

1 **Surface transformations of platinum grains from Fifield, New South Wales, Australia**
2 **(Revision 2)**

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33 **Abstract**

34 A growing literature is demonstrating that platinum (Pt) is transformed under surface conditions;
35 yet (bio)geochemical processes at the nugget-soil-solution interface are incompletely understood.
36 The reactivity of Pt exposed to Earth-surface weathering conditions, highlighted by this study,
37 may improve our ability to track its movement in natural systems, e.g., focusing on nanoparticles
38 as a strategy for searching for new, undiscovered sources of this precious metal. To study
39 dissolution/re-precipitation processes of Pt and associated elements, grains of Pt-Fe alloy were

40 collected from a soil placer deposit at the Fifield Pt-field, Australia. Optical- and electron-
41 microscopy revealed morphologies indicative of physical transport as well as chemical
42 weathering. Dissolution ‘pits’, cavities, striations, colloidal nano-particles and aggregates of
43 secondary Pt platelets as well as acicular, iron (Fe) hydroxide coatings were observed. FIB-
44 SEM-(EBSD) combined with S- μ -XRF of a sectioned grain showed a fine layer of up to 5 μ m
45 thick composed of refined, aggregates of 0.2 to 2 μ m-sized crystalline secondary Pt overlying
46 more coarsely crystalline Pt-Fe-alloy of primary magmatic origin. These results confirm that Pt
47 is affected by geochemical transformations in supergene environments; structural and chemical
48 signatures of grains surfaces, rims and cores are linked to the grains’ primary and secondary
49 (trans)formational histories; and Pt mobility can occur under Earth surface conditions.
50 Intuitively, this nanophase-Pt can disperse much further from primary sources of ore than
51 previously thought. This considerable mineral reactivity demonstrates that the formation and/or
52 release of Pt nanoparticles needs to be measured and incorporated into exploration geochemistry
53 programs.

54 **Keywords:** platinum, weathering, Fifield Pt-Province, secondary mineralization, Australia

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Introduction

57 Platinum is a highly prized noble metal; its resistance to oxidation and corrosion in
58 combination with its unique surface properties makes it an important catalyst in industrial
59 processes and automobile catalytic converters (MacDonald 1987). With ca. 90 % of the world’s
60 production of Pt coming from the Republic of South Africa and the Russian Federation, Pt is a
61 highly strategic resource, important to resource security (Koek et al. 2010). To enhance
62 exploration success, a fundamental understanding of (bio)geochemical processes leading to Pt

63 dispersion in surface environments needs to be developed. Understanding Pt-Fe alloy
64 weathering is one component that will improve our ability to recover Pt from soils and track its
65 movement in nature. This could potentially lead to new, undiscovered sources of this precious
66 metal and to an improved understanding of the cycling of industrial Pt-nanoparticles in the
67 environment.

68 Schneiderhöhn and Moritz (1939) described native Pt that was entirely porous from the
69 oxidized zone of the Merensky Reef, Bushveld Complex, Republic of South Africa that they
70 interpreted as a dissolution feature of a pre-existing mineral, such as sperrylite or cooperite.
71 Native Pt as rims was subsequently observed on both sperrylite (Oberthur et al. 2003, 2013;
72 Melcher et al. 2005) and on cooperite (Oberthur 2002; Oberthur et al. 2004). Platinum
73 mobility can occur in eluvial, alluvial and lateritic environments in tropical and possibly also
74 semi-arid climates (Bowles 1986; Freyssinet et al. 2005). Under supergene conditions Pt may be
75 oxidized, dissolved, complexed by inorganic- and organic- ligands, transported, re-precipitated
76 and deposited, yet these processes are incompletely understood (Fuchs and Rose 1974; Bowles
77 1986; Hanley 2005). The reactivity of platinoids to secondary processing appears to vary based
78 on the reactivity of the starting material. Placer Pt grains are often larger than the primary
79 sources they are derived from (Cousins and Kinloch 1973, 1976) suggesting that secondary
80 processes contribute to growth or aggregation of these materials. Conversely, other studies
81 indicate that Pt-Fe alloy is susceptible to dissolution and will “shrink” in weathering
82 environments (Cabral et al. 2007; Traoré et al. 2008). Evidence, for a biogenic contribution to
83 the formation of the arborescent Pt–Pd nuggets, and the presence of organic matter in these
84 grains, has recently been described (Cabral et al. 2011). This continuum of dissolution versus

85 growth is typically revealed using mineralogical and petrologic analyses of placer Pt-grains,
86 highlight the opposing processes that can transform Pt-grains in natural systems.

87 The internal composition of eluvial and alluvial Pt-Fe alloy from the Fifield site proves a
88 high temperature primary origin (Slansky et al. 1991); however, to better understand the
89 weathering of Pt-Fe alloy in surficial environments, chemical characterization of mineral
90 dissolution-precipitation processes occurring at the solid-solution interface needs to be
91 conducted. In a recent study, Brugger et al. (2013) compared the μm -scale dispersion of Au and
92 Pt within an extraordinary 10 mm-sized fragment of ferruginous palaeochannel material from
93 Fifield that contained a number of native Au- and Pt-Fe alloy (based on the classification scheme
94 of Cabri et al. 1996). While Au grains were surrounded by an abundant dusting of highly pure
95 metallic Au particles ($10\text{ nm} < \text{secondary Au} < 10\ \mu\text{m}$ in diameter), which is indicative of
96 (bio)geochemical transformations (Reith et al. 2007, 2010; Southam et al. 2009), secondary Pt
97 was not observed in this sample. In contrast, the Pt-Fe alloy grains appeared smoother and more
98 rounded, but also displayed signs indicative of supergene transformations, e.g., herringbone-
99 shaped embayments, possibly pointing to the weathering-out of a more reactive material, e.g.,
100 Os-Ir alloy inclusions. However, to establish if Pt itself is mobilized and/or re-precipitated from
101 Pt-Fe alloy in weathering environments, additional research on a larger number of these grains
102 needs to be undertaken using targeted micro-analyses techniques. The specific focus of this
103 study was placed on the examination of mechanical and chemical evidence for nano- and
104 microscale surface transformations resulting the redistribution of Pt, which should be detectable
105 using Electron microprobe mapping, (Focused Ion Beam)-Scanning Electron Microscopy-
106 (Energy Dispersive X-ray Analysis/Electron BackScatter Diffraction) (FIB)-SEM-
107 (EDXA/EBSD) in combination with electron X-ray emission spectroscopy: X-ray Analysis Near

