

1 **Revision 1**

2 **4613 Words**

3 **First widespread occurrence of rare phosphate chladniite in a meteorite, winonaite Graves**

4 **Nunataks (GRA) 12510: implications for phosphide – phosphate redox buffered genesis in**

5 **meteorites**

6 **Brendan A. Anzures^{1,2}, Francis M. McCubbin³, Timmons M. Erickson², Ryan S. Jakubek²,**

7 **Marc D. Fries³, Loan Le²**

8 ¹Lunar and Planetary Institute, USRA

9 ²Jacobs, NASA Johnson Space Center

10 ³ARES, NASA Johnson Space Center

Revision 1

11 **Abstract**

12 The first widespread occurrence of rare Na-, Ca-, and Mg,Mn,Fe-bearing phosphate
13 chladniite was observed in meteorite Graves Nunataks (GRA) 12510, which is a primitive
14 achondrite that sits within the winonaite class. Numerous 1-500 μm chladniite grains were found,
15 often on the margins between silicate clasts and the kamacite portions of the large metal veins
16 that permeated through the sample. The largest chladniite grains are associated with merrillite,
17 kamacite, taenite, troilite, albite, forsterite, diopside, and enstatite, with a few tiny chladniite
18 grains and an apatite grain enclosed within merrillite. GRA 12510's average chladniite
19 composition is $\text{Na}_{2.7}\text{Ca}_{1.25}(\text{Mg}_{10.02}\text{Mn}_{0.69}\text{Fe}_{0.20})_{\Sigma=10.91}(\text{PO}_4)_9$. Electron back scattered diffraction
20 (EBSD) patterns indicate varying degrees of nucleation and growth of chladniite grains.
21 Additionally, the first pure Raman spectrum of chladniite is described here revealing primary ν_1
22 bands at 954, 974, and especially 984 cm^{-1} . The co-occurrence and close association of merrillite,
23 apatite, chladniite, and P-bearing metallic phases within GRA 12510 suggests that the $f\text{O}_2$ of
24 IW-2 to IW-4 is an intrinsic property of the precursor chondritic material, and the phosphate-
25 phosphide reaction may have buffered the final winonaite and IAB iron meteorite phase
26 assemblages. Altogether, chladniite appears to form alongside other phosphates with their
27 chemistries reflecting the diverse environment of their formation. Meteoritic chladniite likely
28 formed through subsolidus oxidation of schreibersite, scavenging Na from albite, Ca from
29 diopside, Mg from enstatite/forsterite, Fe from kamacite/taenite, and Mn from
30 alabandite/chromite when available. A P^0 - P^{5+} redox-buffered environment also has implications
31 for thermometry and fast cooling rates, although more experiments are necessary to extrapolate
32 powder reaction rates to those of larger crystals. Furthermore, phosphide-phosphate buffered
33 experiments may aid in investigating equilibrium chemistry at $f\text{O}_2$'s between IW-2 and IW-4,

Revision 1

34 which have been challenging to explore experimentally due to the limited availability of solid
35 metal-metal oxide buffers between IW (Fe-FeO) and IW-5 (Cr-Cr₂O₃) at temperatures and
36 pressures relevant to planetary interiors. Future investigations of phosphide-phosphate redox-
37 buffered genesis at f_{O_2} 's between IW-2 and IW-4 have important implications for *primitive*
38 *meteorite constituents* (e.g. CAI's), *partially differentiated planetesimals*, and *planets* including
39 Mercury and core formation on Earth.

Introduction

41 The winonaites are a small group of primitive achondrites that provide insights into the
42 early differentiation and partial melting of chondritic planetesimals in the early Solar System
43 (Benedix et al., 1998, 2005; Bild, 1977; Hunt et al., 2017, 2018; Zeng et al., 2019). Winonaites
44 have not been studied in much detail since the discovery of their namesake Winona in 1928,
45 although their number has more than doubled since 2020 from 33 to 82 through 2023
46 (Gattacceca et al., 2023). Winonaites are distinguished from other primitive achondrite groups
47 based on their mineralogy and composition, reflecting reducing conditions intermediate between
48 ordinary and enstatite chondrites (Benedix et al., 1998; Bild, 1977). Winonaites are also
49 distinguished by their oxygen isotopic systematics that bear similarities to silicate inclusions in
50 rare group IAB complex iron meteorites, implying they formed from the same parent body
51 (Benedix et al., 1998; Bild, 1977). Winonaites are highly heterogeneous in grain size, petrologic
52 texture, and modal mineralogy, reflecting a complex and varied geologic history (Benedix et al.,
53 1998; Floss et al., 2007; Hunt et al., 2017; Li et al., 2011). Previous studies have revealed that
54 winonaites experienced extensive thermal metamorphism, limited Fe-Ni-FeS partial melting,
55 possible silicate partial melting, and catastrophic impact, breakup, and reassembly (Benedix et
56 al., 1998, 2005; Bild, 1977; Floss et al., 2007; Hunt et al., 2017, 2018; Zeng et al., 2019; Anzures

Revision 1

57 et al. 2022). Studies of winonaites and IAB iron meteorites have revealed several new minerals,
58 including rare Na- and Mg-bearing phosphates chladniite (McCoy et al., 1994), moraskoite
59 (Karwowski et al., 2015), and czochralskiite (Karwowski et al., 2016). Here, we describe the first
60 widespread occurrence in a meteorite of the rare Mg-rich member of the fillowite-group
61 chladniite ($\text{Na}_3\text{CaMg}_{11}(\text{PO}_4)_9$) (Hatert et al., 2011) and its first identification in a winonaite
62 meteorite, Graves Nunataks (GRA) 12510 (Figure 1).

63 Phosphate minerals make up a minor to trace fraction of the modal mineralogy of most
64 meteorite groups, and the most common phosphates in meteorites are apatite and merrillite
65 (Jones et al., 2014, 2016; McCubbin et al., 2023; McCubbin et al., 2021; McCubbin and Jones,
66 2015; Patiño Douce and Roden, 2006; Ward et al., 2017). Although they are minor phases,
67 phosphates can provide invaluable insights into the petrogenesis of samples as they are often the
68 primary carrier of rare earth elements (REE) (Pan and Fleet, 2002; Piccoli and Candela, 2002).
69 Furthermore, some phosphates can host magmatic volatiles in their structure (i.e., F, Cl, and OH)
70 and can provide insights into the volatile history of a sample, including the isotopic compositions
71 of H and Cl (Barnes et al., 2019, 2020; Boyce et al., 2014; McCubbin and Ustunisik, 2018;
72 Sarafian et al., 2017; Tartèse et al., 2019; Webster and Piccoli, 2015). For reduced systems, like
73 the winonaites, phosphates can also provide important constraints on oxygen fugacity as the
74 phosphate-phosphide transition occurs at about 4 log units below the iron-wüstite (IW) buffer
75 (IW-4) at ~ 700 °C and at about IW-3 at ~ 1300 °C (Pasek, 2015). Very little is known about the
76 phosphate mineral chladniite because it is rare in natural samples. Here we investigate the
77 widespread occurrence of the fillowite-group mineral chladniite in winonaite GRA 12510 and its
78 relation to the petrogenesis of GRA 12510.

Revision 1

79 **Sample Material**

80 The polished thin section studied here, GRA 12510,5, was provided by the
81 Astromaterials Acquisition and Curation Office at NASA's Johnson Space Center and was
82 progressively polished down before a final finish with 50 nm colloidal silica dispersion. The thin
83 section had a 20 nm carbon coat for electron probe microanalysis (EPMA) and scanning electron
84 microscopy (SEM) elemental mapping, which was subsequently removed and recoated with a 5
85 nm carbon coat for electron backscatter diffraction (EBSD). The carbon coat was then polished
86 off for Raman spectroscopy.

87 **Analytical Methods**

88 **Electron probe microanalysis (EPMA)**

Revision 1

89 Phase identification and quantitative major and minor element chemistry measurements
90 were completed using electron probe microanalysis (EPMA) using the JEOL 8530 field emission
91 (FE) electron microprobe at NASA Johnson Space Center (JSC) using a ZAF correction. Silicate
92 minerals were analyzed using a 15 kV accelerating voltage, a 10 nA beam current, and a 5 μm
93 spot size via wavelength-dispersive X-ray spectroscopy (WDS). Metals and sulfides were
94 analyzed using a 15 kV accelerating voltage, 20 nA beam current, and a 1-5 μm spot size.
95 Natural and synthetic standards were used including canyon diablo troilite for S. Phosphates
96 were analyzed using 15 kV accelerating voltage, 20 nA beam current, and 10 μm spot size. The
97 analysis of phosphates, particularly apatite, followed procedures established and described in
98 McCubbin et al., (2021). Natural and synthetic minerals were used as standards including SrF_2 ,
99 albite, quartz, stikin anorthite, springwater olivine, Wilberforce apatite, ilmenite, and rhodonite
100 (crystal setup LDE1: F, TAP (Na, Si, Al, Mg), PET (P, S), PETL (Cl, Ca, Ti), and LIFH (Fe,
101 Mn). Individual EPMA analyses are included in the online supplementary files.

102 **Scanning electron microscopy (SEM)**

103 Modal mineralogy was calculated using elemental maps produced with the JEOL 7600
104 scanning electron microscope (SEM) at NASA JSC. Elemental maps were collected using an
105 accelerating voltage of 15 kV, 20 nA beam current, and 8 mm working distance at a resolution of
106 $< 0.5 \mu\text{m}/\text{pixel}$. Mineral phases were identified by the distribution of 16 elements (Na, Mg, Al,
107 Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, C, O) along with energy-dispersive X-ray spectroscopy
108 (EDS) spot analyses. Modal mineral abundances were determined by converting the elemental
109 maps to mineralogical maps in XMapTools (Lanari et al., 2014, 2019) (Table 1, Figure 2).

110 **Electron backscatter diffraction (EBSD)**

Revision 1

111 Quantitative phase indexing and microstructural maps of chladniite-bearing regions were
112 collected using the JEOL 7900F FE-SEM at NASA JSC. Electron backscatter diffraction
113 patterns (EBSPs) were collected using an Oxford Instruments Symmetry™ crystal metal oxide
114 scintillator detector and an Oxford instruments Aztec 4.1 software package. Acquisition
115 parameters included a 20 kV accelerating voltage, 10 nA beam current, ~20 mm working
116 distance, and a 70° tilt relative to the beam incidence. Phosphate EBSPs were indexed using a
117 fillowite match unit after the crystal structure of Araki and Moore (1981). In addition, a
118 merrillite match unit based on the structural data of Xie et al. (2015) was included in all maps to
119 identify additional phosphates and ensure accurate structural indexing of the grains. Maps were
120 collected with a step size ranging from 0.5 - 0.2 μm.

