

1 **Revision 2**

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3 **Expanding the speciation of terrestrial molybdenum: discovery of polekhovskiyite, MoNiP₂,**
4 **and insights into the sources of Mo-phosphides in the Dead Sea Transform area**

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Abstract

21 Polekhovskiyite, MoNiP_2 , is the first terrestrial Mo phosphide, a phosphorus-rich homologue of
22 meteoritic monipite, MoNiP . The mineral represents a novel, phosphide type of terrestrial Mo
23 speciation. It was discovered among phosphide assemblages in pyrometamorphic rocks of the
24 Hatrurim Formation (the Mottled Zone) in Israel, the area confined to the Dead Sea Transform fault
25 system. Polekhovskiyite occurs in the altered diopside microbreccia, as micrometer-sized euhedral
26 crystals intimately intergrown with murashkoite, FeP , and transjordanite, Ni_2P , in association with
27 Si-rich fluorapatite, hematite and magnetite. In reflected light, the mineral has a bluish-grey colour
28 with no observable bireflectance and anisotropy. Chemical composition (electron microprobe,
29 wt.%): Mo 44.10, Ni 22.73, Fe 4.60, P 29.02, total 100.45, that corresponds to the empirical formula
30 $\text{Mo}_{0.99}(\text{Ni}_{0.83}\text{Fe}_{0.18})_{1.01}\text{P}_{2.01}$ and leads to the calculated density of 6.626 g cm^{-3} . Polekhovskiyite is
31 hexagonal, space group $P6_3/mmc$, a 3.330(1), c 11.227(4) Å, V 107.82(8) Å³, and $Z = 2$. The crystal
32 structure has been solved and refined to $R_1 = 0.0431$ based on 50 unique observed reflections. The
33 occurrence of Mo-bearing phosphides at the Dead Sea Transform area is a regional-scale
34 phenomenon, with the localities tracked across both Israel and Jordan sides of the Dead Sea. The
35 possible sources of Mo required for the formation of Mo-bearing phosphides are herein reviewed;
36 they are likely related to the processes of formation of the Dead Sea Transform fault system. The
37 problem of anthropogenic contamination of geological samples with Mo and Ni is also discussed in
38 the paper, in context of the general aspects of discrimination between natural and technogenic ultra-
39 reduced phases.

40

41 **Keywords:** molybdenum, phosphide, pyrometamorphism, meteorite, carbonaceous chondrite, Ca-
42 Al-rich inclusions, Dead Sea Rift, anthropogenic contamination

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Introduction

45 Molybdenum, as an element, is a sensitive geochemical marker whose redox and isotopic
46 speciation allows tracing diverse planetary processes (Kendall et al. 2017; Greaney et al. 2018). The
47 dominant Mo mineral in the lithosphere is its sulfide, molybdenite MoS_2 , which crystallizes in
48 systems where the nearest relative of Mo, tungsten, appears in the form of tungstate anions, $(\text{WO}_4)^{2-}$
49 (Smedley and Kinniburgh 2017). It is noteworthy that the rich family of oxygen-bearing Mo
50 minerals (more than 60 species) owes its diversity to the secondary oxidation of molybdenite,
51 usually under aquatic environments (Greaney et al. 2018). The rare exceptions not related to
52 molybdenite are confined to volcanic exhalations (Pekov et al. 2020), where pre-sublimation
53 speciation of Mo is obscure. Thiomolybdates – the anions intermediate between $(\text{MoO}_4)^{2-}$ and
54 $(\text{MoS}_4)^{2-}$ – are believed to play an important role in the aquatic behaviour of Mo (Erickson and Helz
55 2000). However, until now, thiomolybdates were not recognized as mineral species in the solid
56 state. Altogether, the fate of Mo in the lithosphere can be expressed as a redox-dependent cycling
57 between its sulfide and oxide forms (Erickson and Helz 2000; Greaney et al. 2018). In meteorites,
58 molybdenite was for a long time the sole known Mo mineral (Fuchs and Blander 1977; Armstrong
59 et al. 1987). It is a rare constituent of specific assemblages called Fremdlinge (El Goresy et al.
60 1978). The latter represent the opaque, μm - to mm-sized droplets consisting of Fe-Ni metal, sulfides
61 with inclusions of refractory metal alloys, oxides, silicates and phosphates (El Goresy et al. 1978).
62 Fremdlinge occur in CV3 carbonaceous chondrites, where they are found within calcium-aluminium
63 rich inclusions (CAI) - the oldest known objects in the Solar System (Amelin et al. 2010). Recent
64 investigations revealed that Fremdlinge may bear a diverse suite of Mo-minerals not limited to
65 sulfides and oxides, including the first natural Mo-phosphide, monipite MoNiP (Ma et al. 2014).

66 In the course of ongoing research of phosphide assemblages of the Hatrurim Formation in
67 Israel and West Jordan, the substantial enrichment in Mo was revealed among phosphides described
68 in this area (Britvin et al. 2020a, 2021b). Phosphide speciation of Mo is quite unusual for Earth, as

69 emphasized by the present discovery of the first known terrestrial Mo-phosphide, MoNiP₂ which is,
70 from the chemical point of view, is a higher phosphide homologue of meteoritic mineral monipite,
71 MoNiP (Ma et al. 2014). We herein present the description of this mineral, named polekhovskiyite in
72 honour of Yury Stepanovich Polekhovskiy (1947–2018), Russian geologist and mineralogist, for his
73 contributions to the studies of opaque minerals, including phosphides (Britvin et al. 2015; 2019a,b;
74 2020a,b). Both the mineral and its name have been approved by the Commission on New Minerals,
75 Nomenclature and Classification, International Mineralogical Association (2018-147). The holotype
76 specimen of polekhovskiyite is deposited in the collections of the Fersman Mineralogical Museum of
77 the Russian Academy of Sciences, Moscow, Russia, with the registration number 5287/1. Besides
78 the report on a new mineral, the sources of Mo in phosphides of the Mottled Zone are herein
79 discussed, which were likely linked to the onset of activity at the Dead Sea Transform fault system.
80 Last but not least, the present article touches on the persistent problem of anthropogenic
81 contamination of heavy mineral concentrates with Ni and Mo, following the discussions raised in
82 the recent works by Litasov et al. (2019, 2020) and Ballhaus et al. (2021).

83

84 **The Hatrurim Formation**

85 This rock complex is located in the Levant region of the Middle East (Britvin et al. 2021a)
86 (Fig. 1). The term "Hatrurim Formation" was originally introduced to describe a suite of
87 metamorphosed sediments constituting the Hatrurim Basin – a hilly terrain that occupies an area of
88 about 50 km² in the vicinity of the Dead Sea, ca. 15 km northwest of Mount Sedom (Gross 1977)
89 (Fig. 1). Another common name for this suite, "the Mottled Zone" (Picard 1931), emphasizes the
90 unusual coloration and patchy structures of its diverse metamorphic lithologies. Today, the names
91 "Hatrurim Formation" and "the Mottled Zone" are often used in a broader sense – to refer to the
92 world's largest suite of pyrometamorphic rocks whose outcrops are exposed over an area of
93 150×200 km around the Dead Sea Transform (traced by the Jordan valley), encompassing central to

94 north Israel, West Bank and central to west Jordan (Fig. 1) (e.g., Burg et al. 1992; Vapnik et al.
95 2007; Novikov et al. 2013).