108 Edge Structure (XANES), micro X-Ray Fluorescence (μ XRF) and micro X-Ray Diffraction
109 (μ XRD).

110

111 **Materials and Methods**

112 **Field Description and Sampling**

113 The Fifield Pt-field, situated about 380 km WNW of Sydney, Australia (Figure 1), was
114 the largest Australian producer of Pt: 650 kg of Pt and 325 kg of Au were recovered from
115 Pleistocene gravels and recent residual soils since its discovery in 1887 (Johan et al. 1989). The
116 Fifield Pt-field is part of the Fifield Pt-province, which contains ca. 40 Alaskan-type mafic-
117 ultramafic intrusions (monzodiorite, gabbro-norite, hornblendite,
118 hornblende/olivine/biotite/magnetite-clinopyroxenite, peridotite and dunite complexes). These
119 late Ordovician to Siluro-Devonian magmatic bodies intrude into Cambro-Ordovician
120 metasediments and, locally, Silurian and Devonian volcanics and sediments (Crawford et al.
121 2007; Johan et al. 1989; Slansky et al. 1991). Mineralization associated with chromite-rich
122 layers within dunites is dominated by Pt-Fe alloy with inclusions of Os-Ir alloy, and rare
123 inclusions of Ru, Rh and Ir sulfides (Johan et al. 1989; Slansky et al. 1991). Landscape
124 evolution at the site commenced in the Early to Middle Devonian, and subsequent periods of
125 weathering, laterization and fluvial erosion have continued since then. Since the Jurassic, Pt and
126 Au grains have been concentrated into a number of paleoplacers that have been reworked
127 throughout the Cenozoic (Teluk 2001). The grains used in this study were obtained from the
128 soils overlying the Platina Deep Lead, which is assumed to be of early Tertiary age. While these
129 grains are considered to be primary, a primary source of mineralization for these grains has not
130 been determined (Slansky et al. 1991; Teluk 2001). The regolith over the Platina Lead Pt-Au

131 bedrock source area is a Pt-Au bearing residual soil, classified as a red podsol, with limited Fe
132 pisolitic pebble development (Northcote 1979).

133 Two hundred and fifty Pt grains, representing the dominant morphotypes, were
134 subsampled from ca. 500 g of placer Pt using a field-sterile sampling procedure described by
135 Reith et al. (2010). Upon collection, 20 grains were immediately submerged in 2 vol. %_(aq)
136 glutaraldehyde to fix any biological materials.

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138 **Micro-analyses of Pt grains**

139 Platinum grains from the Fifield Pt Province were screened by using an optical binocular
140 microscope equipped with a Nikon DXM1200 digital camera. Representative grains reflecting
141 the diversity of morphologies observed in the sample were selected for micro-analytical
142 characterization.

143 Ten representative grains were set in epoxy resin, polished with 1 μm diamond paste, C-
144 coated (15 nm) and subjected to electron microprobe mapping (EPMA) using a Cameca SX51
145 Microprobe (Cameca, France) equipped with five wavelength dispersive spectrometers as
146 described by Fairbrother et al. (2012). Data collection and reduction was performed with the
147 SAMx package. Analyses were conducted at 20 kV and 19.9 nA with a 1 μm beam diameter.

148 To investigate possible biogenic components, the twenty glutaraldehyde-fixed grains
149 were dehydrated using a 25, 50, 75 and 3 times 100 vol. %_(aq) ethanol series for 15 min each,
150 critical point dried using a Tousimis Samdri[®]-PVT-3B drier, and Os-coated (5 nm; Osmium
151 Plasma Coater Model OPC-80T - SPI Supplies). A LEO 1530 field emission gun-scanning
152 electron microscope (FEG-SEM), a Zeiss 1540 XB, a Philips XL30-, and a Hitachi SU 6600
153 analytical FEG-SEM were used to produce high-resolution micrographs. An Oxford

154 Instruments' INCAx-sight energy dispersive spectrophotometer (EDS) on the Zeiss 1540 SEM
155 and an Oxford Xmax Silicon Drift Detector EDS on the Hitachi SU 6600 SEM were used for
156 element identification.

157 Two of the glutaraldehyde fixed grains possessing evidence of weathering and secondary
158 minerals were analyzed at the Pacific Northwest Consortium/X-ray Science division (PNC-XSD)
159 Sector 20 - Insertion Device beamline at the Advanced Photon Source, Argonne National
160 Laboratory, Argonne, IL, USA. X-ray emission spectroscopy was conducted to map the element
161 distribution on grain surfaces. X-ray emission energy reference values from Kortright and
162 Thompson (2001) were used to determine elements present in the scans. X-ray Absorption Near
163 Edge Structure (XANES) energy measurements were conducted at points of interest to determine
164 the oxidation state of iron. Triplicate XANES energy measurements of the Fe-K edge were
165 collected at each spot and compared to the inflection of an Fe-reference foil edge (7112 eV;
166 Williams 2001). Beam energy was set to 10700 eV. Element maps and X-ray emission spectra
167 were analyzed using National Instruments™ LabVIEW™ 2-D Scan Plot v. 4 and National
168 Instruments™ LabVIEW™ 1-D Scan Plot v. 3. XANES data was processed by ATHENA
169 analysis software (Ravel and Newville 2005). The Fe-K edge of the samples was compared to
170 the Fe-K edge of the reference foil.