121 Post-processing of the EBSD data used Oxford Instruments Aztec Crystal 2.2 program.
122 All EBSD data were given a wild-spike noise reduction and a seven nearest neighbor zero-
123 solution correction. An additional correction was applied to remove systematic misindexing of
124 the fillowite data with disorientation relation of 180°<11-20> caused by mirror symmetry normal
125 to the axis. Forescatter electron, EBSD phase and inverse pole figure (IPF) maps can be found in
126 Figure 3. Fillowite pole plots are equal area, lower hemisphere projections.

127 **Raman spectroscopy and Raman spectroscopic imaging**

128 Chladniite and its associated minerals were measured using a WITec alph300R Raman
129 microscope (XMB3000-3003) at NASA JSC. Both single spectra and a Raman image were
130 collected. Incident 532 or 488 nm excitation was generated using a WITec diode laser
131 (XSL3100-1154) producing ~170 μW or ~100 μW of incident power at the sample surface,
132 respectively. For single spectral collections, the incident laser was focused on the sample surface
133 using either a 100X magnification Zeiss EC Epiplan-Neofluar objective producing a 0.9 μm

Revision 1

134 beam spot on the sample surface, or a 50X magnification Zeiss EC Epiplan objective producing a
135 1.2 μm spot size on the sample surface. The Raman scattered light was dispersed using a WITec
136 UHTS600 (XMC3200-0600) spectrometer with a 300 g/mm grating, and the spectrum was
137 detected using a back-illuminated, thermoelectrically cooled (-60°C) CCD (XMC3022-1001).
138 Single spectra were collected by averaging approximately 5-10 accumulations, each with a 10
139 second integration time. The Raman image of 100x100 spectra was collected over a 300x300 μm
140 area of the sample for a Raman image resolution of 3 $\mu\text{m}/\text{pixel}$ and a total of 10,000 individual
141 spectra. The 50X magnification objective was used to collect the Raman image. The
142 accumulation time for each individual Raman spectrum in the image was 5 seconds for an image
143 accumulation time of 14 hours and 8 minutes. Principal component analysis (PCA) of the image
144 was performed using WITec Project FIVE software to identify and map the main component
145 minerals chladniite, merrillite, enstatite, diopside, olivine, and feldspar as shown in Figure 4a.
146 Representative Raman spectra of chladniite and merrillite, as well as fillowite from the literature,
147 are shown in Figure 4b.

Results

Occurrence

150 GRA 12510 is a coarse-grained winonaite with abundant metal veins and pools
151 separating silicate clasts that are either dominated by orthopyroxene or orthopyroxene+olivine.
152 Modal mineralogy is 65.43% silicate (28.27% orthopyroxene, 21.63% olivine, 4.54%
153 clinopyroxene, and 10.87% plagioclase), 30.01% metal (26.08% kamacite, 3.50% taenite, and
154 0.43 % schreibersite), with minor troilite (2.73%), chromite (0.50%), merrillite (1.13%),
155 chladniite (0.32%), and trace apatite (Table 1, Figure 2). Both silicate clast lithologies have
156 similar silicate:metal area% ratios (84.33:8.15 and 85.11:10.77 for the orthopyroxene-rich and

Revision 1

157 orthopyroxene + olivine-rich clasts). However, the orthopyroxene-rich clasts have more
158 orthopyroxene (45.05 vs. 31.68%), less clinopyroxene (5.36 vs. 11.09%), similar abundances of
159 plagioclase (12.85 vs. 11.64%), and less olivine (21.07 vs. 30.70%). A single 5 μm diameter
160 grain of alabandite (MnS) was also found in an orthopyroxene-rich silicate clast in contact with
161 troilite and schreibersite. A single F-rich, Cl-bearing apatite grain was found as an inclusion in
162 merrillite. Notably, the orthopyroxene-rich clast has substantially more phosphate (0.67%
163 chladniite and 1.66% merrillite vs. 0.31% chladniite and 1.23% merrillite) and less phosphide
164 (0.09% vs. 0.81% schreibersite).

165 Numerous 1-500 μm chladniite grains were found, often on the margins between silicate
166 clasts and the kamacite portions of the large metal veins. The largest chladniite grains are
167 associated with merrillite, kamacite, taenite, troilite, albite, forsterite, diopside, and enstatite
168 (Figure 2). Rarely, chladniite encloses <3 μm merrillite grains as seen in Figure 2b. Additionally,
169 even though chladniite in this meteorite contains Mn, the areas immediately surrounding
170 chladniite are mostly Mn-free. However, several Mn-rich chromite grains (7.89 wt% MnO) and
171 one tiny alabandite grain (MnS) are found elsewhere in the section.

172 **Composition of chladniite**

173 The average composition of 37 analyses of 7 grains of chladniite in GRA 12510 is shown
174 in Table 2. These chladniite grains include those near metal, merrillite, and silicates, as well as
175 inclusions in merrillite and albite. Based on these analyses, the calculated mineral formula for
176 chladniite in GRA 12510 is $\text{Na}_{2.7}\text{Ca}_{1.25}(\text{Mg}_{10.02}\text{Mn}_{0.69}\text{Fe}_{0.20})_{\Sigma=10.91}(\text{PO}_4)_9$ after Hatert et al.
177 (2021)'s stoichiometry $\text{Na}_3\text{CaMg}_{11}(\text{PO}_4)_9$.

178 **EBSD**

Revision 1

179 EBSD analyses of GRA 12510 revealed that the chladniite structure agreed well with
180 fillowite (Araki and Moore, 1981) thus falling within the fillowite-type phosphate group.
181 Chladniite areas were found using foreshatter electron images (Figure 3). Diffraction patterns
182 were collected from one large chladniite grain in area A, as well as chladniite areas with multiple
183 grain boundaries in area A and B (areas A and B matching those identified in BSE images in
184 Figure 1). The mean angular deviation values of the electron backscatter patterns for the maps
185 ranged between 0.87 to 0.63 for fillowite-structure materials, corroborating the chladniite-type
186 phosphate.

187 Crystallographic orientations displayed as IPP maps and pole plots showed a single 40 x
188 60 μm chladniite grain in area A (Figure 3a). Other chemically coherent chladniite areas
189 including a 100 x 100 μm area (Figure 3b) and a ~ 500 μm diameter area (Figure 3c) were
190 actually revealed through EBSD to be monomineralic granular aggregates with grain sizes down
191 to 3 μm . The pole plots do not show a systematic pattern consistent with preferred growth
192 orientation, rather with multiple random orientations, indicating nucleation and coalescence of
193 grains (Prior et al., 1999).

Raman Spectroscopy

195 Here, the Raman spectra of pure chladniite is described for the first time revealing a
196 diagnostic peak centered at 982 cm^{-1} as shown in Figure 4b. A previous attempt at collecting a
197 Raman spectrum of chladniite in a type III silicate-phosphate (PG) inclusion in the Elga IIE iron
198 meteorite resulted in a dominantly merrillite spectrum with a chladniite shoulder at 984 cm^{-1}
199 (Litasov and Podgornykh, 2017). Phosphates typically have a main peak corresponding to the ν_1
200 symmetric stretching mode of PO_4^{3-} at 950-990 cm^{-1} , an antisymmetric ν_3 vibration at 1000-1175
201 cm^{-1} , as well as weaker bands due to the ν_2 bending mode at 400-500 cm^{-1} , ν_4 bending mode at

Revision 1

202 550-640 cm^{-1} , and lattice modes at wavenumbers lower than 300 cm^{-1} (Litasov and Podgornykh,
203 2017). Chladniite appears to have three strong overlapping ν_1 bands at 954 cm^{-1} , 974 cm^{-1} , and
204 984 cm^{-1} , ν_3 bands at 1063, 1129, 1138, and 1154 cm^{-1} , ν_2 bands at 441 and 486 cm^{-1} , ν_4 bands at
205 563, 583, and 602 cm^{-1} , and lattice mode bands at 282 cm^{-1} . Although chladniite is isostructural
206 with fillowite, the substitution of Mg for Mn^{2+} in chladniite affects the ν_1 vibrational frequencies.
207 Fillowite has three ν_1 bands at 943, 959, and 974 cm^{-1} (RRUFF database) whereas chladniite
208 shows ν_1 bands at 954, 974, and 984 cm^{-1} . Three strong overlapping ν_1 bands indicate that the
209 PO_4 tetrahedra inhabit three non-equivalent positions with slight structural/environmental
210 heterogeneity rather than a more uniform location in its crystal structure.

211 Discussion

212 Winonaite Parent Body Pressure-Temperature-Redox Conditions

213 There are some thermodynamic constraints on the formation conditions of the winonaite
214 parent body that can be used to elucidate the formation of chladniite. The winonaite parent body
215 has been estimated to be a small body with a radius of ~ 100 km (Benedix et al., 2005) that
216 corresponds to a maximum pressure of 0.01 GPa (Lucas et al., 2020). The winonaite parent body
217 is also fairly reduced, with silicates recording oxygen fugacities ($f\text{O}_2$) from IW-2.3 to IW-3.2
218 calculated using the FeO content of olivine (quartz-iron-fayalite) and pyroxene (quartz-iron-
219 ferrosillite) (Benedix et al., 2005). In their study, Benedix et al. (2005) notes that that winonaite
220 and IAB $f\text{O}_2$ estimates do not fall along any traditional metal-metal oxide buffers or the
221 temperature and pressure dependent graphite-carbon monoxide buffer. However, this $f\text{O}_2$ range
222 calculated from the silicates is consistent with the phosphide-phosphate oxidation transition of
223 IW-3 to IW-4 designated by the schreibersite (Fe_3P)-whitlockite ($\text{Ca}_3(\text{PO}_4)_2$) buffer (Bindi et al.,
224 2023; Pasek, 2015) as shown in Figure 5. Recent experiments also suggest that at temperatures

Revision 1

225 >900 °C, the phosphide to phosphate reaction occurs rapidly with complete oxidation from
226 phosphide within a week and a few percent reduction of phosphate on the same timescale (Feng
227 and Pasek, 2023). The co-occurrence and close association of merrillite, chladniite, apatite, and
228 P-bearing metallic phases within GRA 12510 suggests that the fO_2 of IW-2 to IW-4 is an
229 intrinsic property of the precursor chondritic material and the phosphate-phosphide reaction may
230 have buffered the final winonaite and IAB iron meteorite phase assemblages.

231 The prevailing model for winonaite-IAB parent body formation is that it underwent
232 incomplete differentiation followed by catastrophic impact, breakup, and reassembly (Benedix et
233 al., 2000). Most recently, the proposed layered structure of the winonaite-IAB iron meteorite
234 parent body from the surface to the core was 1) precursor chondritic material, 2) diverse
235 lithologies that experienced limited metamorphism and FeNi-FeS partial melting, 3) residues of
236 silicate partial melting, and 4) incompletely differentiated molten metal represented by IAB iron
237 meteorites (Hunt et al., 2017; Zeng et al., 2019). Adding onto this model, winonaite and IAB iron
238 meteorites record rapid cooling rates of 0.48-1.75 °C/year, and therefore cooled from their peak
239 magmatic temperatures as collisional fragments during breakup prior to reassembly (Anzures et
240 al. 2022). Finally, the winonaite parent body also experienced multiple impact events that caused
241 liberation from the parent body before impacting and being found on Earth. Cosmic-ray exposure
242 ages for winonaites range from 0.02 to 0.08 Ga (Benedix et al., 1998), while IAB iron meteorites
243 range from 0.4 to 1.0 Ga (Voshage, 1967).