96 The rugged terrain of the Hatrurim Basin in the Negev desert, Israel, is composed of
97 numerous hills up to 80 m in relief, dissected by a system of dry wadi – tributaries to the Dead Sea
98 (e.g., Britvin 2021b). The lack of vegetation and quaternary cover (Fig. 2a, 2c) affords favorable
99 conditions for the sampling of metamorphic rocks. The latter appear as cliffs and lenses composed
100 of diverse lithologies produced by combustion metamorphism (pyrometamorphism) – a process
101 involving high-temperature and low-pressure calcination and fusion of the sediments (e.g., Vapnik
102 et al. 2015). The conditions of metamorphism corresponded to sanidinite facies; the local
103 temperatures might reach 1200–1450 °C at near-atmospheric pressure (Sharygin et al. 2016). The
104 main types of pyrometamorphic rocks are spurrite, gehlenite, larnite marbles, and anorthite–
105 pyroxene hornfelses (Gross 1977). The fused rocks, called paralavas (Vapnik et al. 2007), are less
106 common. The total preserved thickness of metamorphic complex is about 100 m (Fig. 3). The
107 stratigraphic equivalent of the Mottled Zone in Israel is the Ghareb and Taqiye chalky–marly
108 sequence of Maastrichtian to Paleocene age (Gross 1977) (Fig. 3). The upper contacts of
109 phosphorites of the Mishash Formation (Campanian age) underlying the Mottled Zone (Fig. 3) are
110 sporadically affected to pyrometamorphic alteration.

111 The largest pyrometamorphic massif of the Hatrurim Formation is the Daba-Siwaqa
112 complex, which occupies 330 km² of the Transjordan Plateau, 25–80 km south of Amman, Jordan
113 (Fig. 1). The metamorphic rocks of Daba-Siwaqa appear as a chain of 30–80 m high hills on the
114 plateau composed of Maastrichtian–Danian bituminous chalk, Paleocene limestone (Muwaqqar
115 Formation) and Eocene chert and limestone (Umm Rijam Formation) (Novikov et al. 2013; Al-
116 Tawalbeh et al. 2017) The total preserved thickness reaches 200 m (Fig. 3). Pyrometamorphic rocks
117 are represented by spurrite and fluorapatite marbles with a few occurrences of larnite marbles.
118 Paralavas were revealed at one locality.

119 Pyrometamorphic lithologies of the Mottled Zone, both in Israel and Jordan, were subjected
120 to pronounced hydrothermal alteration and weathering (Gross 1977; Burg et al. 1992; Khoury 2020).
121 Altogether, superposition of various processes has resulted in an unprecedented mineral diversity
122 (more than 240 species), ranging from reduced associations of phosphides and Ca-sulfides (Britvin
123 et al. 2015; Galuskina et al. 2017) to extremely oxidized assemblages containing chromate(VI) and
124 selenate(VI) ions, $(\text{CrO}_4)^{2-}$ and $(\text{SeO}_4)^{2-}$ (Juroszek et al. 2020).

125 According to K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating of pyrometamorphic rocks of the Hatrurim Basin,
126 the major metamorphic events at the Mottled Zone might occur in Miocene (16 Ma) and Pliocene–
127 Pleistocene (4.0–1.5 Ma), although age determinations of 200 Ka were also reported (Burg et al.
128 1992; Gur et al. 1995 and the references cited therein). The Miocene event chronologically coincides
129 with the separation of Israel from the Arabian Plate by the Dead Sea Transform fault (Ben-Avraham
130 et al. 2008). Although the Mottled Zone was studied since the beginning of the last century (Picard
131 1931), the origin of this rock complex is still a matter of debates. The most popular hypotheses
132 include the spontaneous combustion of dispersed organic matter in the chalky–marly sequence of
133 the Maastrichtian and Paleocene age (Gross 1977) or oil-gas (methane) firing induced by mud
134 volcanism (Novikov et al. 2013). The recent mineralogical records evidence for possible high-
135 pressure processes that could take place in this region, where the pressures could reach 25 GPa
136 (Britvin 2021b, 2022). This might open new insights into the primary event(s), such as large-scale
137 earth-meteoroid collision, which could be responsible for the initiation of combustion processes in
138 the Mottled Zone.

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140 **Phosphides of the Mottled Zone**

141 Phosphides are the principal carriers of reduced phosphorus in the solar system, but until the
142 findings in the Hatrurim Formation, these minerals were practically unknown on Earth (Britvin et al.
143 2021c). Since the first report on phosphide occurrences in the Mottled Zone (Britvin et al. 2015),

144 these minerals were recognized at three localities on both sides of the Dead Sea (Fig. 1): in natural
145 outcrops at wadi Halamish and wadi Zohar in the southern part of the Hatrurim Basin, Israel (Britvin
146 et al. 2015; Galuskin et al. 2020) (Fig. 2a, 2c) and in the phosphorite quarry which exposes
147 pyrometamorphic rocks of the Daba-Siwaqa complex in Jordan (Britvin et al. 2015) (Fig. 2e). In the
148 Hatrurim Basin, phosphide-bearing lithologies were primarily found in several detrital blocks, and
149 subsequently revealed in a ~2×2 m bedrock outcrop (Fig. 2a and 2c). In Jordan, phosphide
150 assemblages can be found in the quarry highwalls and in the detached meter-sized rock blocks (Fig.
151 2e). In wadi Halamish (Israel) and Daba-Siwaqa quarry (Jordan), phosphides are confined to
152 diopside-dominant rocks - paralavas and microbreccias (the latter likely represent hydrothermally
153 altered paralavas) (Fig. 2b and 2f). Chemical and mineral composition of these rocks was previously
154 reviewed by Britvin et al. (2019b). In wadi Zohar (Israel), phosphide assemblages were found in
155 gehlenite rocks – microbreccias and paralavas described by Galuskin et al. (2020) and Britvin et al.
156 (2022) (Fig. 2d). In all reported localities, mineral assemblages are often much enriched in
157 phosphides, whose nests, resembling sulfides in appearance, can reach 1 cm in size (Fig. 4). In total,
158 nine phosphide species belonging to the system Fe-Ni-P were discovered, among those six minerals
159 are new in nature (Britvin et al. 2020c). Molybdenum phosphides are represented by
160 polekhovskiyite, MoNiP_2 described herein, nickolayite FeMoP (Murashko et al. 2019) and
161 orishchinite, $(\text{Ni,Fe,Mo})_2\text{P}$ (Britvin et al. 2019c), which are rare but were found on both sides of the
162 Dead Sea – in Israel (polekhovskiyite) and in Jordan (nickolayite and orishchinite). Subordinate
163 contents of Mo (up to 3 wt.%) are typical in the most common phosphides belonging to the
164 transjordanite-barringerite series, $\text{Ni}_2\text{P-Fe}_2\text{P}$, both in Israel and Jordan (Britvin et al. 2020a, 2021b).

165 Phosphide assemblages, once formed, were affected by a subsequent high-temperature
166 alteration – oxidative pyrolysis, which resulted in the formation of specific phosphate minerals, such
167 as pyrophosphates and cyclophosphates, with further oxidation to hematite (Britvin et al. 2021a).
168 The geochemical processes which could lead to the emergence of phosphides in the Hatrurim

169 Formation were discussed by Britvin et al. (2015, 2021a). The suggested pathways are focused on
170 the co-reduction of phosphates with Fe and Ni oxides. Phosphates could be represented by
171 fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, which is ubiquitous in the Mottled Zone (Gross 1977), and less common
172 keplerite, $\text{Ca}_9(\text{Ca}_{0.5}\square_{0.5})\text{Mg}(\text{PO}_4)_7$ (Britvin et al. 2021d). The oxide concentrators of Ni are trevorite,
173 NiFe_2O_4 , and bunsenite, NiO (Britvin et al. 2015; Sokol et al. 2020). The formation of phosphides
174 *via* phosphate reduction by dihydrogen, carbon or methane was well explored in synthetic chemistry
175 and metallurgy (Lazoryak et al. 2003; Voncken et al. 2006; Burns et al. 2007). The lowermost
176 thermal limits required for the initiation and maintenance of reduction processes (550–750 °C) agree
177 with the formation temperatures of natural phosphides, which were below 850–900 °C (Britvin et al.
178 2020b, 2021b). Based on the current hypotheses on the genesis of the Mottled Zone (Gross 1977;
179 Novikov et al. 2013), one can suggest that either dispersed bitumen or natural methane could serve
180 as reducing agents. The recent discovery of encapsulated molecular dihydrogen in phosphide-
181 bearing assemblages of wadi Zohar (Galuskin et al. 2020) (Fig. 2c) suggests that native dihydrogen
182 could also play a role of reductant. Consideration of lightning strikes (Pasek and Block 2009) as
183 reduction drivers can not be ruled out (Britvin et al. 2015), although the confinement of phosphide
184 mineralization to the deep zones of metamorphosed strata (e.g., in the Jordan quarry) makes this
185 hypothesis less realistic.