171 Three Pt grains possessing nanophase and μm -scale surface Pt were selected for detailed
172 structural analysis of ion milled grains using a focused ion beam-secondary electron microscope
173 (FIB-SEM; Helios NanoLab DualBeam, FEI, Netherlands). Images were collected from 3 to 15
174 kV, with sectioning and cleaning carried out at 30 kV and 21 nA and 20 kV and 2.8 to 0.34 nA,
175 respectively.

176 Electron backscatter diffraction (EBSD) analyses were performed after milling a small,
177 rounded Pt grain using an EDAX-TSL EBSD system fitted to a FEI Helios NanoLab platform.
178 The sample (a FIB-sectioned Pt-grain) was rotated to face to the Hikari EBSD camera and tilted
179 to 70° with respect to the camera. EBSD patterns were collected on milled regions at 20 kV and
180 2.7 nA with a working distance of ~9 mm and a step-size of 0.1 μm. OIM Data Collection
181 (V5.2) and OIM Analysis (V4.5) were used for data collection and interpretation. This FIB-
182 sectioned grain was also examined using S-μXRF at the ID22NI beamline - European
183 Synchrotron Research Facility (ESRF). ID22NI is an undulator beamline with X-ray optics
184 designed to focus the beam to nm size in pink beam mode operation. The beamline has a Si
185 mirror at an incident angle about 2.6 mrad for high harmonic rejection. In the Kirkpatrick-Baez
186 geometry used in this experiment, the focusing system comprises of two elliptically shaped
187 mirrors, with a graded multilayer coating the first one, thus functioning both as monochromator
188 and vertical focusing optics. The beam was focused to 120 nm, with an incident energy of 17500
189 eV. The sample was mounted on a XY-piezo-nano-positioner stage and scanned at the focal
190 plane, while the emitted X-ray fluorescence data were measured with a single-element Si Drift
191 detector. S-μXRF data were analyzed with GeoPIXE II (Ryan et al. 2005), using the dynamic
192 analysis (DA) method to project quantitative elemental images from the full fluorescence spectra
193 (Ryan 2000; Ryan et al. 2009).

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Results

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The morphology of the Fifield native Pt grains (based on Cabri et al. 1996 - composition
> 80% Pt; determined using EDS; data not shown) ranged from subhedral to well-rounded, and
included grains with and without negative crystal imprints (Figure 2 a-f). Pitting, cavities and

199 striations are common on the surfaces of many grains, and demonstrate that the ‘nugget-soil-
200 solution’ interface is an important site of mechanical and chemical weathering (Figures 2-5).
201 EPMA mapping of polished whole mounts (e.g., Figure 3) provided evidence for exsolution of
202 Os-Ir alloys indicative of primary material derived from differentiation of the melt; however, no
203 zones of enrichment or depletion of Pt were observed along the rims at the spatial resolution of
204 EPMA.

205 Tens of μm -scale dissolution pits and cavities were observed using FEG-SEM, some of
206 which were in-filled with organic matter and clay-sized materials (Figures 4 and 5). In fact, most
207 of the depressions in the grain surfaces that were partially coated by visible orange/red to dark
208 brown layers of Fe-hydroxides, with aluminosilicates, clay-sized minerals, and organic material
209 (Figures 2 and 4). Using FEG-SEM, acicular Fe-hydroxides were detected primarily within the
210 clay patches, but they were also directly affixed to the Pt-grain surfaces (Figures 4g and 5cd).
211 Energy-dispersive spectroscopy (Figures 4fg and 5e) and XANES spectra (Figure 5f) confirmed
212 that the acicular, Fe-bearing minerals exist in an oxidized Fe^{3+} state, and are likely oxygen-
213 bound, as indicated by the *K*-edge located approximately 13 eV up-energy shift from the Fe^0
214 standard (O’Day et al. 2004). XANES and EDS detected trace amounts of Cu and Rh in these
215 grains (Figures 4 and 5). SEM micrographs show fine-grained, 150 nm cubic Pt-Cu minerals
216 suggesting the presence of sub-micrometer tulameenite ($\text{PtFe}_{0.5}\text{Cu}_{0.5}$; based on their cubic
217 structure and chemistry, demonstrating that hydrothermal alteration of these grains has occurred
218 (see Cabri et al. 1996); no bacteria were observed on the surface of these Pt grains. An attempt
219 to extract and recover these cubic minerals using sonication was not successful; micro-XRD was
220 also unsuccessful in identifying these cubic minerals over the background isoferroplatinum
221 signal.

222 BSE-SEM-imaging of grain surfaces nanophase to μm -scale Pt (Figure 6) highlighted the
223 presence of low numbers of spheroidal and elongated nanophase Pt typically ranging from 50 to
224 200 nm in diameter (Figure 6b). Aggregates of Pt-platelets were also observed on the surface of
225 some grains, individual platelets were between 0.2 and 4 μm in diameter (Figure 6c). FIB-SEM
226 showed that a zone of μ -crystalline Pt was common beneath the Fe-hydroxide with crystal sizes
227 becoming larger towards the center of the slice (Figure 6 d-f).

228 EBSD analyses on the small, FIB-milled cross section demonstrated the occurrence and
229 distribution of secondary Pt, (Figure 7a). While the core of the grain consisted of a large set of
230 twinned crystals, consistent with a magmatic origin, a narrow layer (up to 5 μm) of
231 microcrystalline-Pt was observed coating part of the grain (Figure 7ab). In these areas,
232 distinctive electron backscattered patterns (EBSD) were obtained from individual crystals, down
233 to 200 nm in size, which displayed highly variable orientations compared to adjacent crystals
234 (Figure 7b). Synchrotron- μXRF at a spot size of 100 nm was used to assess the chemical
235 gradient from surface to interior and provide clues to the dissolution and precipitation processes
236 affecting Pt grains (Figure 7). Using μXRF , a quantifiable difference of Pt/Fe contents of the
237 thin layer of finely crystalline secondary Pt compared to the primary bulk elemental composition
238 was detected (Figure 7c-f). The fine layer of secondary Pt consisted of up to 91 wt. %, Pt
239 concentrations in the bulk lay around 85 wt. %.