244 **Origin of Chladniite**

245 The only other occurrences of chladniite have been as a single large grain in a complex
246 silicate-bearing inclusion in IAB iron meteorite Carlton (McCoy et al., 1994), a minor phase in
247 lodranite GRA 95209 (Floss, 1999; Grew et al., 2010; McCoy et al., 2006; McCoy and Carlson,

Revision 1

248 1998), as inclusions in merrillite-dominated phosphate aggregate in a IIE iron meteorite Elga
249 (Litasov and Podgornykh, 2017), in a couple of terrestrial pegmatites in Argentina (Vallcorba et
250 al., 2016) and Brazil (Hatert et al., 2021), and as a REE-bearing Y-chladniite in a granulite from
251 Antarctica (Grew et al., 2006). The first terrestrial identification of chladniite was found in a
252 pegmatite from Córdoba, Argentina, as up to 200 μm diameter inclusions in beusite, the Mn
253 analog of the graftonite phosphate structural group (Vallcorba 2016). Based on chemical and
254 textural evidence, the association of beusite and chladniite was interpreted as a replacement
255 product of garnet during the magmatic stage (Vallcorba 2016) caused by destabilization of garnet
256 due to phosphorous buildup (Colombo et al., 2012). Chladniite has also been found in another
257 pegmatite in Sapucaia, Brazil (Hatert et al., 2021). Y-chladniite was also found in a granulite in
258 Larsemann Hills, Antarctica as up to 250-1000 μm inclusions in fluorapatite associated with
259 wagnerite, xenotime-(Y), monazite-(Ce), P-bearing K-feldspar, biotite, sillimanite, quartz, and
260 pyrite. Y-chladniite was inferred to have formed at 800-860 $^{\circ}\text{C}$ and 0.6-0.7 GPa by reaction of
261 biotite with an anatectic melt with phosphorous buildup by interaction with fluorapatite (Grew et
262 al., 2006). However, terrestrial chladniite likely has a different mode of formation than
263 meteoritic chladniite because of the much higher pressures and more oxidizing environments on
264 Earth as well as the inferred differences in geological processes that occur on small asteroids
265 versus the Earth's crust.

266 For meteoritic chladniite formation, two hypotheses for its formation are either as a 1)
267 replacement product of a phosphate (either graftonite (Floss, 1999) or panethite (Litasov and
268 Podgornykh, 2017), which originated by reaction of olivine and orthopyroxene with metallic iron
269 containing P or 2) crystallization from the reaction of plagioclase and pyroxene with metallic
270 iron or schreibersite (Floss, 1999). In lodranite GRA 95209, chladniite is also associated with a

Revision 1

271 graffonite structural group phosphate in the iron analog graffonite as < 50 μm thick veins
272 intersecting silicate phases adjacent to remnant metal or troilite (Floss, 1999). However, in IAB
273 iron meteorite Carlton, the single chladniite grain (175 x 975 μm) is not associated with a
274 graffonite group phosphate, rather with chlorapatite. In IIE iron meteorite Elga, chladniite was
275 found in only one site as <10 μm inclusions in merrillite surrounded by schreibersite rims and
276 enclosed within kamacite-taenite metal (Litasov and Podgornykh, 2017). In Elga, chladniite was
277 suggested to be poorly crystalline due to its Raman spectra always being contaminated by
278 merrillite peaks (Litasov and Podgornykh, 2017).

279 Chladniite in winonaite GRA 12510 is much more abundant and found in larger grain
280 sizes here compared with other meteorites. Numerous 1-500 μm chladniite grains were found,
281 often on the margins between silicate clasts and the kamacite portions of the large metal veins.
282 The largest chladniite grains are associated with merrillite, kamacite, taenite, troilite, albite,
283 forsterite, diopside, and enstatite (Figure 2). Additionally, unlike Elga where a few tiny poorly
284 crystallized chladniite grains are included in merrillite (Litasov and Podgornykh, 2017),
285 sometimes chladniite in GRA 12510 encloses <3 μm merrillite grains as seen in Figure 2b.

286 Chladniite compositions differ widely, which suggests that the composition is controlled
287 by the geologic environment of formation rather than by crystal-chemical constraints (Vallcorba
288 et al., 2016). Terrestrial pegmatitic chladniite has high Mn and Fe (13.96-14.42 wt% MnO and
289 15.98-17.37 wt% FeO) reflective of its pegmatitic environment (Hatert et al., 2021; Vallcorba et
290 al., 2016) and association with Mn-phosphate beusite in Argentina (Vallcorba et al., 2016).
291 Terrestrial granulite chladniite has similar Fe content (15.88 wt% FeO) but virtually no Mn (0.26
292 wt% MnO) due to its almost Mn-free environment (Grew et al., 2006). Lodranite GRA 95209's
293 chladniite is also rich in Fe with a little less Mn (8.61 wt% MnO and 14.4 wt% FeO (Floss,

Revision 1

294 1999)) reflective of its association with Fe-phosphate graftonite. Chladniite in silicate clasts of
295 iron meteorites have very low Mn and Fe including IAB iron Carlton (0.30 MnO and 2.23 wt%
296 FeO respectively) (McCoy et al., 1994) and IIE Elga (1.37 MnO and 5.11 wt% FeO) (Litasov
297 and Podgornykh, 2017). GRA 12510's chladniite also has relatively low overall Mn and Fe (3.92
298 wt% MnO and 1.14 wt% FeO respectively). However, GRA 12510's chladniite is 10 times
299 higher in Mn than in Carlton, which could have been scavenged from MnS or Mn-rich chromite
300 that are spatially anticorrelated with abundant chladniite in the sample. Interestingly, this
301 composition plots slightly within the proposed miscibility gap in a Fe²⁺-Mn-Mg ternary for
302 fillowite-type phosphates (Fransolet et al., 1998; Hatert et al., 2021) as shown in Figure 6. This
303 possible miscibility gap has been hypothesized because of the larger difference in ionic radii
304 between Mg and Mn compared with their similarities to Fe²⁺, although this could also be due to
305 small sample bias with only seven total occurrences of chladniite.

306 Altogether, chladniite appears to form alongside other phosphates with their chemistries
307 reflecting the diverse environment of their formation. Meteoritic chladniite likely formed through
308 subsolidus oxidation of schreibersite (Fe,Ni)₃P scavenging Na from albite, Ca from diopside, Mg
309 from enstatite/forsterite, Fe from kamacite/taenite, and Mn from alabandite/chromite when
310 available. Near Mg-endmember enstatite and forsterite (Mg#>90) is generally the most abundant
311 mineral aside from metal in winonaites, IAB irons, and lodranites, consistent with the Mg-,
312 rather than Fe- or Mn-, endmember of the fillowite group being present in GRA 12510. Whereas
313 Carlton likely formed in a Cl-rich environment with chlorapatite present (McCoy et al., 1994),
314 and GRA 95209 forming in a Cl-poor and Fe-rich environment (Floss, 1999). Although Elga has
315 both chladniite, merrillite, and schreibersite like GRA 12510, its silicates appear to be more
316 oxidized with an average orthopyroxene composition of En₇₆Fs_{21.5}Wo_{2.5}. Elga's lower Mn in

Revision 1

317 chladniite compared with GRA 12510 is also reflected in its Mn-poor chromite (2.15 wt% vs.
318 7.89 wt% MnO) and presence of only troilite rather than troilite and alabandite respectively.

319 **Implications**

320 This schreibersite-chladniite reaction appears to have buffered the redox state of GRA
321 12510 with the recorded fO_2 using FeO content of olivine (quartz-iron-fayalite) and pyroxene
322 (quartz-iron-ferrosillite) in winonaites/IAB iron meteorites (Benedix et al., 2005) corresponding
323 to the fO_2 -T curve of the phosphide-phosphate buffer (Bindi et al., 2023; Pasek, 2015). The
324 primary texture of the schreibersite and secondary texture of the chladniite suggest that GRA
325 12510 was initially more reduced. Furthermore, within a single section of GRA 12510 studied
326 here, chladniite makes up a higher fraction of the modal mineralogy than schreibersite,
327 suggesting that this reaction was proceeding toward oxidation at the time of closure.
328 Schreibersite-chladniite and more broadly schreibersite-phosphate assemblages in other
329 meteorites including IAB iron Carlton, IIE iron Elga, lodranite GRA 95209, indicate they formed
330 in a P^0 - P^{5+} redox-buffered environment with an oxygen fugacity of \sim IW-3 to IW-4 dependent on
331 temperature.

332 A P^0 - P^{5+} redox-buffered environment also has implications for thermometry and cooling
333 rates. Recent experiments found that at >900 °C (close to the closure temperatures of common
334 silicates such as clinopyroxene, orthopyroxene, and plagioclase), the phosphide to phosphate
335 reaction occurs rapidly with a few % oxidation from phosphide within days and complete
336 oxidation within a week, along with a few percent reduction of phosphate on the same timescale
337 (Feng and Pasek, 2023). These experiments using powdered reagents suggest that a phosphide-
338 phosphate phase assemblage would only be preserved if cooling rates were quite fast in the
339 presence of an available oxidant, much faster than the fastest cooling rates estimated for high-

Revision 1

340 temperature meteorite equilibration at 10-100 °C/year for ordinary chondrites (Lucas et al.,
341 2020). However, those estimated cooling rates may not be a good analogy for the larger crystals
342 that are present in the interiors of asteroid parent bodies. Given that closure temperatures are
343 proportional to grain size squared (Dodson, 1973), grains twice as large will cool four times
344 more slowly for a given closure temperature. Therefore, to truly constrain cooling rates of
345 phosphide-phosphate phase assemblages, more experiments are needed to constrain solid-state
346 phosphide oxidation and phosphate reduction timescales for realistic grain sizes in meteorites.