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Analytical methods

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The rock piece containing phosphide assemblages was cut into a few slices, which were
polished and coated with carbon film. It should be emphasized that none of the phosphide-bearing
samples was affected to any mechanical grinding or crushing – all phosphide grains were found *in-*
situ in the polished sections. The thick section containing polekhovskiyte was first examined under
scanning electron microscope (Hitachi S-3400N) and chemically characterized using an Oxford
Instruments AzTec Energy X-Max 20 EDX spectrometer at 10 kV acceleration voltage and 0.2 nA

194 beam current. The metal analytical standards were used to measure Fe, Ni, Co ($K\alpha$ -series) and Mo
195 ($L\alpha$), whereas P was measured against InP standard ($PK\alpha$). The absence of S and Co was further
196 confirmed qualitatively using an INCA WAVE 500 WDX spectrometer (20 kV, 15 nA). After
197 removal of carbon coating, phosphide assemblages were examined in reflected light under optical
198 microscope. A grain containing the biggest polekhovskite crystals was manually removed from the
199 section and was subjected to X-ray single-crystal study. Because of the small size of polekhovskite
200 crystals (2 to 3 μm , Fig. 5), we did not attempt to extract a single crystal of the mineral. Instead, the
201 whole phosphide assemblage (murashkoite with the embedded polekhovskite crystals) was used for
202 data collection. A hemisphere of reciprocal space was collected by means of a Bruker Kappa APEX
203 DUO CCD diffractometer using $MoK\alpha$ radiation (frame width 0.5° ; exposure time 360 s per frame).
204 Subsequent data processing was performed using CrysAlisPro v.171.41 program package (Rigaku
205 Oxford Diffraction). The CrysAlisPro software allows extracting and independent refinement of up
206 to 8 orientation (UB) matrices related to separate single crystal domains. In our case, one could
207 recognize 1 UB matrix related to the host murashkoite crystal and 4 randomly oriented UB matrices
208 of $MoNiP_2$. Subsequent integration of each of the four $MoNiP_2$ matrices allowed selection of the
209 best integrable domain, which was used for structure solution and refinement. The crystal structure
210 of polekhovskite has been solved by the dual space method and refined to $R_1 = 0.0431$ using a
211 *SHELX-2018* set of programs (Sheldrick 2015), via an Olex2 v.1.2.8 graphical user interface
212 (Dolomanov et al. 2009). The details of data collection, integration procedures and structure
213 refinement can be retrieved from the crystallographic information file (CIF) included into
214 Supplementary data. Powder X-ray diffraction pattern of polekhovskite was calculated with Stoe
215 WinXPOW software (Stoe and Cie GmbH).

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Occurrence, appearance and chemical composition

218 Polekhovskite was found in phosphide-bearing rocks collected at the Nahal Halamish – a
219 wadi passing approximately in longitudinal direction through the southern part of the Hatrurim
220 Basin, Negev desert, Israel (Britvin et al. 2015) (Fig. 1, 2a). Phosphide assemblages are confined to
221 severely altered diopside microbreccias enriched in hematite and magnetite (Fig. 2b). Thauasite,
222 tobermorite and a suite of other, poorly defined Ca- and Mg-Fe hydrous secondary silicates serves
223 as a binder for diopside crystals. A complete list of rock-forming minerals and their compositions
224 was reported by Britvin et al. (2019b). Si-Fe-bearing fluorapatite,
225 $(\text{Ca}_{4.37}\text{Fe}^{2+}_{0.16})_{4.48}(\text{P}_{2.88}\text{Si}_{0.16})_{3.04}\text{O}_{11.49}\text{F}_{1.02}$, commonly occurs in the same association (Fig 5a).
226 Polekhovskite appears as euhedral crystals up to 3 μm in size intimately intergrown with
227 murashkoite (FeP) or rimming transjordanite grains (Ni_2P) (Fig. 5). It has a bluish-grey colour in
228 reflected light (Fig. 5b), with no observable bireflectance and anisotropy. Reflectance and
229 microhardness could not be measured because of the small crystal size. Chemical composition of the
230 mineral is given in Table 1. Taking into account the results of structure refinement, the empirical
231 formula can be written as $\text{Mo}_{0.99}(\text{Ni}_{0.83}\text{Fe}_{0.18})_{1.01}\text{P}_{2.01}$ (based on 4 atoms per formula unit),
232 corresponding to the ideal one MoNiP_2 . The density calculated from the empirical formula and unit-
233 cell parameters is 6.626 g cm^{-3} . From the chemical point of view, polekhovskite can be regarded a
234 higher phosphide homologue of meteoritic monipite, MoNiP (Ma et al. 2014).

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236 **X-ray powder diffraction and crystal structure**

237 The insufficient amount of polekhovskite precluded obtaining X-ray powder diffraction
238 data. However, its calculated powder pattern conforms to synthetic MoNiP_2 (Guérin 1976) (Table
239 2). Taking into account that natural polekhovskite has a mixed (Ni,Fe) site population, its unit-cell
240 parameters can be regarded as identical to the parameters of synthetic MoNiP_2 (Table 3). The crystal
241 structure of polekhovskite belongs to its own, MoNiP_2 structure type (Guérin et al. 1975; Guérin
242 and Sergent 1976). The structural framework is built up of the two kinds of $[\text{MP}_6]$ polyhedra (Fig.

243 6a), whose population refinement revealed the perfect ordering between Mo and (Ni,Fe).
244 Molybdenum incorporates into trigonal prisms [MoP₆] [$d(\text{Mo-P}) = 2.462(4) \text{ \AA}$], whereas Ni and Fe
245 populate [(Ni,Fe)P₆] octahedra [$d(M-P) = 2.304(3) \text{ \AA}$] (Fig. 6a). The coordination numbers of Mo
246 and (Ni,Fe) in polekhovskiyite are higher than those in synthetic analogue of monipite (Guérin and
247 Sergent 1977) (Fig. 6b) – a structural consequence of the lower metal-to-phosphorus ratio in
248 MoNiP₂ (1:1) relative to MoNiP (2:1).

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250 **Polekhovskiyite, MoNiP₂, vs. monipite, MoNiP: formation factors**

251 A lack of sufficient knowledge of the phase relations in the Mo–Ni–P system (Oryshchyn et
252 al. 2001) allows only rough assessment of the conditions that governed the formation of
253 polekhovskiyite, MoNiP₂ instead of its nearest chemical relative, monipite, MoNiP. The synthesis of
254 both phosphides is accomplished under the same oxygen-free environment, in the solid state at 800-
255 1200 °C (Guérin and Sergent 1976, 1977). Therefore, the factor which likely determined the
256 emergence of a certain phosphide is a metal-to-phosphorus ratio: crystallization of polekhovskiyite
257 apparently proceeded at higher phosphorus potential than crystallization of monipite. The deficiency
258 of phosphorus during monipite formation is supported by the presence of (Ru,Mo,Ni) alloy and
259 awaruite in the same Fremdling (Ma et al. 2014). In contrast, polekhovskiyite assemblages do not
260 contain metal alloys, but include murashkoite that has the same $M:P$ atomic ratio equal to 1 ($M = \text{Fe},$
261 Ni, Mo). The morphological relationships between phosphides evidence that polekhovskiyite was
262 formed after transjordanite but prior to murashkoite, according to the sequence: Ni₂P ($M:P = 2$) →
263 MoNiP₂ ($M:P = 1$) → FeP ($M:P = 1$). Therefore, one can assume that polekhovskiyite crystallization
264 was realized due to the excess of phosphorus not accommodated by already crystallized Ni₂P
265 (transjordanite). In this respect, one should emphasize the extreme level of Mo fractionation
266 between these phosphides. Transjordanite contains less than 1.4 wt.% Mo, in contrast to 44 wt.% in
267 polekhovskiyite (Table 1). However, it was shown that transjordanite is capable of incorporating

268 more than 3 wt.% Mo (Britvin et al. 2020a), by substitution of five-coordinated Ni towards
269 isostructural monipite: $\text{Ni}^{\text{IV}}\text{Ni}^{\text{V}}\text{P}$ (transjordanite) \rightarrow $\text{Ni}^{\text{IV}}\text{Mo}^{\text{V}}\text{P}$ (monipite). Therefore, transjordanite
270 in the given assemblages is undersaturated with respect to Mo. Consequently, it can be inferred that
271 the growth of polekhovskyite proceeded under unequilibrated conditions: it was either very fast or
272 was accomplished at low temperature precluding interphase Mo diffusion.