240

241

Discussion

242 Large-scale differences were observed in surface fracturing and pitting. This
243 heterogeneity suggests that the grains were subjected to differing degrees of (bio)geochemical
244 and physical weathering, e.g., abrasion. A number of fluvial and lateritic environments affected

245 the Fifield Pt Province throughout the Cenozoic, and the diverse morphologies characterized by
246 this and previous work, are indicative of those conditions (Teluk 2001).

247 Deep weathering scars, pits and cavities demonstrate that the surfaces of Pt grains are
248 important sites of mechanical and more importantly, geochemical weathering. Long, ‘ordered’
249 parallel scars mar the placer grain in Figures 2a and 4a, and may relate to the preferential
250 weathering of Os-Ir alloy via exsolution from the Pt-Fe alloy (Figure 3 and 4; see Slansky et al.
251 1991). SEM micrographs show delicate, 150 nm cubic Pt-Cu minerals; the focal series in Figure
252 4 (a-c) reveals 150 nm-sized cubic minerals embedded within the surface of the grain. The
253 presence of these cubic minerals extending out from the surface of the Pt grain, combined with
254 similar-sized ‘pits’ in the surface (Figure 4f), suggests that they were physically plucked out
255 from the more massive Pt-Fe alloy, (presumably as the matrix dissolved) releasing sub-
256 micrometer tulameenite ($\text{PtFe}_{0.5}\text{Cu}_{0.5}$) into the environment. The apparent dissolution of the
257 bulk nugget around these minerals demonstrates that weathering is not homogenous, reflecting
258 the geological conditions of the field site, and that nanophase minerals may be left in, or
259 transported out from the regolith or farther within alluvium.

260 The color of the Fe-hydroxides differed slightly between grains (Figure 2), which
261 suggests that an array of insoluble Fe-hydroxides possessing various hydration states coat the
262 grains; Fe-hydroxides, e.g., limonite, goethite, and Fe-oxides have been detected on Pt nuggets
263 (Bowles 1986; Ottemann and Augustihus 1967; Suárez et al. 2008) and that weathering
264 conditions may vary within this deposit. More importantly, the presence of acicular Fe-
265 hydroxides provides evidence that acidic conditions occur at the grain surface, which presents a
266 possible mechanism for chemical dissolution of platiniferous materials (Guilbert 1986; Sillitoe
267 2005). The oxidation of Fe promotes the formation of acid through subsequent hydrolysis of

268 water, which can alter the local chemical conditions (see Dockrey et al., 2014), forming acid,
269 which can enhance Pt solubilization (Sillitoe 2005); in particular, the precipitation of acicular Fe-
270 hydroxides immediately on grain surfaces (Figure 4) may produce an acidic nano-environment
271 (interface) contributing to grain dissolution and the release of additional Fe from the Pt-Fe alloy
272 surface (Guilbert 1986; Hattori et al. 2010). Hattori et al.'s (2010) suggestion that the surface of
273 the weathered Pt-Fe grains they studied consisted of a physical mixture of relict Pt-Fe alloy and
274 newly precipitated Fe³⁺-O-OH is corroborated with imaging and chemical analysis using FEG-
275 SEM; see Figures 4 and 5). Based on the detailed spectral analysis by Hattori et al. (2010), our
276 Fe *K*-edge absorption spectrum, with a larger peak at 7122 eV vs. 72128 eV suggests that only
277 trace iron exists on the surface of these Pt-Fe alloys, i.e., less weathering is occurring in the arid
278 Australian environment vs. New Caledonia.

279 Similar to gold (Reith et al., 2007; Southam et al., 2009), we see evidence for both
280 dissolution and re-precipitation occurring on individual Pt-Fe alloy grains. In Au-Ag systems,
281 Ag is leached and gold dissolution re-precipitation results in the formation of octahedral gold.
282 For Pt-Fe alloys, the leaching and oxidation of iron may contribute to the dissolution-re-
283 precipitation of Pt (see Traoré et al. 2008), resulting in occurrence of nanophase and
284 microcrystalline secondary aggregates of Pt (Figure 6 bc) revealed using EBSD analysis (Figure
285 7). Pt-Fe alloys may respond in the same manner as Au-Ag alloys, where the enrichment of Pt
286 (or Au) at the surface of these grains (respectively) may relate to the preferentially leaching, i.e.,
287 higher solubility of Fe (and Ag; Groen et al., 1990).

288 A model for near surface transformation of Pt, i.e., the dissolution, transportation and
289 precipitation of Pt, in soils and weathering profiles (Anthony and Williams 1994; Cabral et al.
290 2011) must continue to be developed to better understand placer Pt formation (see Fuchs and

291 Rose 1974; Bowles 1986; Azaroual et al. 2001; Bowles et al. 2004; Cabri et al. 1996; Hanley
292 2005; Reith et al. 2009; Cabral et al. 2011) and the mobility of Pt in Earth surface environments.

293

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Implications

295 The physico-chemical extraction of intact, cubic Pt-Cu minerals from the surface of one,
296 Pt-Fe alloy grain, and the development of secondary microcrystalline Pt at the surface of other Pt
297 grains represent a strong case for the occurrence of nanophase Pt minerals in soils at Fifield. The
298 dissolution and precipitation of secondary Pt also demonstrates that Pt is chemically mobile in
299 surface weathering environments. The transport of these materials through gravity movement of
300 soils, fluvial movement of sediment, and solution transport in water, will create a geochemical
301 halo ‘downgradient’ from surface and near-surface Pt deposits. Methods development, targeting
302 the recovery and quantification of these microscopic materials and/or soluble compounds from
303 soils and sediments will increase the likelihood of detecting geochemical anomalies of Pt, which
304 can serve as a means to vector in on Pt-deposits.

305

306

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476 California, Berkeley, California.

477

478 **List of Figure Captions**

479 **Figure 1.** Map of Australia with Fifield study site indicated by a circle in state of New South
480 Wales.