Revision 1

347 Furthermore, phosphide-phosphate buffered experiments may aid in investigating
348 equilibrium chemistry at fO_2 's between IW-2 and IW-4, which have been challenging to explore
349 experimentally due to the limited availability of solid metal-metal oxide buffers between IW (Fe-
350 FeO) and IW-5 (Cr-Cr₂O₃) at temperatures and pressures relevant to planetary interiors. This fO_2
351 range is of particular interest for understanding changes in S speciation that have been
352 highlighted by (Brendan A. Anzures et al., 2020) where the dominant S species in silicate melt
353 changes from FeS at $fO_2 > IW-2$ to MgS at $fO_2 < IW-4$, with a few experiments suggesting that
354 CaS/Na₂S are the major species at IW-2 to IW-4. There is a growing recognition that such low
355 fO_2 conditions (IW-2 to IW-4) were widespread and had a significant control on the formation
356 of planetary bodies in the early solar system, including *primitive meteorite constituents* CAI's,
357 type I CR chondrites, and CM refractory inclusions, *partially differentiated planetesimals* that
358 sourced the winonaite-IAB iron, lodranite-acapulcoite, ureilite, IIE iron, and IIICD iron
359 meteorites (Righter et al., 2016), and finally *planets* on the oxidized range for Mercury (IW-3 to
360 IW-7) (McCubbin et al., 2012; Nittler et al., 2023; Zolotov et al., 2013) and reduced estimate for
361 Earth's core formation (IW-2 to IW-3.5) (Badro et al., 2015; Dauphas, 2017; Fischer et al.,
362 2017).

Acknowledgements

363
364 FMM acknowledges support from NASA's Planetary Science Research Program during
365 this work. We are grateful to the Meteorite Working Group, now the Antarctic Meteorite Review
366 Panel of the Astromaterials Allocation Review Board, for carefully evaluating our sample
367 requests, and we thank the curatorial staff at NASA Johnson Space Center for allocation of the
368 Antarctic meteorites used in this study. The U.S. Antarctic meteorite samples are recovered by
369 the Antarctic Search for Meteorites (ANSMET) program which has been funded by NSF and

Revision 1

370 NASA and characterized and curated by the Department of Mineral Sciences of the Smithsonian
371 Institution and Astromaterials Acquisition and Curation Office at NASA Johnson Space Center,
372 respectively.

373 **References**

- 374 Anzures, B.A., Dygert, N., and Lucas, M. (2022). Thermochemical evolution of the winonaite
375 and IAB iron meteorite parent body. Proceedings of the 53rd Lunar and Planetary Science
376 Conference, p. 2696. Lunar and Planetary Institute, Woodlands, TX.
- 377 Anzures, Brendan A., Parman, S. W., Milliken, R. E., Namur, O., Cartier, C., and Wang, S.
378 (2020). Effect of Sulfur Speciation on Chemical and Physical Properties of Heavily
379 Reduced Mercurian Melts. *Geochimica et Cosmochimica Acta*, 286, 1–18.
- 380 Araki, T., and Moore, P. B. (1981). Fallowite, Na₂Ca(Mn, Fe)₇₋₈(PO₄)₆: its crystal
381 structure. *American Mineralogist*, 66.7-8, 827–842.
- 382 Badro, J., Brodholt, J. P., Piet, H., Siebert, J., and Ryerson, F. J. (2015). Core formation and core
383 composition from coupled geochemical and geophysical constraints. Proceedings of the
384 National Academy of Sciences, 112.40, 12310–12314.
- 385 Barnes, J. J., Franchi, I. A., McCubbin, F. M., and Anand, M. (2019). Multiple reservoirs of
386 volatiles in the Moon revealed by the isotopic composition of chlorine in lunar basalts.
387 *Geochimica et Cosmochimica Acta*, 266, 144–162.
- 388 Barnes, J. J., McCubbin, F. M., Santos, A. R., Day, J. M. D., Boyce, J. W., Schwenger, S. P., Ott,
389 U., Franchi, I. A., Messenger, S., Anand, M., and Agee, C. B. (2020). Multiple early-formed
390 water reservoirs in the interior of Mars. *Nature Geoscience*, 13.4, 260–264.
- 391 Benedix, G. K., Lauretta, D. S., and McCoy, T. J. (2005). Thermodynamic constraints on the
392 formation conditions of winonaites and silicate-bearing IAB irons. *Geochimica et*

Revision 1

- 393 Cosmochimica Acta, 69.21, 5123–5131.
- 394 Benedix, G. K., McCoy, T. J., Keil, K., Bogard, D. D., and Garrison, D. H. (1998). A petrologic
395 and isotopic study of winonaites: Evidence for early partial melting, brecciation, and
396 metamorphism. *Geochimica et Cosmochimica Acta*, 62.14, 2535–2553.
- 397 Benedix, G. K., McCoy, T. J., Keil, K., and Love, S. G. (2000). A petrologic study of the IAB
398 iron meteorites: Constraints on the formation of the IAB-Winonaite parent body.
399 *Meteoritics and Planetary Science*, 35.6, 1127–1141.
- 400 Bild, R. W. (1977). Silicate inclusions in group IAB irons and a relation to the anomalous stones
401 Winona and Mt Morris (Wis). *Geochemica et Cosmochemica Acta*, 41, 1439–1456.
- 402 Bindi, L., Feng, T., and Pasek, M. A. (2023). Routes to reduction of phosphate by high-energy
403 events. *Communications Earth and Environment*, 4.1.
- 404 Boyce, J. W., Tomlinson, S. M., McCubbin, F. M., Greenwood, J. P., and Treiman, A. H. (2014).
405 The lunar apatite paradox. *Science*, 344.6182, 400–402.
- 406 Colombo, F., Sfragulla, J., and Del Tánago, J. G. (2012). The garnet - phosphate buffer in
407 peraluminous granitic magmas: A case study from pegmatites in the Pocho district,
408 Córdoba, Argentina. *Canadian Mineralogist*, 50.6, 1555–1571.
- 409 Dauphas, N. (2017). The isotopic nature of the Earth’s accreting material through time. *Nature*,
410 541.7638, 521–524.
- 411 Feng, T., and Pasek, M. A. (2023). Thermal phosphide mineral oxidation chemistry. Proceedings
412 of the 54th Lunar and Planetary Science Conference, p. #1322. Lunar and Planetary
413 Institute, Woodlands, TX.
- 414 Fischer, R. A., Campbell, A. J., and Ciesla, F. J. (2017). Sensitivities of Earth’s core and mantle
415 compositions to accretion and differentiation processes. *Earth and Planetary Science*

Revision 1

- 416 Letters, 458, 252–262.
- 417 Floss, C. (1999). Fe,Mg,Mn-bearing phosphates in the GRA 95209 meteorite: Occurrences and
418 mineral chemistry. *American Mineralogist*, 84.9, 1354–1359.
- 419 Floss, C., Jolliff, B. L., Benedix, G. K., Stadermann, F. J., and Reid, J. (2007). Hammadah al
420 Hamra 193: The first amphibole-bearing winonaite. *American Mineralogist*, 92.4, 460–467.
- 421 Fransolet, A. M., Fontan, F., Keller, P., and Antenucci, D. (1998). La Serie johnsomervilleite-
422 fillowite dans les associations de phosphates de pegmatites granitiques de l’Afrique
423 Centrale. *Canadian Mineralogist*, 36, 355–366.
- 424 Gattacceca, J., McCubbin, F. M., Grossman, J. N., Schrader, D. L., Chabot, N. L., D’Orazio, M.,
425 Goodrich, C., Greshake, A., Gross, J., Joy, K. H., Komatsu, M., and Miao, B. (2023). The
426 Meteoritical Bulletin, No. 111. *Meteoritics and Planetary Science*, 58.6, 901–904.
- 427 Grew, E. S., Armbruster, T., Medenbach, O., Yates, M. G., and Carson, C. J. (2006). Stornesite-
428 (Y), (Y, Ca) \square Na₆(Ca,Na)₈(Mg,Fe)₄₃(PO₄)₃₆, the first terrestrial Mg-dominant member
429 of the fillowite group, from granulite-facies paragneiss in the Larsemann Hills, Prydz Bay,
430 East Antarctica. *American Mineralogist*, 91.8–9, 1412–1424.
- 431 Grew, E. S., Yates, M. G., Beane, R. J., Floss, C., and Gerbi, C. (2010). Chopinite-sarcopside
432 solid solution, $[(Mg, Fe)_{3\square}](PO_4)_2$, in GRA95209, a transitional acapulcoite: Implications
433 for phosphate genesis in meteorites. *American Mineralogist*, 95.2–3, 260–272.
- 434 Hatert, F., Grew, E. S., Vignola, P., Rotiroti, N., Nestola, F., Keller, P., Bajjot, M., Bruni, Y.,
435 Fransolet, A. M., Dal Bo, F., and Depret, M. (2021). Crystal chemistry and nomenclature of
436 fillowite-type phosphates. *Canadian Mineralogist*, 59.4, 781–796.
- 437 Hunt, A. C., Benedix, G. K., Hammond, S. J., Bland, P. A., Rehkämper, M., Kreissig, K., and
438 Strekopytov, S. (2017). A geochemical study of the winonaites: Evidence for limited partial

Revision 1

- 439 melting and constraints on the precursor composition. *Geochimica et Cosmochimica Acta*,
440 199, 13–30.
- 441 Hunt, A. C., Cook, D. L., Lichtenberg, T., Reger, P. M., Ek, M., Golabek, G. J., and
442 Schönbächler, M. (2018). Late metal–silicate separation on the IAB parent asteroid:
443 Constraints from combined W and Pt isotopes and thermal modelling. *Earth and Planetary
444 Science Letters*, 482, 490–500.
- 445 Jones, R. H., McCubbin, F. M., Dreeland, L., Guan, Y., Burger, P. V., and Shearer, C. K. (2014).
446 Phosphate minerals in LL chondrites: A record of the action of fluids during metamorphism
447 on ordinary chondrite parent bodies. *Geochimica et Cosmochimica Acta*, 132, 120–140.
- 448 Jones, R. H., McCubbin, F. M., and Guan, Y. (2016). Phosphate minerals in the H group of
449 ordinary chondrites, and fluid activity recorded by apatite heterogeneity in the Zag H3-6
450 regolith breccia. *American Mineralogist*, 101.11., 2452–2467.
- 451 Karwowski, Ł., Kryza, R., Muszyński, A., Kusz, J., Helios, K., Drożdżewski, P., and Galuskin,
452 E. V. (2016). Czochralskiite, Na₄Ca₃Mg(PO₄)₄, a second new mineral from the Morasko
453 IAB-MG iron meteorite (Poland). *European Journal of Mineralogy*, 28.5, 969–977.
- 454 Karwowski, Ł., Kusz, J., Muszyński, A., Kryza, R., Sitarz, M., and Galuskin, E. V. (2015).
455 Moraskoite, Na₂Mg(PO₄)₂F, a new mineral from the Morasko IAB-MG iron meteorite
456 (Poland). *Mineralogical Magazine*, 79.2, 387–398.
- 457 Lanari, P., Vho, A., Bovay, T., Airaghi, L., and Centrella, S. (2019). Quantitative compositional
458 mapping of mineral phases by electron probe micro-analyser. *Geological Society Special
459 Publication*, 478.1, 39–63.
- 460 Lanari, P., Vidal, O., De Andrade, V., Dubacq, B., Lewin, E., Grosch, E. G., and Schwartz, S.
461 (2014). XMapTools: A MATLAB©-based program for electron microprobe X-ray image

