	0.99	1.00	1.00	1.012	-

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 600 <sup>a</sup>Abbreviations: Tj, transjordanite, max. Ni content; Br, barringerite, max. Fe content; Tj-Br, average  
 601 composition of transjordanite-barringerite aggregates; Schr, schreibersite, average of 33 analyses;  
 602 Tro, troilite, average of 6 analyses; Km, “kamacite”. Standard deviations (esd, wt. %) are given in  
 603 parentheses. The bar ‘-’ denotes values below detection limit (~0.05 wt. %).  
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**Table 3. Crystal parameters, data collection, structure refinement details and bond lengths for holotype transjordanite**

<b>Crystal data</b>	
Chemical formula	$(\text{Ni}_{1.73}\text{Fe}_{0.27})_{\Sigma=2.00}\text{P}^a$
Crystal size (mm)	$0.08 \times 0.06 \times 0.05$
Crystal system, space group	Hexagonal, $\bar{P}62m$
$a, c$ (Å), $V$ (Å <sup>3</sup> ), $Z$	5.8897(3), 3.3547(2), 100.78(1), 3
$D_x$ (g/cm <sup>3</sup> )	7.297
<b>Data collection and refinement</b>	
Instrument	Bruker APEX DUO (CCD detector)
X-ray source and optics	MoK $\alpha$ , microfocus tube, 50 kV, 0.60 mA
$2\Theta$ range (°)	8.0–70.0 (truncated at 70 °)
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	3524, 192, 190
$h, k, l$ range	–9→9, –9→9, –5→5
$R_{\text{int}}, R_{\sigma}$	0.057, 0.022
$R_1$ ( $ F_o  \geq 4\sigma_F$ ), $wR_2$ , $S=GoF$	0.013, 0.024, 1.156
$\Delta\sigma_{\text{min}}, \Delta\sigma_{\text{max}}$ (e/Å <sup>3</sup> )	–0.57, 0.47
<b>Bond lengths (Å)</b>	
$M(1)$ —P1	2.2080(4) × 2
$M(1)$ —P2	2.2744(4) × 2
$M(2)$ —P1	2.4622(2) × 4
$M(2)$ —P2	2.3464(7)

<sup>a</sup> Determined by the site occupancy refinement.

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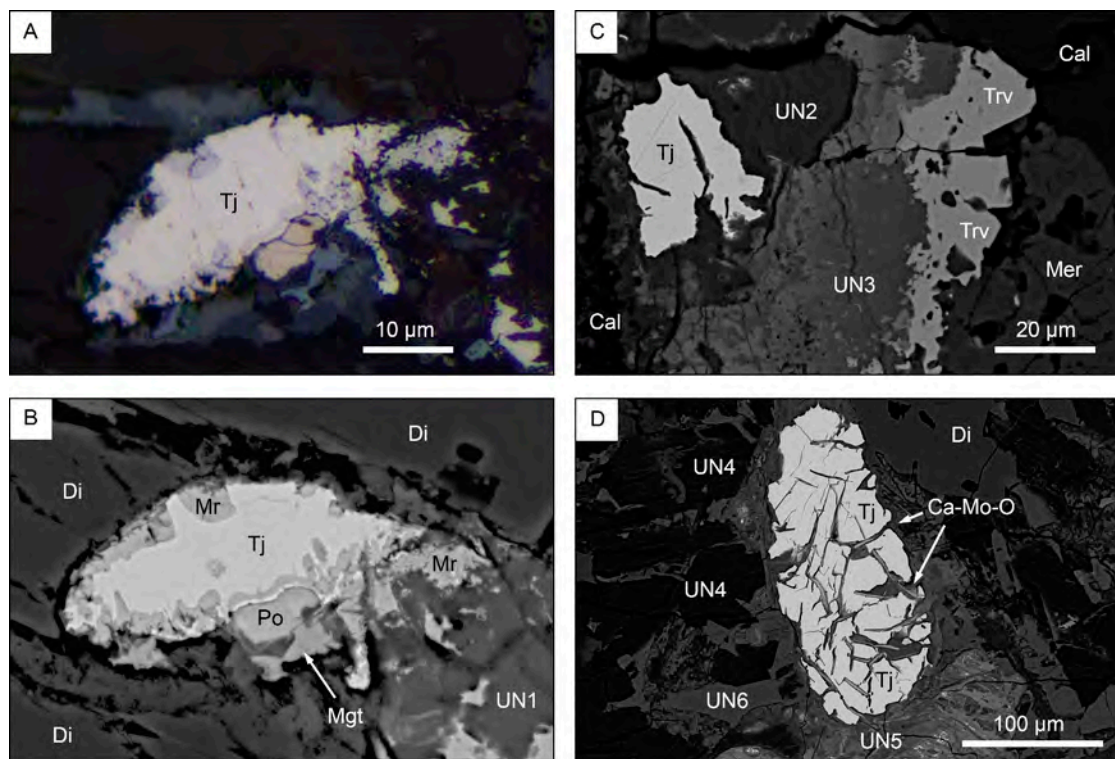
**Table 4. Fractional atomic coordinates and displacement parameters ( $\text{\AA}^2$ ) for holotype transjordanite**