273

274 **Some insights into the origin of Mo phosphides in the Mottled Zone**

275 The available data suggest that the enrichment of phosphide assemblages in Mo is a regional-
276 scale phenomenon, which encompasses the localities separated by a distance of ~100 km, on both
277 Israel and Jordan sides of the Dead Sea (Britvin et al. 2020a, 2021b) (Fig. 1). Molybdenum contents
278 up to 3 wt.% are commonly detected in the minerals related to the join barringerite-transjordanite –
279 hexagonal $\text{Fe}_2\text{P-Ni}_2\text{P}$ (Britvin et al. 2020a), and in allabogdanite – the high-pressure modification of
280 $(\text{Fe,Ni})_2\text{P}$ (Britvin et al. 2021b). Other associated phosphides related to the Fe-Ni-P system do not
281 contain Mo in the amounts detectable by EMPA, but sometimes exhibit the presence of thin
282 molybdenite lamellae (Fig. 7a, 7b). In addition, powellite, CaMoO_4 , is common in the same
283 associations (Fleurance et al. 2013; Khoury 2020) (Fig. 7c). In view of a relatively diverse Mo
284 mineralisation, it looks surprising that in total, pyrometamorphic lithologies of the Hatrurim Basin
285 (Israel) are depleted in this element, showing no more than 4 ppm Mo (Bogoch et al. 1999).
286 Therefore, it can be concluded that Mo tends to selectively concentrate within phosphide phases and
287 powellite.

288 In Jordan, sedimentary sequences stratigraphically juxtaposed to the Mottled Zone are
289 enriched in polymetallic mineralization, where Mo content may reach 950 ppm (Fleurance et al.
290 2013). The data available for phosphorites of the Mishash Formation in Israel, which underlies the
291 Mottled Zone, show Mo contents of 8 to 70 ppm (Nathan et al. 1979), whereas chalks and marls of
292 the Ghareb Formation contain up to 30 ppm Mo (Geller et al. 2012). However, there are the spatially

293 occurring lithologies on the Israel side of the Dead Sea which exhibit extreme enrichment in Mo.
294 Contents of this element up to 1000 ppm were first determined in the dolomite-chert breccia body
295 outcropping near the Arad town (Issar et al. 1969). Further prospecting has revealed a series of
296 similar outcrops of ferruginous dolomite-chert breccias, tracked in NW direction across the
297 northeastern Negev desert. The breccia bodies, being exposed on the areas from a few to several
298 dozens of square meters (Fig. 8a), are hosted by the chalky limestones, dolomites and chalks of the
299 Bina and Menuha Formations, both of Late Cretaceous age (Magaritz et al. 1983; Ilani et al. 1985)
300 (Fig. 3). The breccias are composed of irregular dolomite blocks up to 30-40 cm in size and chert
301 fragments cemented by a mixture of finely dispersed hematite and goethite, along with calcite and
302 barite (Fig. 8b). Molybdenum anomalies are confined to the cement, where as much as 1.9 wt.% Mo
303 (18900 ppm) was determined (Ryb et al. 2009) – the concentration rarely attainable even in rich Mo
304 ores. Molybdenum is disseminated among dispersed iron oxides, with no own mineral phases
305 resolvable at the level of conventional scanning electron microscope (our data). Besides the
306 abnormally high overall Mo content, ferruginous dolomite breccias are characterized by
307 unprecedented Mo isotopic variations ($\delta^{97/95}\text{Mo}$ from -0.6 to $+2.3$ ‰) – the largest spread reported
308 in geological systems (Ryb et al. 2009). The origin of the breccias was explained by the influence of
309 hydrothermal solutions – the subsurface brines circulated in the sediments before the onset of the
310 Dead Sea rifting (Margaritz et al. 1983; Gilat 1994). It is noteworthy that the most significant Mo
311 anomaly is situated in the Zohar anticline, ~2 km away from the Hatrurim Basin (Ryb et al. 2009).
312 Although direct contacts between the sediments of the Bina and Menuha Formations and the
313 Mottled Zone were not observed (Fig. 3), one can suggest that Mo-rich dolomite breccias could be
314 entrapped and uplifted during pyrometamorphic processes. The upward transport of underlying
315 sediments through the clastic dykes and explosion pipes was reported in the Hatrurim Basin (Sokol
316 et al. 2007). The composition of ferruginous breccias is well suited for the pyrolytic transformation
317 into diopside rocks: dolomite and chert as the source of Ca, Mg and Si for diopside; hematite and

318 goethite as precursors for magnetite. An addition, the breccias are enriched in Ni, up to 1000 ppm
319 (Issar et al. 1969), while the source of phosphorus can be ascribed to the phosphorites of the
320 underlying Mishash Formation (Fig. 3). In the Jordan, the sediments of the Belqa group are the
321 obvious source of both Mo and Ni (Fleurance et al. 2013). As a consequence, one can suggest that
322 Mo-rich phosphide mineralization of the Mottled Zone is linked to the processes of polymetallic
323 enrichment of the sediments related to the development of the Dead Sea Transform fault system
324 (Ben-Avraham 2014). The subsequent formation of Mo-phosphides in pyrometamorphic rocks could
325 be accomplished *via* the co-reduction of phosphates and Mo- and Ni-bearing phases (powellite,
326 CaMoO_4 , trevorite, FeNi_2O_4 , bunsenite, NiO) with natural hydrocarbons or molecular dihydrogen,
327 as it was demonstrated on synthetic Mo-Ni-P systems (Burns et al. 2007).

328

329 **Mo and Ni as anthropogenic contaminants**

330 Zaccarini et al. (2019) recently described a mineral named tsikourasite, a Ni-Mo phosphide
331 found in the heavy mineral concentrate from chromitites of the Othrys ophiolite, Greece. This report
332 follows the growing number of articles on “super-reduced” or “ultra-reduced” mineral phases,
333 whose reliability was arguably doubted in the recent papers (Litasov et al. 2018, 2019; Ballhaus et
334 al. 2021). It appears symptomatic that the majority of these minerals, like those reported by
335 Zaccarini et al. (2019) or Xiong et al. (2020), come from mechanically ground probes taken from
336 chromitites of ophiolite complexes. Concerning the contents of our work, we have to give some
337 critical comments on the findings made by Zaccarini et al. (2019). It is noteworthy that
338 contamination of geological probes from grinding equipment is a well known problem (Butler et al.
339 2017). Molybdenum and nickel, being the constituents of heavy-duty superalloys (e.g., Darolia
340 2019), are proven contaminants of the probes prepared with the usage of mechanical grinders (e.g.,
341 Schmidt and Pearce 1981; Sertek et al. 2015). Besides superalloys as such, Ni-Mo and Ni-Co-Mo
342 compositions are used as the metal binders in diamond drilling tools (Loginov et al. 2019) and in the