481

482 **Figure 2.** Dominant Pt-Fe alloy morphologies occurring in sample of grains collected at the from
483 Fifield Platina Deep Lead, NSW, Australia: **(a)** anhedral grain, with dissolution channels; **(b)**
484 knobby grain with remnants of minerals and negative imprints of crystals; **(c)** platy subhedral
485 grain with abundant coatings of red-brown Fe-hydroxides; **(d)** anhedral grain coated by orange-
486 red Fe-hydroxides; **(e)** smooth well-rounded apparently alluvially worn, grain with polished
487 surface; **(f)** anhedral grain with highly transformed surface.

488

489 **Figure 3. (a-d)** A representative series of electron microprobe maps showing the distribution of
490 Pt (max. 86.7 wt. %), Fe (max. = 21.9 wt. %), Ir (max. 54.9 wt. %) and Os (max. 32.3 wt. %) in a
491 rounded Pt-Fe alloy grain from Fifield, New South Wales Australia.

492

493 **Figure 4. (a-c)** A SEM micrograph focal series of weathered Pt-Fe alloy; note the ca. 150 nm
494 cubic minerals in panel **c**. **(d and e)** Fe and Cu element maps of grain, respectively. Color scales
495 in **d** and **e** show relative element concentrations and transition upward from low concentration
496 (black) to high concentration (white). Note the rectangular area in **e**, which shows a streak of
497 copper that corresponds to the Cu-rich cubic minerals observed in panel **b**. **(f)** SEM micrograph
498 of cubic ‘pits’ and EDS spectra comparing the elemental composition of the bulk grain and cubic
499 mineral rich areas. The bulk grain is Pt-Fe alloy (with trace Cu and Rh) while the cubic minerals
500 show elevated Cu. **(g)** SEM and EDS of the acicular, Fe-hydroxides with co-precipitated trace
501 Ce and Rh.

502

503 **Figure 5. (a)** SEM micrographs of sub-rounded Pt-Fe alloy; note dented and scratched surface,
504 in-filled with clay and organics-darker grey coating); **(b)** a deeply pitted sub-rounded Pt-Fe alloy
505 with relatively deep circular pits in-filled with secondary minerals; **(c and d)** micrographs of Pt-
506 Fe alloy coated with acicular, Fe-hydroxides. **(e)** EDXA spectrum of the acicular Fe hydroxides
507 indicates that cerium and rhodium is present in these samples. **(f)** experimental XANES spectrum
508 and standard spectra for oxidized Fe-species demonstrating that the iron rich coating is
509 comprised of Fe-oxides, intuitively iron hydroxide based on the rust-coloration on the grain.