Revision 1

- 462 processing and geothermobarometry. *Computers and Geosciences*, 62, 227–240.
- 463 Li, S., Wang, S., Bao, H., Miao, B., Liu, S., Coulson, I. M., Li, X., and Li, Y. (2011). The
464 Antarctic achondrite, Grove Mountains 021663: An olivine-rich winonaite. *Meteoritics and*
465 *Planetary Science*, 46.9, 1329–1344.
- 466 Litasov, K. D., and Podgornykh, N. M. (2017). Raman spectroscopy of various phosphate
467 minerals and occurrence of tuite in the Elga IIE iron meteorite. *Journal of Raman*
468 *Spectroscopy*, 48.11, 1518–1527.
- 469 Lucas, M. P., Dygert, N., Ren, J., Hesse, M. A., Miller, N. R., and McSween, H. Y. (2020).
470 Evidence for early fragmentation-reassembly of ordinary chondrite (H, L, and LL) parent
471 bodies from REE-in-two-pyroxene thermometry. *Geochimica et Cosmochimica Acta*, 290,
472 366–390.
- 473 McCoy, T. J., and Carlson, W. D. (1998). Opaque minerals in the GRA 95209 lodranite: A
474 snapshot of metal segregation. *Proceedings of the 29th Lunar and Planetary Science*
475 *Conference*, p. 1675. Lunar and Planetary Institute, Woodlands, TX.
- 476 McCoy, T. J., Carlson, W. D., Nittler, L. R., Stroud, R. M., Bogard, D. D., and Garrison, D. H.
477 (2006). Graves Nunataks 95209: A snapshot of metal segregation and core formation.
478 *Geochimica et Cosmochimica Acta*, 70.2, 516–531.
- 479 McCoy, T. J., Steele, I. M., Keil, K., Leonard, B. F., and Endress, M. (1994). Chladniite,
480 Na₂CaMg₇(PO₄)₆: A new mineral from the Carlton (IIICD) iron meteorite. *American*
481 *Mineralogist*, 79, 375–380.
- 482 McCubbin, F. M., and Jones, R. H. (2015). Extraterrestrial apatite: Planetary geochemistry to
483 astrobiology. *Elements*, 11.3, 183–188.
- 484 Mccubbin, F. M., Lewis, J. A., Barnes, J. J., Boyce, J. W., Gross, J., Mccanta, M. C., Srinivasan,

Revision 1

- 485 P., Anzures, B. A., Lunning, N. G., Elardo, S. M., Keller, L. P., Prissel, T. C., and Agee, C.
486 B. (2023). On the origin of fluorine-poor apatite in chondrite parent bodies. American
487 Mineralogist, 108, 1185–1200.
- 488 McCubbin, F. M., Lewis, J. A., Barnes, J. J., Elardo, S. M., and Boyce, J. W. (2021). The
489 abundances of F, Cl, and H₂O in eucrites: Implications for the origin of volatile depletion in
490 the asteroid 4 Vesta. *Geochimica et Cosmochimica Acta*, 314, 270-293.
- 491 McCubbin, F. M., Riner, M. A., Vander Kaaden, K. E., and Burkemper, L. K. (2012). Is Mercury
492 a volatile-rich planet? *Geophysical Research Letters*, 39.9, 1–5.
- 493 McCubbin, F. M., and Ustunisik, G. (2018). Experimental investigation of F and Cl partitioning
494 between apatite and Fe-rich basaltic melt at 0 GPa and 950-1050 °C: Evidence for steric
495 controls on apatite-melt exchange equilibria in OH-poor apatite. *American Mineralogist*,
496 103.9, 1455–1467.
- 497 Nittler, L. R., Boujibar, A., Crapster-Pregont, E., Frank, E. A., McCoy, T. J., McCubbin, F. M.,
498 Starr, R. D., Vorburger, A., and Weider, S. Z. (2023). Chromium on Mercury: New Results
499 From the MESSENGER X-Ray Spectrometer and Implications for the Innermost Planet's
500 geochemical evolution. *Journal of Geophysical Research: Planets*, e2022JE007691.
- 501 Pan, Y., and Fleet, M. E. (2002). Compositions of the apatite-group minerals: Substitution
502 mechanisms and controlling factors. *Phosphates: Geochemical, Geobiological and Materials*
503 *Importance*, 48, 13–50.
- 504 Pasek, M. A. (2015). Phosphorus as a lunar volatile. *Icarus*, 255, 18–23.
- 505 Patiño Douce, A. E., and Roden, M. (2006). Apatite as a probe of halogen and water fugacities in
506 the terrestrial planets. *Geochimica et Cosmochimica Acta*, 70.12, 3173–3196.
- 507 Piccoli, P. M., and Candela, P. A. (2002). Apatite in igneous systems. *Reviews in mineralogy*

Revision 1

- 508 and Geochemistry, 48.1, 255-292..
- 509 Prior, D. J., Boyle, A. P., Brenker, F., Cheadle, M. C., Austin, D., Lopez, G., Peruzzo, L., Potts,
510 G. J., Reddy, S., Spiess, R., Timms, N. E., Trimby, P., Wheeler, J., and Zetterström, L.
511 (1999). The application of electron backscatter diffraction and orientation contrast imaging
512 in the SEM to textural problems in rocks. *American Mineralogist*, 84.11–12, 1741–1759.
- 513 Righter, K., Sutton, S. R., Danielson, L., Pando, K., and Newville, M. (2016). Redox variations
514 in the inner solar system with new constraints from vanadium XANES in spinels. *American*
515 *Mineralogist*, 101, 1928–1942.
- 516 Sarafian, A. R., John, T., Roszjar, J., and Whitehouse, M. J. (2017). Chlorine and hydrogen
517 degassing in Vesta’s magma ocean. *Earth and Planetary Science Letters*, 459, 311–319.
- 518 Tartèse, R., Anand, M., and Franchi, I. A. (2019). H and Cl isotope characteristics of indigenous
519 and late hydrothermal fluids on the differentiated asteroidal parent body of Grave Nunataks
520 06128. *Geochimica et Cosmochimica Acta*, 266, 529–543.
- 521 Vallcorba, O., Casas, L., Colombo, F., Frontera, C., and Rius, J. (2016). First terrestrial
522 occurrence of the complex phosphate chladniite: crystal-structure refinement by
523 synchrotron through-the-substrate microdiffraction. *European Journal of Mineralogy*, 29.2,
524 287–293.
- 525 Voshage, H. (1967). Bestrahlungsalter und Herkunft der Eisenmeteorite. *Zeitschrift Fur*
526 *Naturforschung - Section A Journal of Physical Sciences*, 22.4, 477–506.
- 527 Ward, D., Bischoff, A., Roszjar, J., Berndt, J., and Whitehouse, M. J. (2017). Trace element
528 inventory of meteoritic Ca-phosphates. *American Mineralogist*, 102.9, 1856–1880.
- 529 Webster, J. D., and Piccoli, P. M. (2015). Magmatic apatite: A powerful, yet deceptive, mineral.
530 *Elements*, 11.3, 177–182.

Revision 1

- 531 Xie, X., Yang, H., Gu, X., and Downs, R. T. (2015). Chemical composition and crystal structure
532 of merrillite from the Suizhou meteorite. *American Mineralogist*, 100.11–12, 2753–2756.
- 533 Zeng, X., Shang, Y., Li, S., Li, X., Wang, S., and Li, Y. (2019). The layered structure model for
534 winonaite parent asteroid implicated by textural and mineralogical diversity. *Earth, Planets
535 and Space*, 71.1, 1-15.
- 536 Zolotov, M. Y., Sprague, A. L., Hauck, S. A., Nittler, L. R., Solomon, S. C., and Weider, S. Z.
537 (2013). The redox state, FeO content, and origin of sulfur-rich magmas on Mercury. *Journal
538 of Geophysical Research: Planets*, 118.1, 138–146.

539

540

Figure Captions

541 **Figure 1.** BSE image of two areas ((a) area A and (b) area B) of chladniite with associated
542 minerals merrillite, kamacite, taenite, troilite, albite, forsterite, diopside, and enstatite.

543

544 **Figure 2.** Mineralogical map of GRA 12510. Chladniite grains from 1-200 μm are scattered
545 throughout the section often on margins between silicate clasts and metal. The areas immediately
546 surrounding chladniite are mostly Mn-free, but several Mn-rich chromite grains (7.89 wt% MnO)
547 and one tiny alabandite grain (MnS) are found elsewhere in the section. Schreibersite is also anti-
548 correlated with chladniite. Black box insets correspond to areas A and B in figure 1. White
549 circles are 75-150 μm LA-ICP-MS pits from previous trace element analyses.

550

551 **Figure 3.** EBSD data of three occurrences of chladniite ((a) area A, (b) area A, (c) area B) and
552 its associated mineral assemblages with forward scattered electron diode (FSD), phase overlay,
553 and inverse pole (IPF) images along with the Kikuchi patterns, Kikuchi bands, and Kikuchi
554 solutions as well as pole figures $\{0001\}$, $\{10-10\}$, and $\{11-20\}$.

555

556 **Figure 4.** (a) Raman image overlaying an optical microscope image exhibiting the distribution of
557 chladniite and merrillite in area B of GRA 12510. (b) Raman spectra of chladniite compared
558 with merrillite and fillowite (RRUFF ID: R110143).

559

560 **Figure 5.** Plot of oxygen fugacity ($\log f\text{O}_2$) vs. temperature ($10000/T(\text{K})$) for IAB irons and a
561 winonaite along with appropriate oxygen fugacity buffers adapted from Benedix et al. (2005).
562 Oxygen fugacity determined from orthopyroxene (blue) and olivine (red) for meteorites Cad
563 (Caddo County), CdC (Campo del Cielo), Cop (Copiapo), Lue (Lueders), Ude (Udei Station),
564 Win (Winona) with data falling along the dashed best fit line. Winonaite and IAB iron meteorite
565 oxygen fugacities fall along the schreibersite (Fe_3P) – whitlockite ($\text{Ca}_3(\text{PO}_4)_2$) buffer purple line
566 (Pasek 2015; Bindi et al. 2023) indicating these meteorites were likely redox buffered by the

Revision 1

567 present phase assemblage of phosphide (P valence state of 0) and phosphate (P valence state of
568 5+). Also shown are three CO-C fugacity buffers at different pressures that fall on a different
569 slope.

570

571 **Figure 6.** Ternary Fe²⁺-Mn-Mg diagram of natural fillowite-type phosphates. The most Mn-rich
572 analysis of chladniite in GRA 12510 falls slightly within the proposed miscibility gap of Hatert
573 et al. (2021).