343 so-called *cermets* – composite ceramic/metal materials prepared from superhard carbides or nitrides
344 (WC, TiC, Mo₂C, TiN etc.) bound by the superalloy matrix. Cermets are commonly served as wear-
345 resistant parts in grinders, milling and drilling equipment (Agnew et al. 2017; Ghasali et al. 2018;
346 Panov 2020). In order to tighten the contacts between steel parts and superalloys, many types of
347 brazing alloys (fillers) were introduced in industry. For the purposes of Ni-Mo alloys brazing, AWS
348 BNi-6 composition is often used (American Welding Society 2007). Besides, this filler is used for
349 brazing of diamond-based tools (Rabinkin et al. 2013). BNi-6 is a nickel-phosphorus eutectic
350 containing 10-12 wt.% P and Ni by balance, that corresponds to the stoichiometry intermediate
351 between Ni₅P and Ni₄P. An example of surficial contamination of the drill core with BNi-6 is given
352 in Supplementary Fig. S1. It should be emphasized that BNi-6, while melted during brazing, is
353 capable of selective extraction of Mo from Ni-Mo-Cr alloys, yielding Ni-Mo and Mo-phosphides
354 (Jalilian et al. 2013). BNi-6 is not the only possible source of contamination with Mo-Ni
355 phosphides. Protective Ni-P and Ni-Mo-P coatings prepared by electroless deposition are widely
356 used in industry since the fifties of the XX century (Krishnan et al. 2006; Vargas et al. 2006).
357 Because in both cases (brazing and coating) the whole system is phosphorus-deficient, the resultant
358 phosphides are also phosphorus-deficient ($M:P > 1$).

359 Zaccarini et al. (2019) give no details on the grinding procedures they employed for the
360 separation of phosphide grains. However, in the next article, the same authors indicate that the
361 grinding equipment contained the parts made of some Mo-Cr superalloy, which they termed by the
362 indefinable name “Alloy 1” (Bindi et al. 2020). Consequently, Zaccarini et al. (2019) used high-Mo
363 superalloy during grinding procedures that would inevitably result in Mo contamination. That is,
364 along with the low-phosphorus composition of tsikourasite, Mo₃Ni₂P_{1+x} and associated phases, e.g.,
365 melliniite-like phosphide ~Ni₄P (= BNi-6), altogether with abnormally high Co contents, allows
366 suggesting that phosphide assemblages described by Zaccarini et al. (2019) have anthropogenic
367 origin. They likely represent the chunks of brazed Mo-superalloy joints, which were trapped by

368 chromite ore at the unknown stage of the grinding/separation process. The “intergrowths” between
369 phosphide/metal and rock-forming minerals must not obfuscate the observer: the pressures attained
370 in drilling/grinding operations are high enough for the alloy phases to be imprinted into (or spread
371 over) the chromite or silicate grains (see Supplementary Fig. S1).

372

373 **Implications**

374 Polekhovskiyite is a striking example of a new type of terrestrial Mo mineralization confined
375 to phosphides of the Dead Sea Transform area. Mineral assemblages of this region are unique on
376 Earth with regard to a diverse speciation of redox-sensitive elements. Further comparison of isotopic
377 Mo ratios in phosphides and surrounding sediments (Ryb et al. 2009) would shed light on the likely
378 sources of this element in the rocks of the Hatrurim Formation. The genesis of this world’s largest
379 pyrometamorphic complex, which encompasses an area of 150×200 km in the Middle East, remains
380 enigmatic. The problem of the source of the incoming heat, which has led to the calcination and
381 fusion of 200 m thick sedimentary sequence, is still unresolved. There is also no answer to the
382 question whether the combustion of the carbon-bearing sediments was a spontaneous process or was
383 it induced by some external event (Britvin et al. 2021b, 2022).

384 Yet another implication of the present work is a discussion of anthropogenic contamination
385 of geological probes with Mo and Ni – a problem related to the use of superalloys in the mining
386 industry and in the laboratory reprocessing of geological samples. This problem is exemplified by
387 analysis of the origin of “ultra-reduced” phosphide assemblages reported from chromite
388 concentrates (Zaccarini et al. 2019; Bindi et al. 2020). In this respect, our article complements the
389 discussion opened by Litasov et al. (2018, 2019) and Ballhaus et al. (2021). Unfortunately, the
390 manufacturers of grinding and drilling equipment avoid disclosing the compositions of superalloys,
391 coatings or brazing fillers. As a consequence, obtaining this information relies upon a good will of
392 mineralogists who are working with ore concentrates. The main problem here is that discrimination

393 between “atypical yet natural” and technogenic phases implies a deep involvement in the specific
394 branches of materials science, outside of the areas covered by geosciences. Besides, tracking the
395 sources of industrial contamination across the ore processing flowcharts implies high analytical
396 costs, which may become comparable with the budgets of corresponding scientific projects.
397 However, ignoring the prerequisites listed above may result in the lack of sufficient due diligence in
398 revelation of anthropogenic factor. This tendency, quite typical of the “Anthropocene Epoch”
399 (Hazen et al. 2017), may have long-lasting consequences: the niche currently occupied by the
400 natural mantle minerals can be gradually superseded by a diverse collection of super-reduced
401 anthropogenic phases.

402

403

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- 641

642 **List of figure captions**

643

644 **Figure 1.** An overview map of the southern Levant. The small Mottled Zone outcrops are marked
645 with red circles. The Hatrurim Basin and Daba-Siwaqa complex are shown as outlined areas.

646 Modified from Britvin et al. 2021a (CC-BY).

647

648 **Figure 2.** Phosphide localities and phosphide-bearing lithologies of the Mottled Zone. (a) Wadi
649 Halamish in the Hatrurim Basin, Israel – a type locality for a variety of phosphides, including
650 polekhovskiyite. Adapted from Britvin et al. (2015) (CC-BY). (b) A piece of hydrothermally altered
651 diopside microbreccia from wadi Halamish – the rock host for phosphide assemblages. Dark areas
652 are coloured with hematite and magnetite. The patches of olive color indicate secondary phosphate
653 mineralization. (c) A 2×2 m outcrop of phosphide-bearing rocks at wadi Zohar, Hatrurim Basin,
654 described in Galuskin et al. (2020). (d) Polished plate of a fused gehlenite rock containing
655 phosphides, wadi Zohar. (e) A block of pyrometamorphic rock where the dark areas bear phosphide
656 mineralization. Phosphorite quarry at the Daba-Siwaqa complex, west Jordan. (f) Polished plate of
657 brecciated phosphide-bearing paralava from this phosphorite quarry. The black areas trace the
658 inclusions of phosphide minerals.

659

660 **Figure 3.** Stratigraphic position of the Hatrurim Basin, Israel, and Daba-Siwaqa complex, Jordan, in
661 the Late Cretaceous–Paleogene sequence of the southern Levant. The stratigraphic equivalents of
662 the Mottled Zone are highlighted by color. Drawn based on the data of Gross 1977, Novikov et al.
663 2013, and Al-Tawalbeh et al. 2017.

664

665 **Figure 4.** A centimeter-sized phosphide nest (resembling sulfides) in the diopside rock. Phosphorite quarry at
666 the Daba-Siwaqa complex, West Jordan (cf. Fig. 2e, 2f).

667 **Figure 5.** Polekhovskiyite crystals in phosphide assemblage within the altered diopside paralava. (a)
668 SEM BSE image. (b) The same area in reflected light, after removal of carbon coating. Wadi
669 Halamish, Hatrurim Basin, Israel. Abbreviations: Pkh – polekhovskiyite; Muh – murashkoite; Tjrd –
670 transjordanite; Ap – fluorapatite.

671
672 **Figure 6.** Crystal structures of (a) polekhovskiyite, MoNiP_2 , and (b) synthetic analogue of monipite,
673 MoNiP . In the structure of polekhovskiyite, face-sharing $[\text{NiP}_6]$ octahedra (green) and $[\text{MoP}_6]$ trigonal
674 prisms (red) alternate along the *c*-axis. In MoNiP , perforated layers of corner-sharing $[\text{NiP}_4]$
675 tetrahedra (green) alternate with perforated layers of corner- and edge-sharing $[\text{MoP}_5]$ square prisms
676 (red). Drawn in ATOMS v.6 (Dowty 2006).