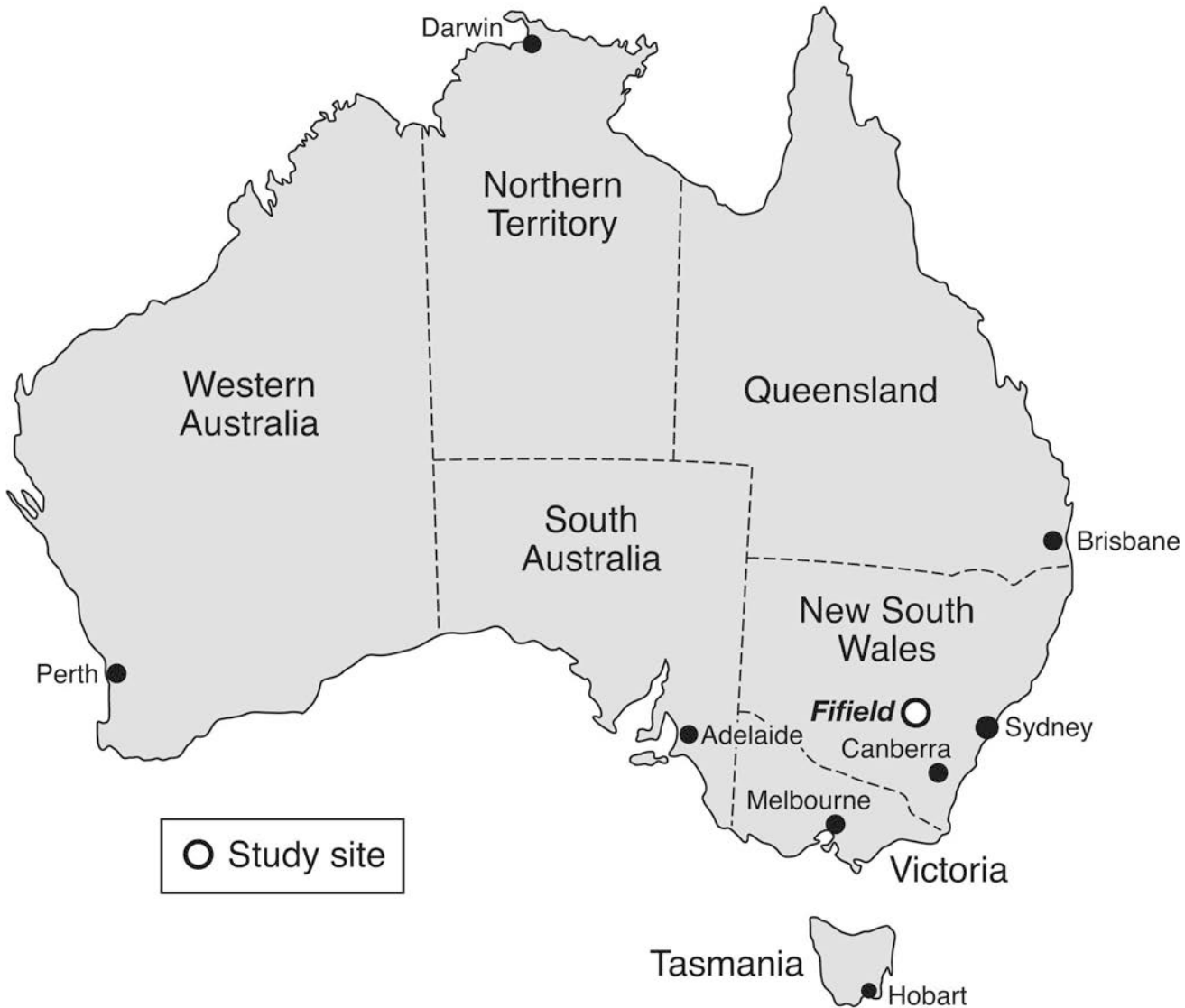
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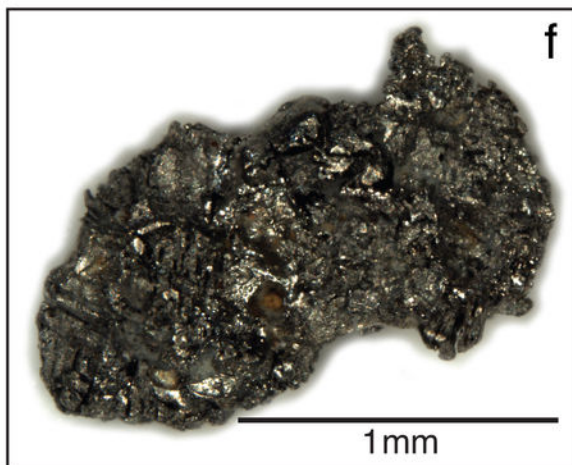
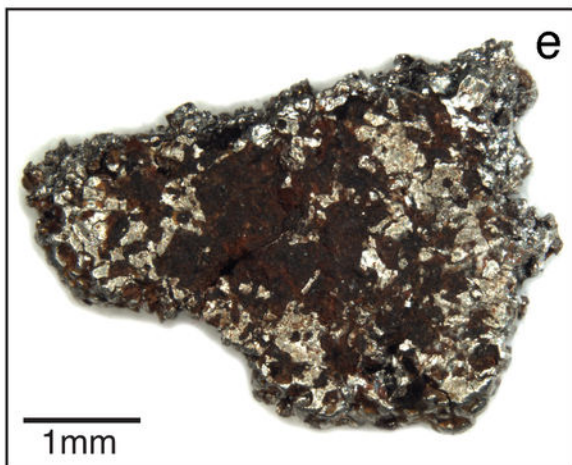
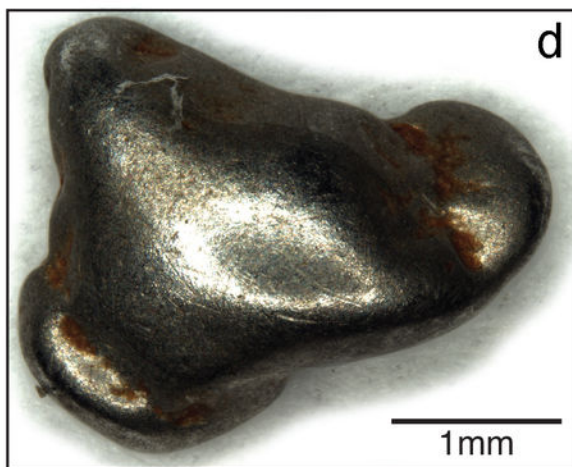
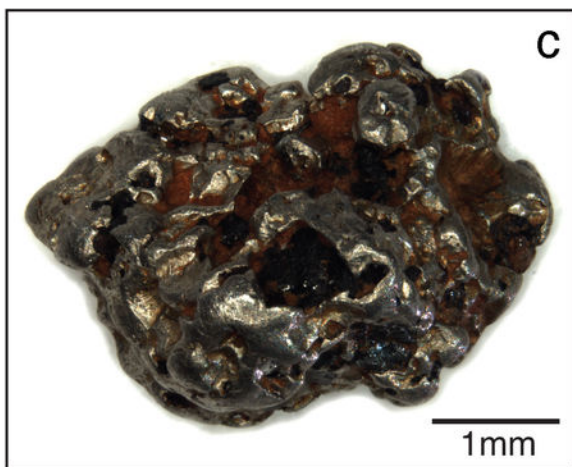
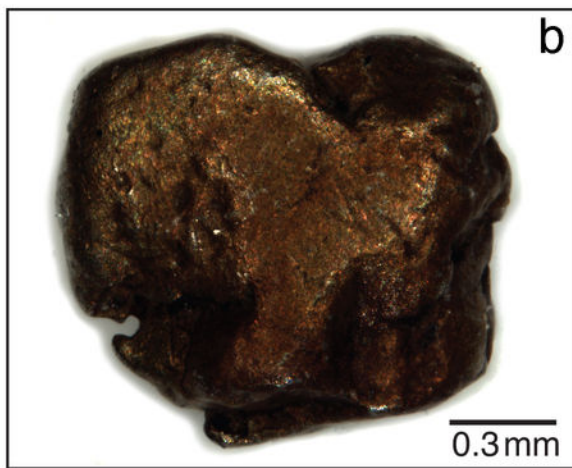
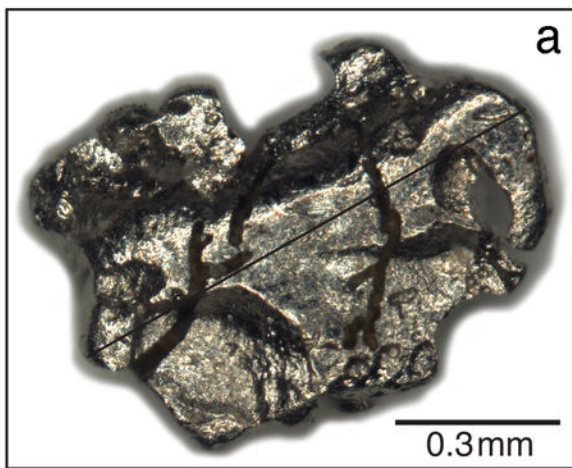
511 **Figure 6. (a and b)** Low and high magnification BSE-SEM micrographs of a weathered Pt-Fe
512 alloy focusing on the grain surface, highlighting the presence of sub-micrometer-scale Pt. **(c)**
513 SEM of aggregate, native Pt consisting of Pt-platelets within an organic film on the surface of Pt-
514 Fe alloy; **(d)** SEM micrograph of a FIB-milled Pt-fe alloy showing increasing native Pt crystal
515 size as you get closer to the rim; **(e and f)** high magnification SEM micrographs of the rim of the