574

Revision 1

Table 1. Modal abundance of minerals in GRA 12510 (by area %)

enstatite	27.89
diopside	4.10
albite	11.49
forsterite	20.04
chromite	0.83
kamacite	25.92
taenite	4.54
schreibersite	1.09
troilite	2.88
alabandite	Trace
chladniite	0.78
merrillite	0.45
apatite	Trace

Table 2. Average major element compositions (wt%) of phosphates (chladniite, merrillite, and apatite), silicates and oxides (forsterite, enstatite, diopside, albite, and chromite), metals (kamacite, taenite, schreibersite), and sulfides (troilite, alabandite) in GRA 12510 from EPMA

Phosphates					
wt%	chladniite	merrillite	apatite		
SiO₂	0.25 (16)	<i>b.d.</i>	<i>b.d.</i>		
TiO₂	0.03 (00)	<i>b.d.</i>	<i>b.d.</i>		
FeO	1.14 (10)	0.32 (30)	0.75		
MnO	3.92 (12)	0.19 (3)	0.16		
MgO	32.58 (26)	3.78 (6)	0.13		
CaO	5.62 (3)	46.23 (21)	53.57		
Na₂O	6.75 (5)	2.75 (3)	0.08		
P₂O₅	51.22 (25)	47.14 (39)	42.02		
F^a			2.38		
Cl			2.51		
S			0.01		
-O = F + Cl + S			1.65		
Total	101.51 (31)	100.42 (33)	99.96		
N	37	20	1		
Silicates and Oxides					
wt%	forsterite	enstatite	diopside	albite	chromite
SiO₂	42.06 (21)	59.95 (9)	54.91 (20)	65.55 (52)	0.02 (1)
TiO₂	<i>b.d.</i>	0.02 (0)	0.68 (4)	0.04 (1)	0.20 (6)
Al₂O₃	<i>b.d.</i>	0.03 (0)	0.81 (6)	21.38 (17)	0.46 (47)
Cr₂O₃					70.38 (52)

Revision 1

FeO	3.11 (84)	0.48 (2)	1.06 (14)	0.29 (17)	13.77 (64)
MnO	0.97 (31)	0.24 (0)	0.36 (3)	0.01 (1)	7.89 (79)
MgO	55.51 (92)	40.18 (0)	18.73 (17)	0.01 (1)	6.05 (16)
CaO	0.02 (1)	0.65 (13)	22.09 (26)	2.38 (22)	0.01 (1)
Na₂O	<i>b.d.</i>	0.01 (1)	0.72 (5)	9.89 (16)	
V₂O₃					0.40 (13)
ZnO					1.30 (4)
Total	101.67	101.55	99.36	99.56	100.48
N	4	2	6	12	13
Metals and sulfides					
wt%	kamacite	taenite	schreibersite	troilite	alabandite
S	<i>b.d.</i>	<i>b.d.</i>		36.16 (71)	36.80 (10)
P	0.04 (2)	0.01 (1)	15.02 (4)	0.01 (1)	
Si	0.02 (1)	0.02 (2)	0.01 (0)	0.04 (1)	0.03 (2)
Mg	0.01 (1)	<i>b.d.</i>		0.02 (1)	0.02 (1)
Ca	0.01 (1)	0.01 (1)		0.07 (5)	0.01 (1)
Mn	0.01 (1)	<i>b.d.</i>		0.02 (2)	58.03 (29)
Ni	6.17 (34)	25.34 (70)	48.28 (71)	0.02 (2)	0.14 (6)
Cr	<i>b.d.</i>	<i>b.d.</i>		0.06 (2)	<i>b.d.</i>
Mo	<i>b.d.</i>	0.01 (1)		<i>b.d.</i>	<i>b.d.</i>
Fe	93.59 (133)	75.63 (63)	36.73 (60)	62.36 (52)	4.81 (19)
Co	0.55 (2)	0.25 (2)	0.11 (1)	0.08 (1)	
Total	100.42 (140)	101.29 (23)	100.14 (40)	98.84 (92)	99.83 (32)
N	29	5	20	7	5

^aX-site sum exceeded 1 structural formula unit so F was computed assuming $X_F = 1 - X_{Cl}$ using the methods outlined in McCubbin et al., (2021)