677
678 **Figure 7.** Non-phosphide Mo minerals in pyrometamorphic rocks of the Mottled Zone. (a)
679 Molybdenite (exsolution?) lamellae in a grain of murashkoite, FeP . (b) Molybdenite lamella in
680 zuktamrurite, FeP_2 . (c) Euhedral grains of powellite, CaMoO_4 , in association with magnetite,
681 aragonite and keplerite, $\text{Ca}_9(\text{Ca}_{0.5}\square_{0.5})\text{Mg}(\text{PO}_4)_7$ (Britvin et al. 2021d). SEM BSE images. Localities:
682 (a,c) Halamish wadi, Hatrurim basin, Negev desert, Israel. (b) Phosphorite quarry, Daba-Siwaqa
683 complex, Transjordan Plateau, Jordan. Abbreviations: Mol – molybdenite, Muh – murashkoite, Zuk
684 – zuktamrurite, Pwl – powellite, Arg – aragonite, Kep – keplerite.

685
686 **Figure 8.** (a) An outcrop of ferruginous dolomite breccia at the northern part of the Zohar anticline,
687 Negev desert, Israel (ca. 2 km away from the Hatrurim Basin). (b) A piece of the breccia composed
688 of dolomite fragments cemented with Mo-bearing goethite.

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Tables

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Table 1. Chemical composition (wt. %) of polekhovskiyite and associated phosphides.

	Polekhovskiyite <i>n</i> = 4 (range)	Murashkoite	Transjordanite
Mo	44.10 (43.78–44.34)	< 0.2	1.36
Ni	22.73 (22.55–22.96)	18.84	70.31
Fe	4.60 (4.52–4.66)	45.72	7.20
Co	< 0.2	< 0.2	< 0.2
P	29.02 (28.84–29.13)	35.63	21.24
Total	100.45	100.19	100.11
Formula amounts			
	$\Sigma = 4$ <i>apfu</i>	$\Sigma = 2$ <i>apfu</i>	$\Sigma = 3$ <i>apfu</i>
Mo	0.99		0.02
Ni	0.83	0.28	1.77
Fe	0.18	0.72	0.19
P	2.01	1.00	1.02

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Table 2. Calculated powder X-ray diffraction pattern for polekhovskite (d in Å) in comparison with the reference pattern of synthetic MoNiP₂.

Polekhovskite ^a		MoNiP ₂ ^b		
I_{calc}	d_{calc}	I_{meas}	d_{meas}	hkl
4	5.614	10	5.610	002
71	2.884	80	2.880	100
14	2.807	40	2.796	004
9	2.793			101
8	2.565	25	2.562	102
8	2.284	15	2.285	103
100	2.011	100	2.012	104
1	1.871	3	1.870	006
1	1.772	2	1.773	105
35	1.665	80	1.665	110
1	1.596	5	1.596	112
1	1.570	3	1.569	106
7	1.442	13	1.442	200
9	1.432	20	1.432	114
1	1.430			201
6	1.403	17	1.403	008
2	1.402			107
1	1.397			202
1	1.346			203

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^a This work; calculated for CuK α -radiation on the basis of structural data, using Atoms v.6 (Dowty 2006). ^b Experimental pattern of synthetic MoNiP₂, CuK α -radiation (Guérin 1976).

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Table 3. Crystal parameters of polekhovskiyite, synthetic MoNiP₂ and MoNiP.

	Ideal formula	Structure type	Space group	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>Z</i>
Polekhovskiyite [1] ^a	MoNiP ₂	MoNiP ₂	<i>P6₃/mmc</i>	3.330(1)	11.227(4)	107.8(8)	2
Synthetic [2]	MoNiP ₂	MoNiP ₂	<i>P6₃/mmc</i>	3.329(3)	11.22(1)	107.7	2
Synthetic [3]	MoNiP	Fe ₂ P	<i>P$\bar{6}$2m</i>	5.861	3.704	110.2	3

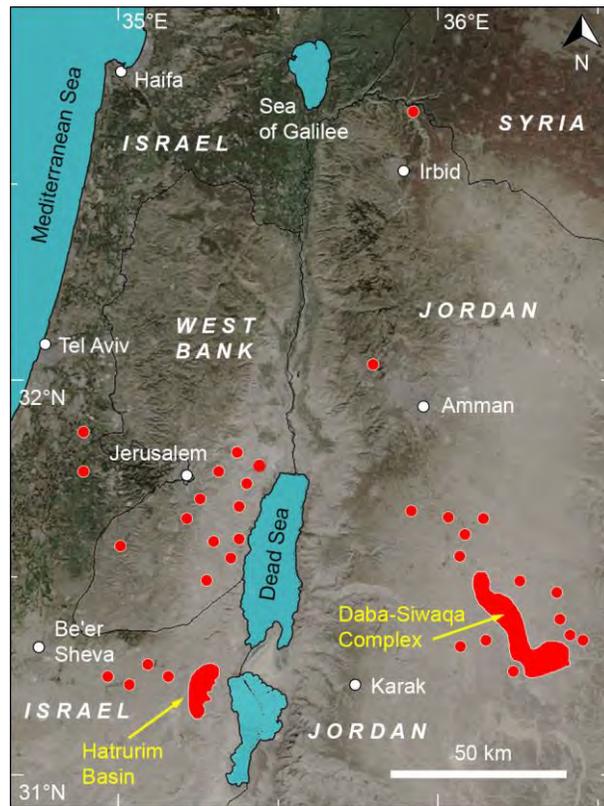
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^a References: [1] This work; [2] Guérin and Sergent (1976); [3] Guérin and Sergent (1977).

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Figures

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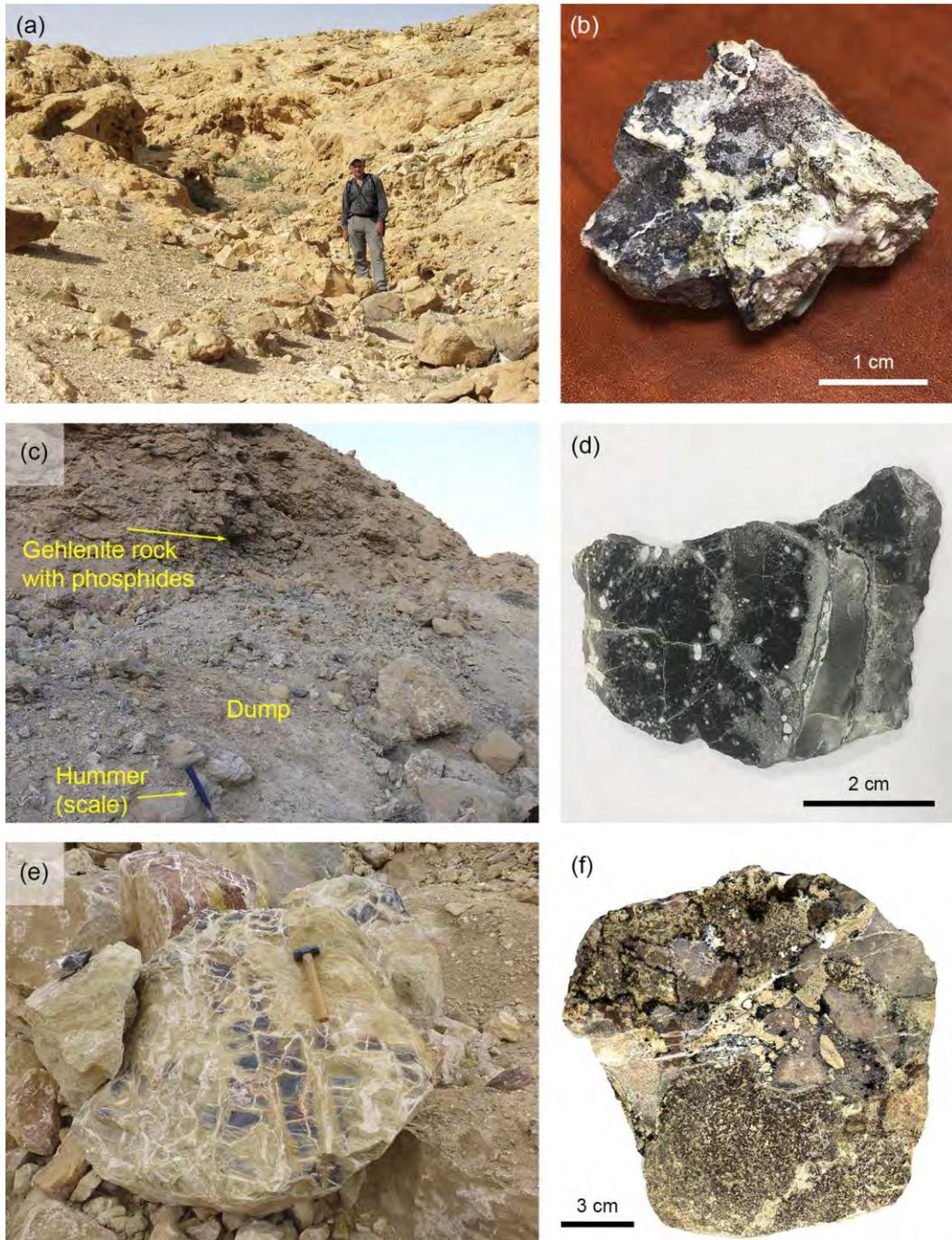
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Figure 1