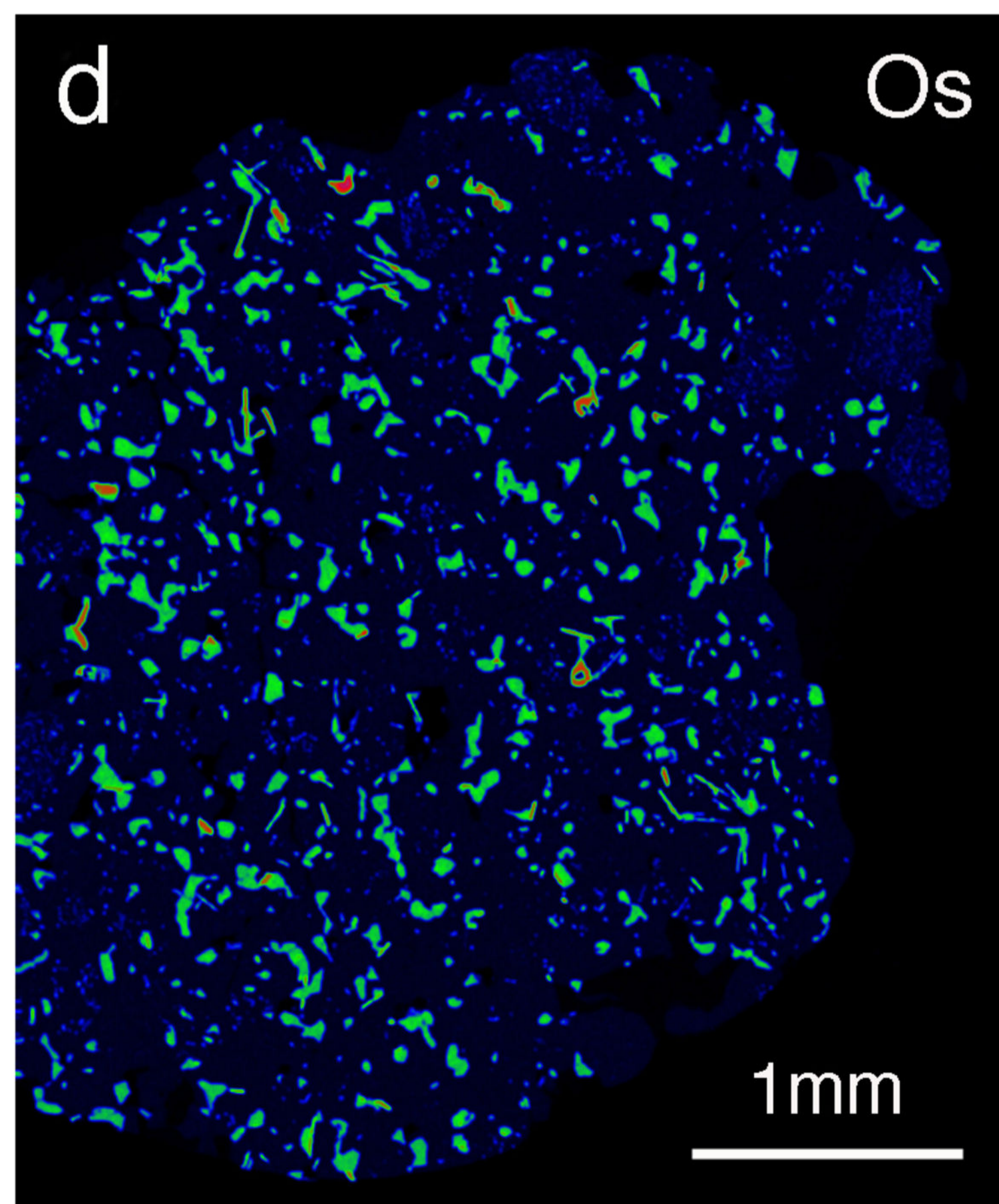
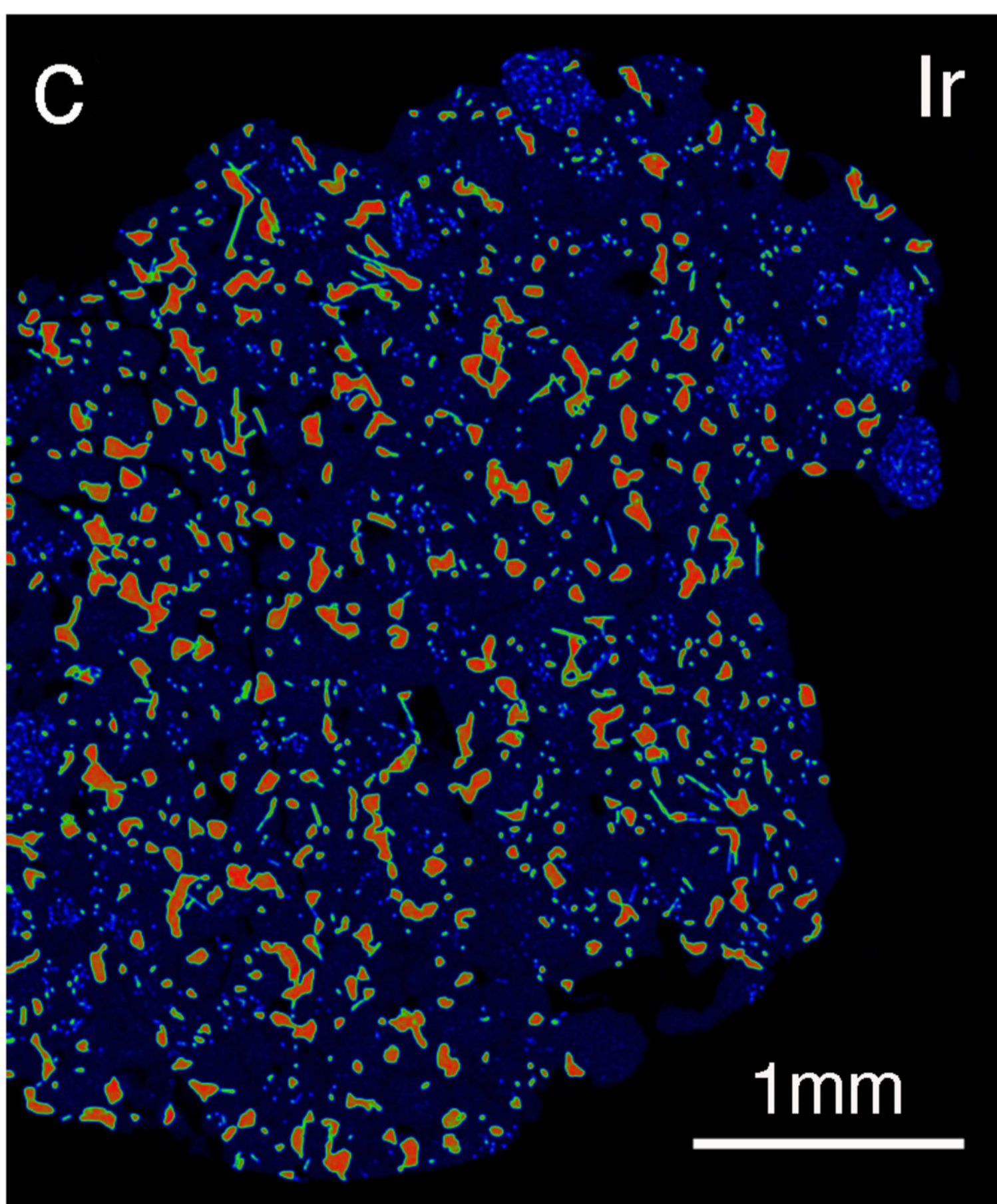