Site <sup>a</sup>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>	<i>U</i> <sup>11</sup>	<i>U</i> <sup>22</sup>	<i>U</i> <sup>33</sup>	<i>U</i> <sup>12</sup>
<i>M</i> (1) (3 <i>f</i> ) <sup>b</sup>	0.73920(9)	0	0	0.00727(15)	0.0062(2)	0.0064(2)	0.0093(2)	0.00318(12)
<i>M</i> (2) (3 <i>g</i> )	0.39839(11)	0	1/2	0.01063(17)	0.0089(2)	0.0157(3)	0.0095(2)	0.00785(14)
P1 (2 <i>c</i> )	2/3	1/3	0	0.0075(2)	0.0058(3)	0.0058(3)	0.0107(5)	0.00292(15)
P2 (1 <i>b</i> )	0	0	1/2	0.0067(3)	0.0066(4)	0.0066(4)	0.0070(6)	0.0033(2)

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<sup>a</sup>Site multiplicities and Wyckoff symbols are given in parentheses. <sup>b</sup>Metal site occupancies: *M*(1), (Ni<sub>0.73</sub>Fe<sub>0.27</sub>); *M*(2), Ni<sub>1.00</sub>. *U*<sup>13</sup> and *U*<sup>23</sup> are equal to 0 by default.

623 **Figures**  
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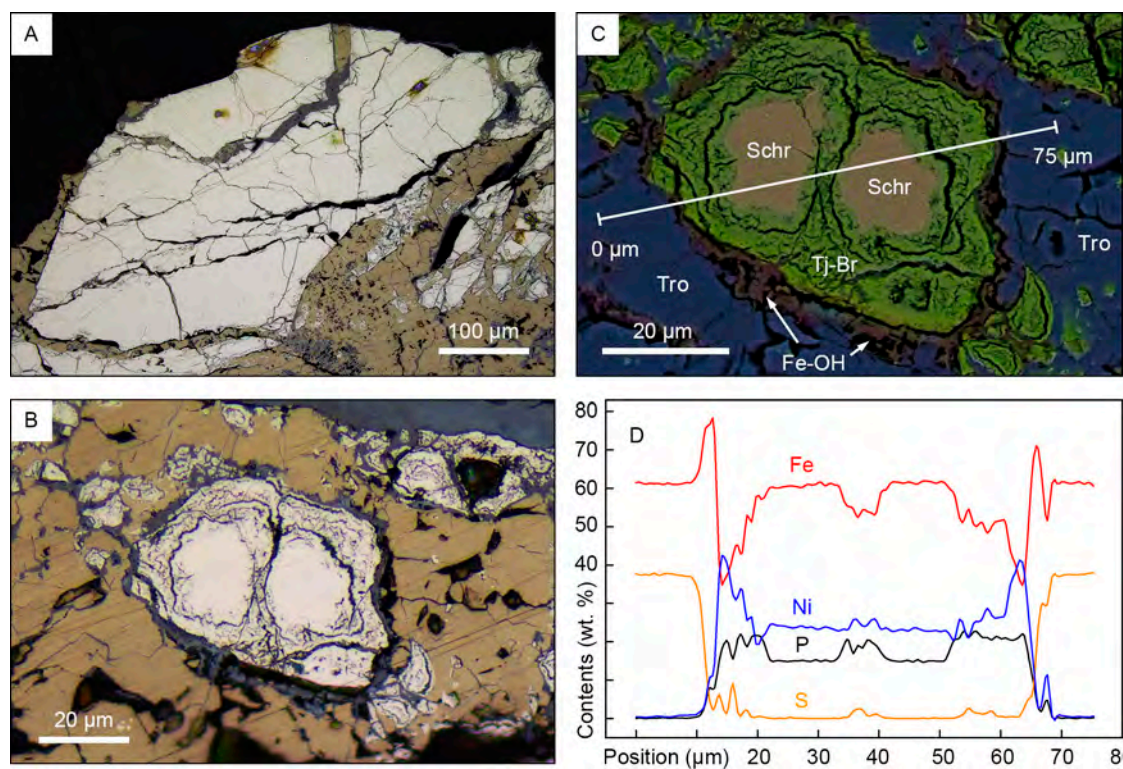


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**Figure 1**

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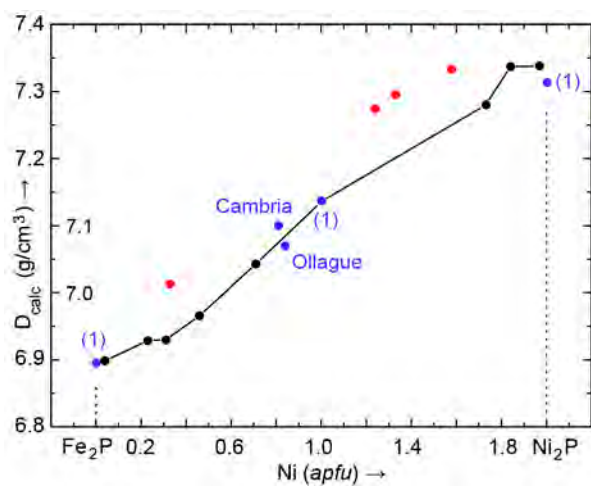
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Figure 2