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Figure 2

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	Age	Israel		Jordan	
		Formation, thickness (m)	Normal facies	Formation, thickness (m)	Normal facies
Paleogene	Eocene			Umm Rijam (45)	Chert Marl Chalk
	Paleocene	Taqiye (30)	Chalk Marl	Muwwaqqar (150)	Marl Limestone
	Maastrichtian	Ghareb (70)	Chalk		
Late Cretaceous	Campanian	Mishash (80)	Phosphorite Chalk Chert	Al Hisa (70)	Phosphorite Limestone Chert
	Santonian	Menuha (50)	Chalk		Wadi Umm Ghudran (40)
	Coniacian				
	Turonian	Bina (70)	Limestone Dolomite	Wadi As Sir (120)	Limestone Dolomite Marl

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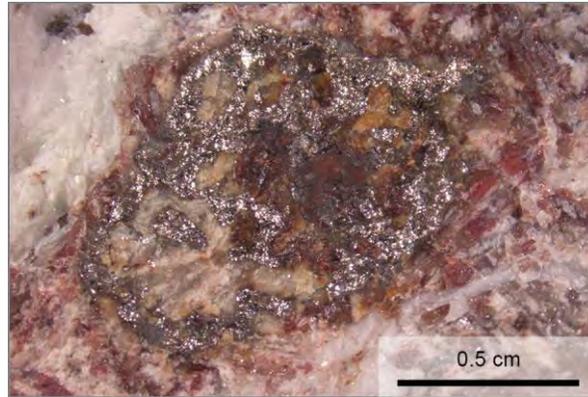
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Figure 3

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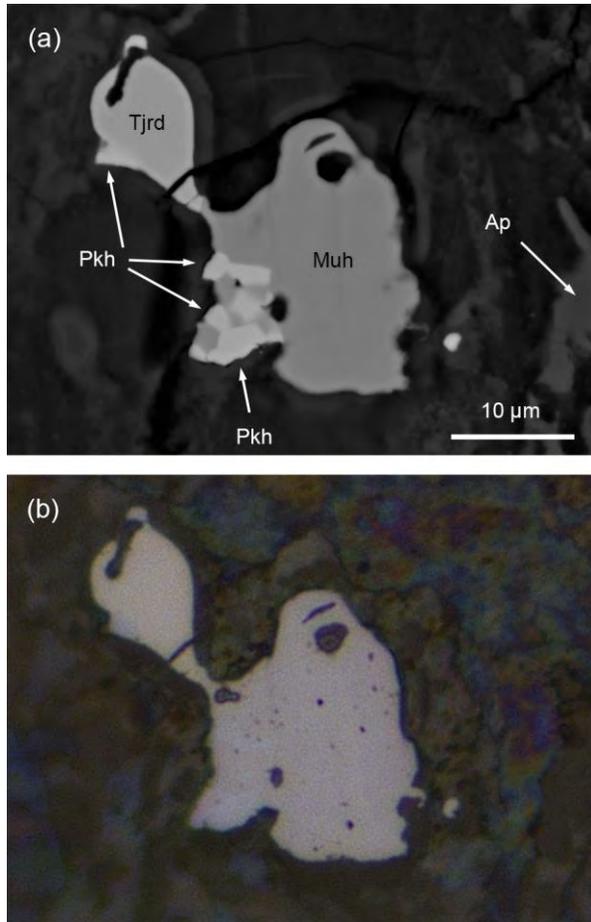
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Figure 4

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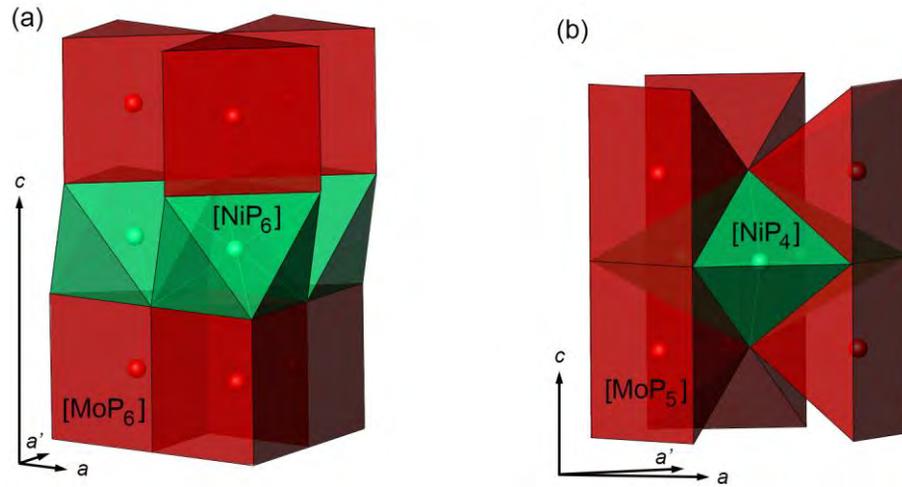
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Figure 5

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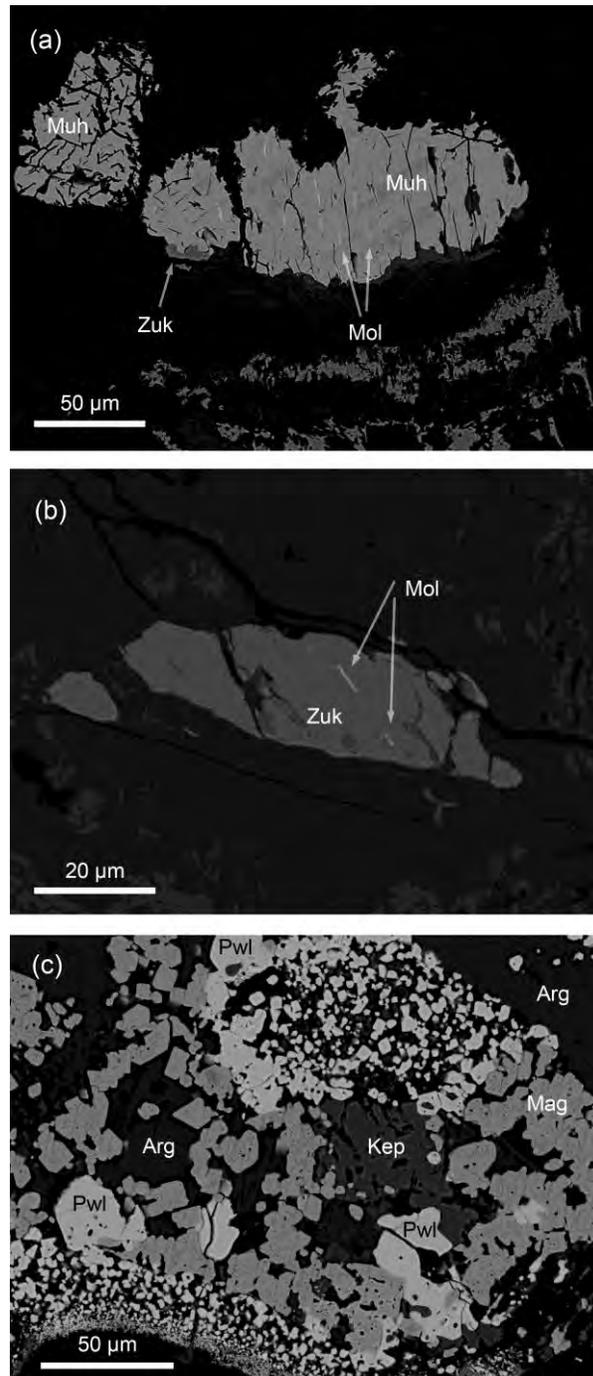
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Figure 6