N – number of analyses

b.d. – abundance was below detection limit

All parenthetical values represent 1-sigma standard deviation of the mean

Figure 1

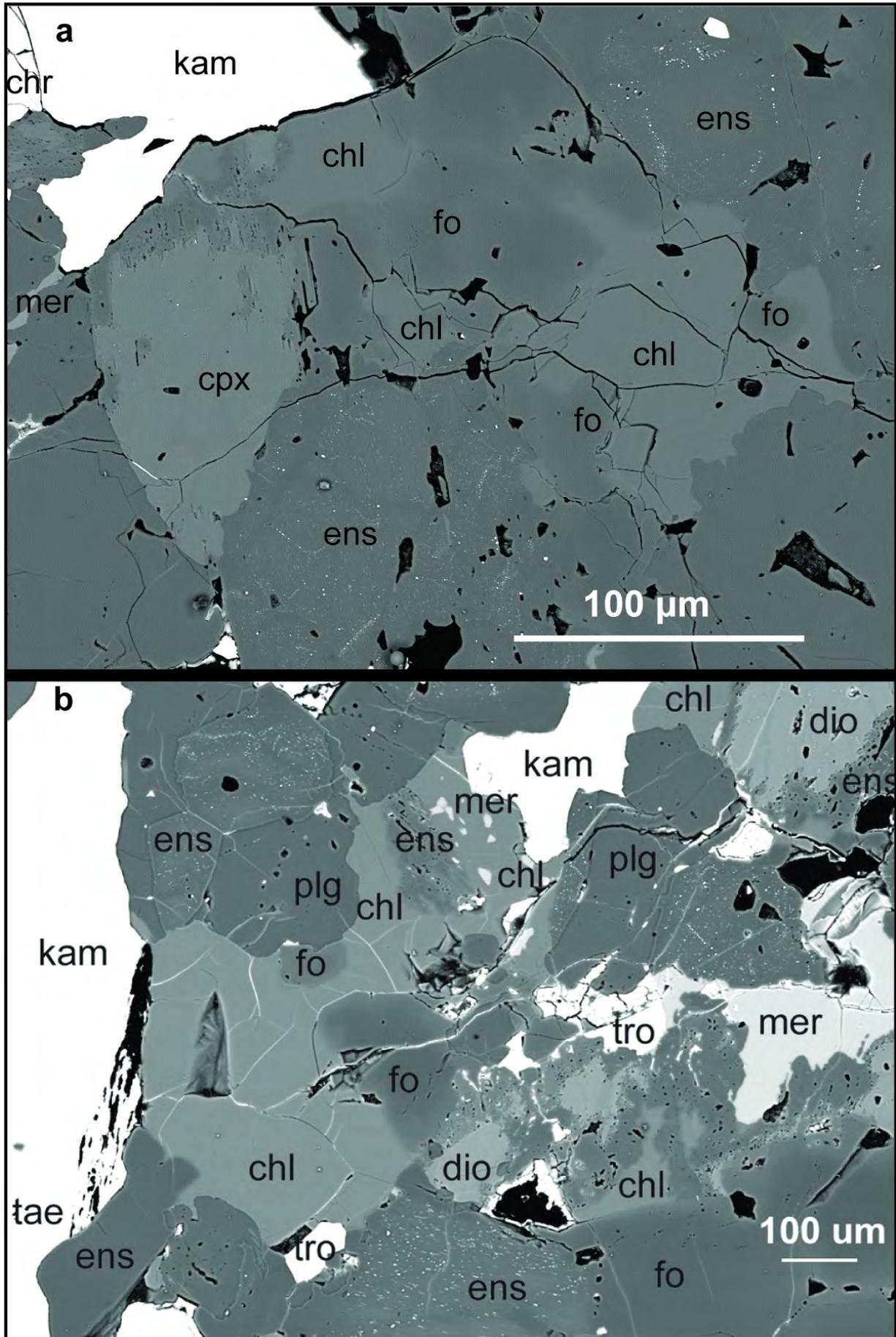


Figure 2

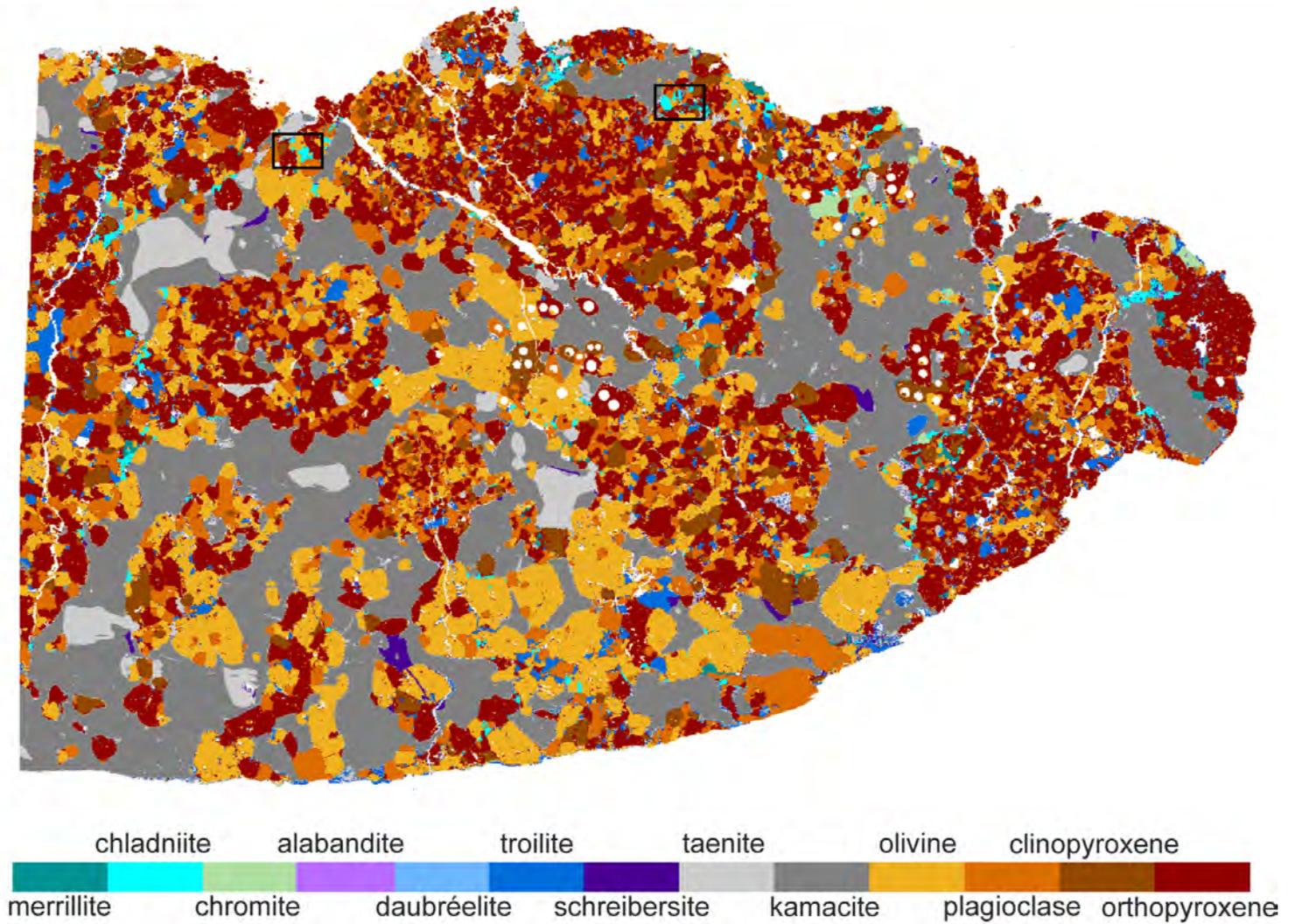


Figure 3a

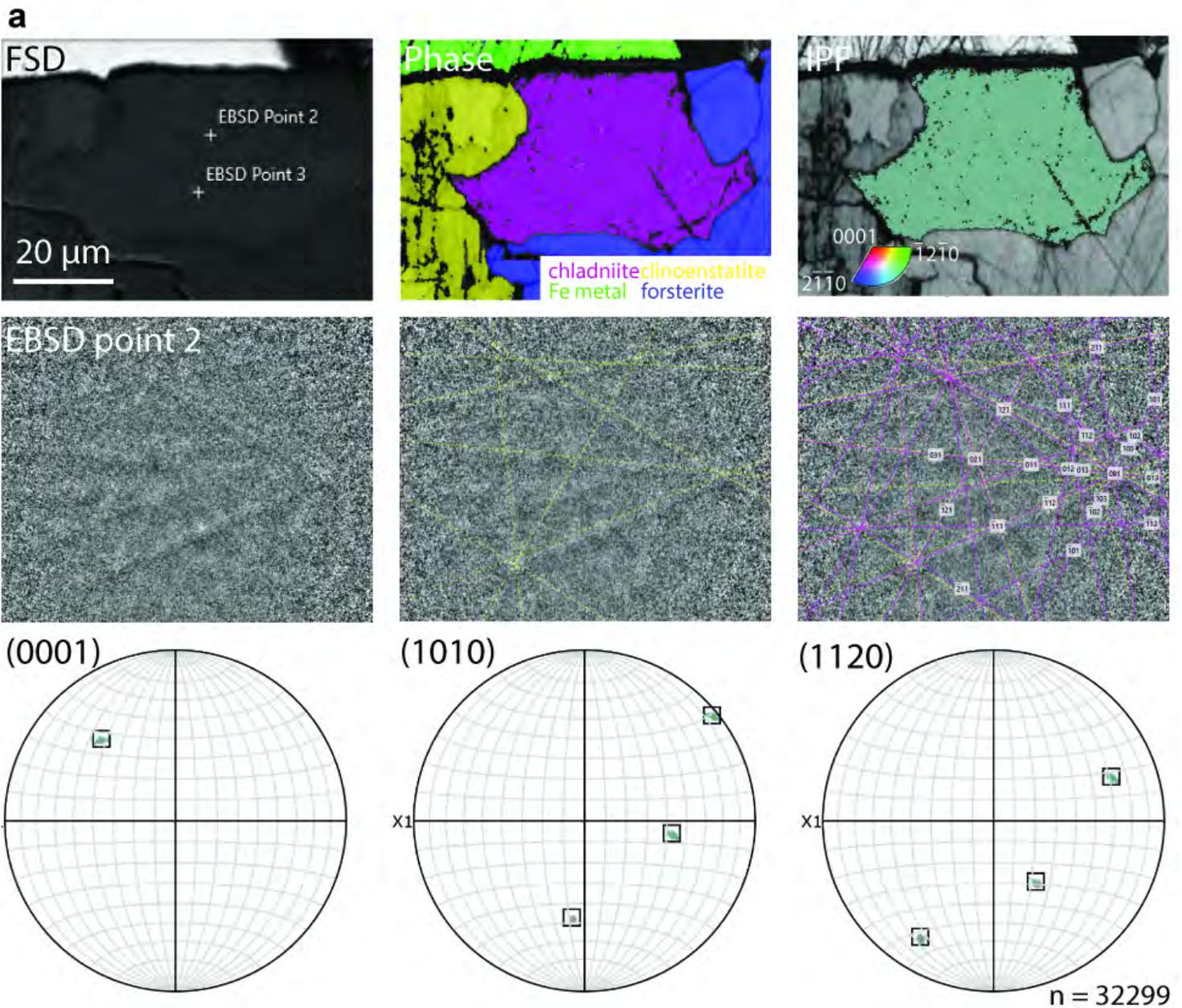