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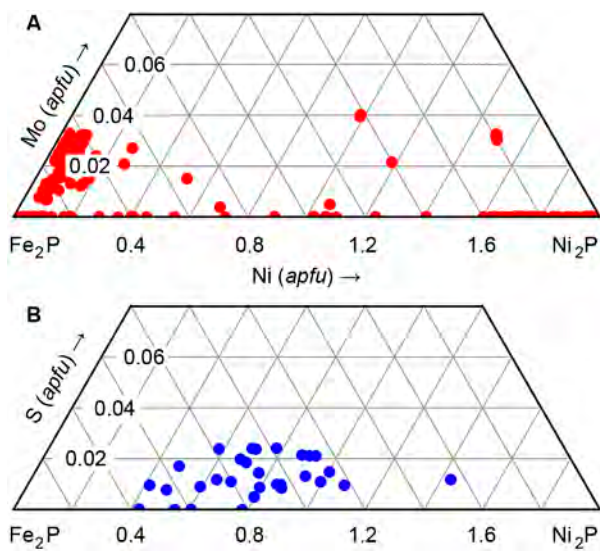
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Figure 3

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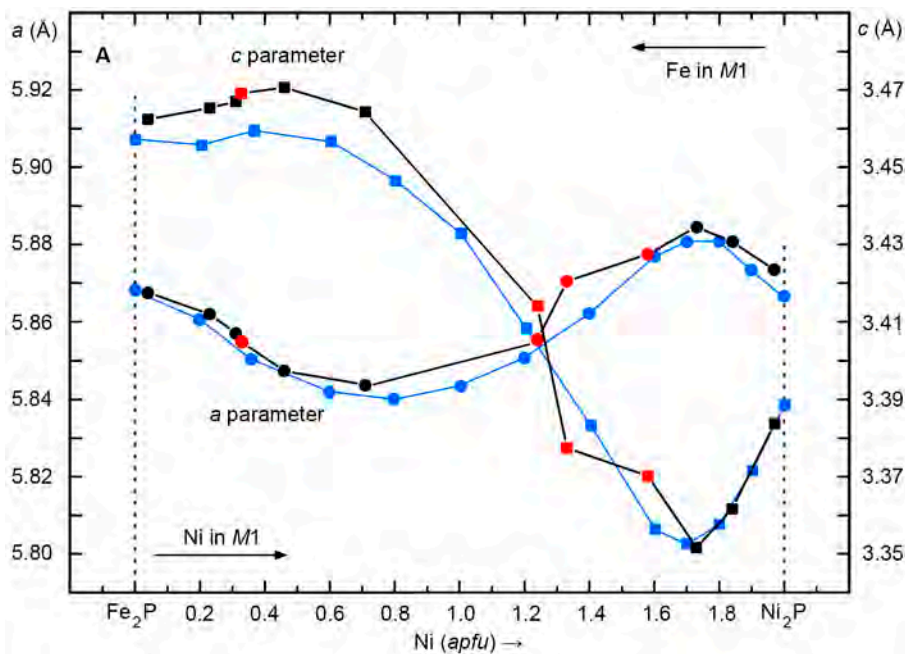
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Figure 4



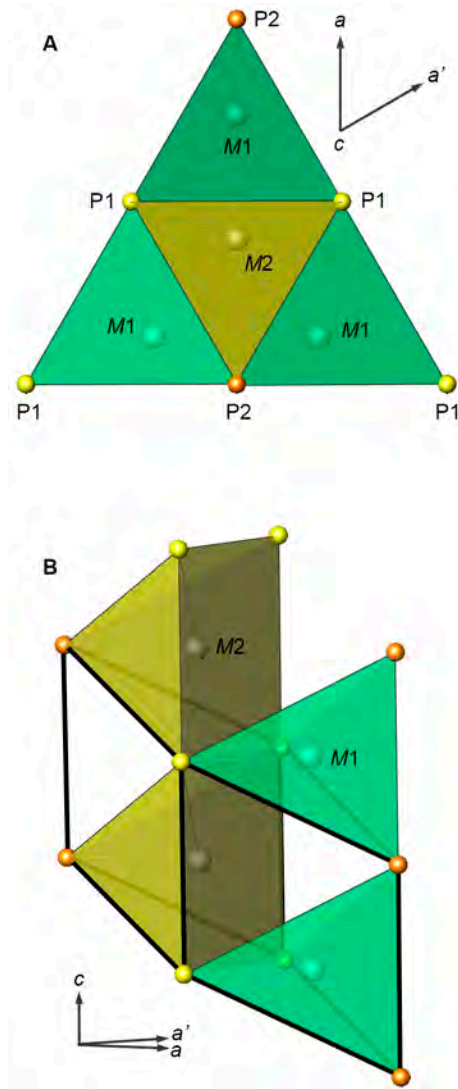
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Figure 5



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**Figure 6**