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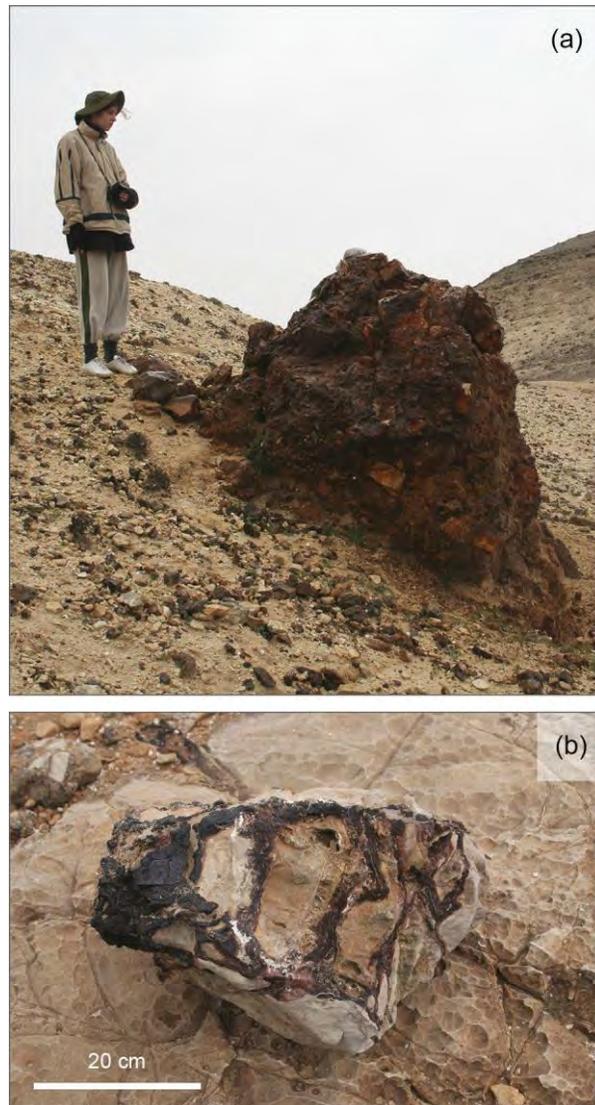
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Figure 7

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Figure 8

Expanding the speciation of terrestrial molybdenum: discovery of polekhovskiyite, MoNiP_2 , and insights into the sources of Mo-phosphides in the Dead Sea Transform area

Sergey N. Britvin, Mikhail N. Murashko, Oleg S. Vereshchagin, Yevgeny Vapnik, Vladimir V.

Shilovskikh, Natalia S. Vlasenko, Vitalii V. Permyakov

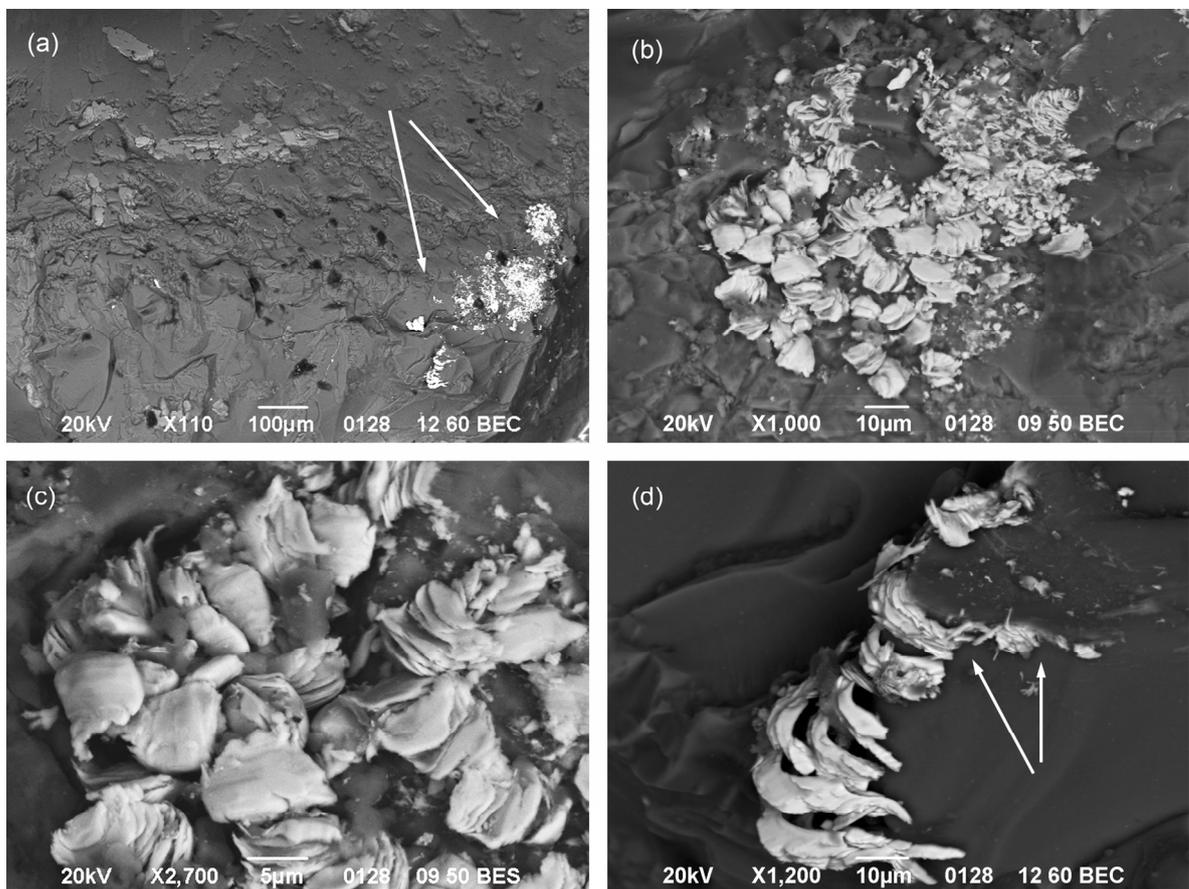


Figure S1. An example of anthropogenic contamination of geological sample with nickel-phosphorus brazing alloy. BNi-6 alloy of the composition $(\text{Ni}_{3.89}\text{Fe}_{0.03})_{3.92}\text{P}_{1.08}$ is spread over the face of the drill core. (a) An overview showing the BNi-6 field on the drill core surface (indicated by arrows). (b,c) Detailed views of the texture of BNi-6 boring scrap on silicate matrix. (d) An illustration of the case where BNi-6 particles are impressed into the matrix cracks (marked by arrows), mimicking the “intergrowths” between brazing alloy and host silicate minerals. SEM BSE images.