Figure 3b

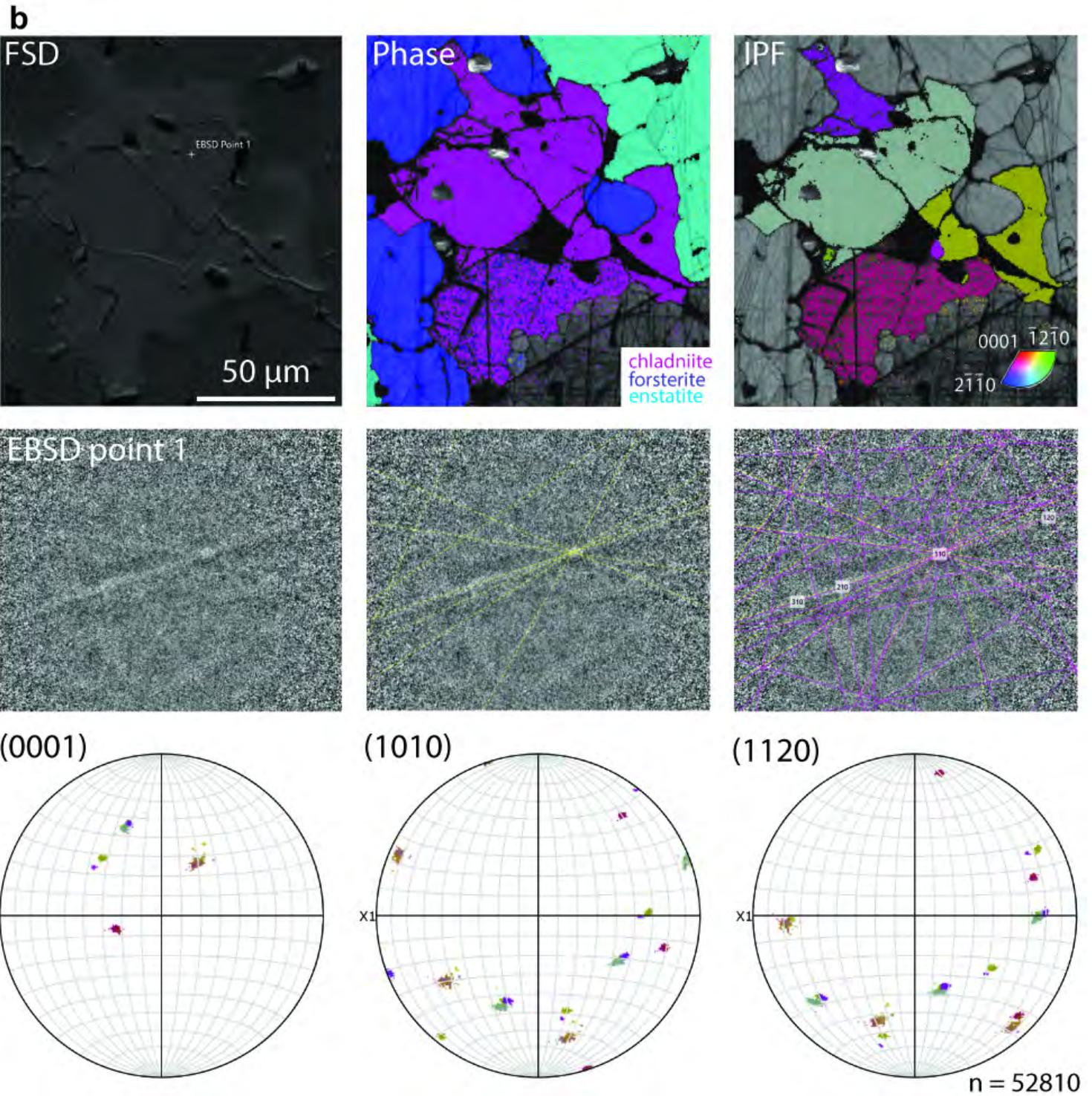


Figure 3c

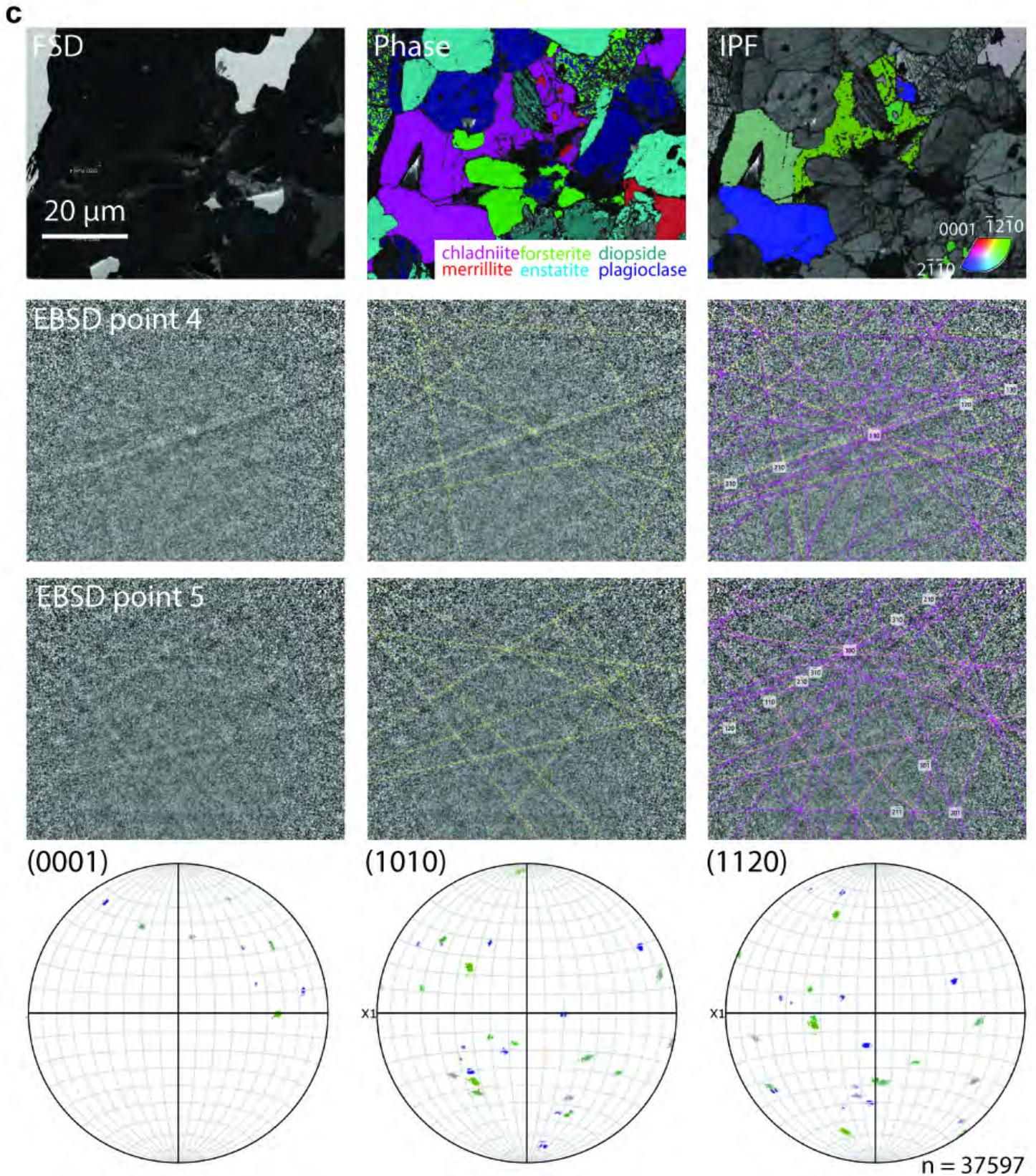


Figure 4

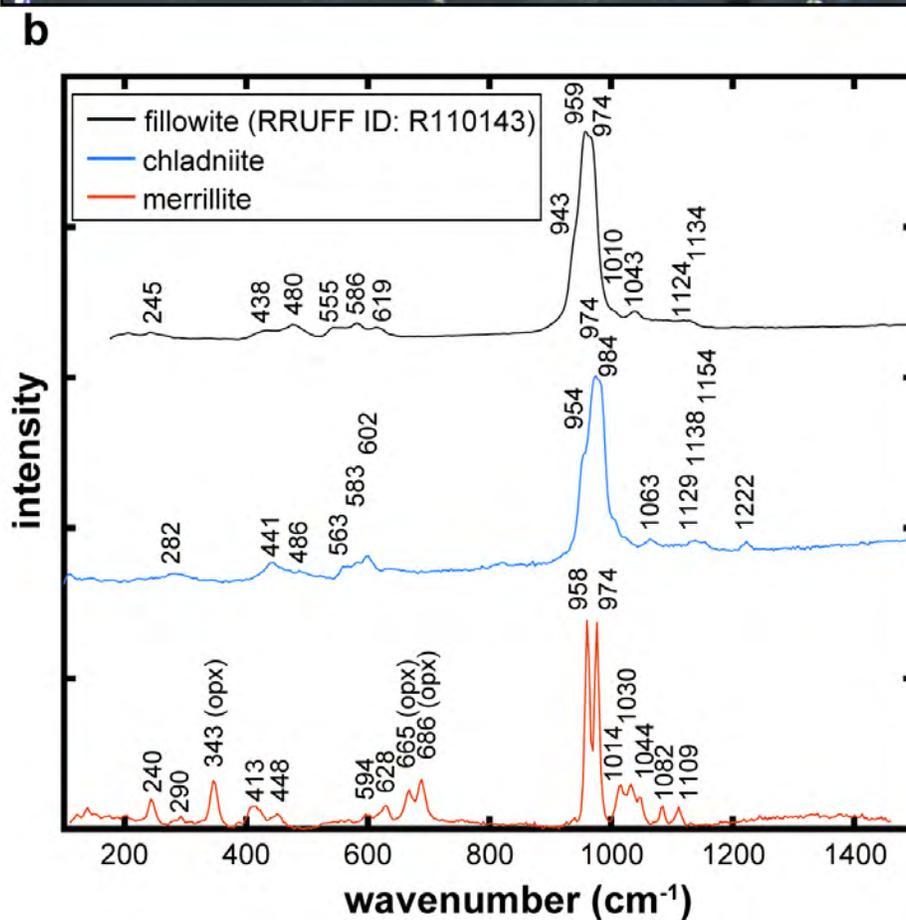
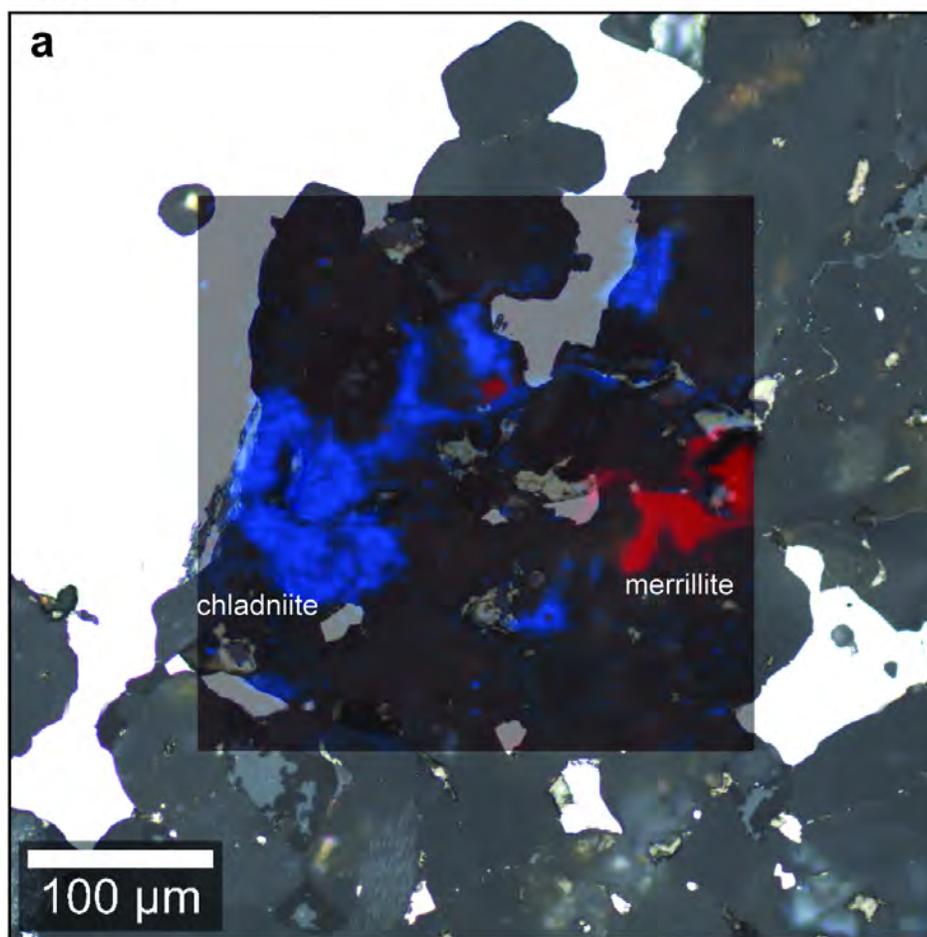


Figure 5

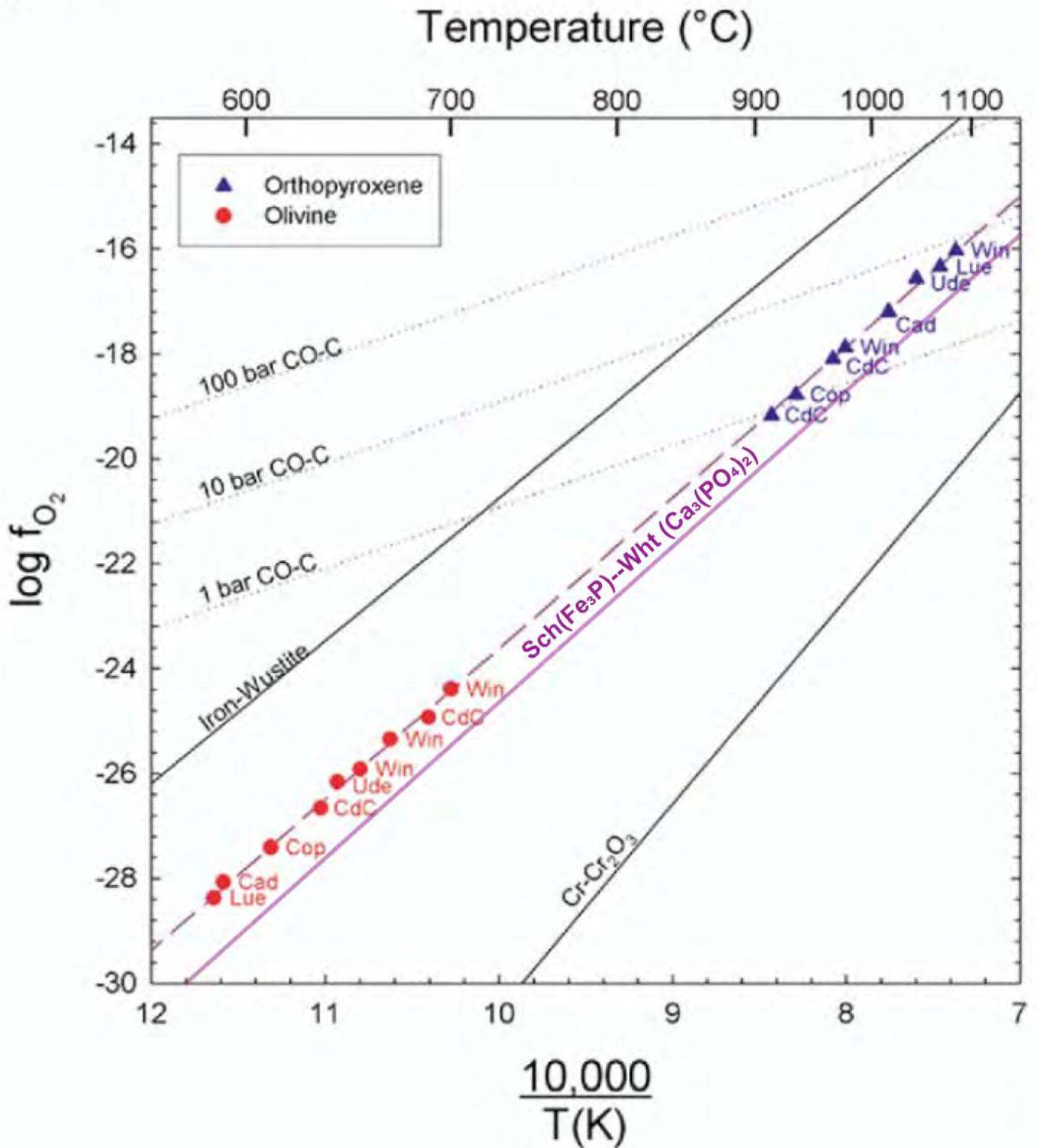


Figure 6