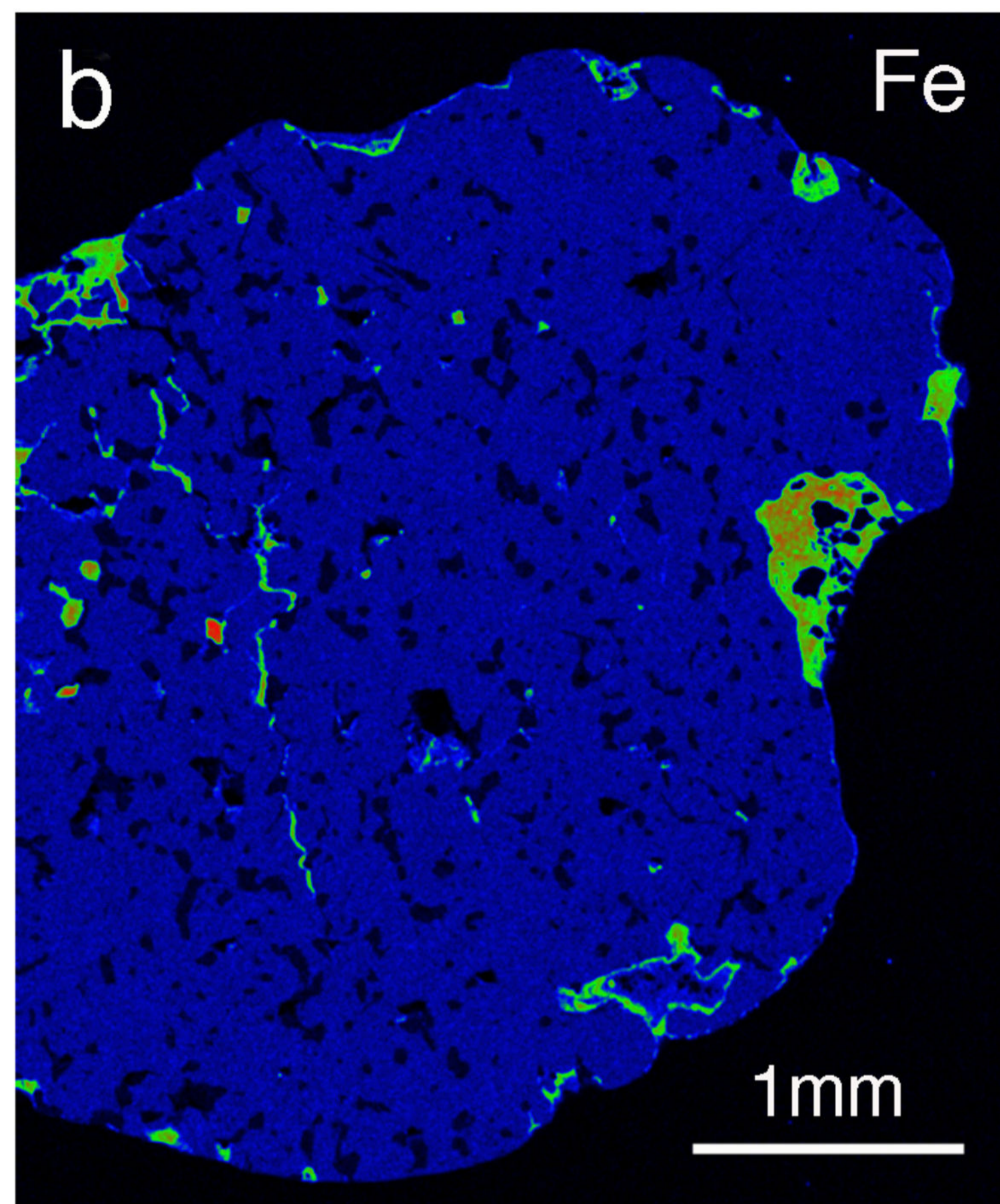
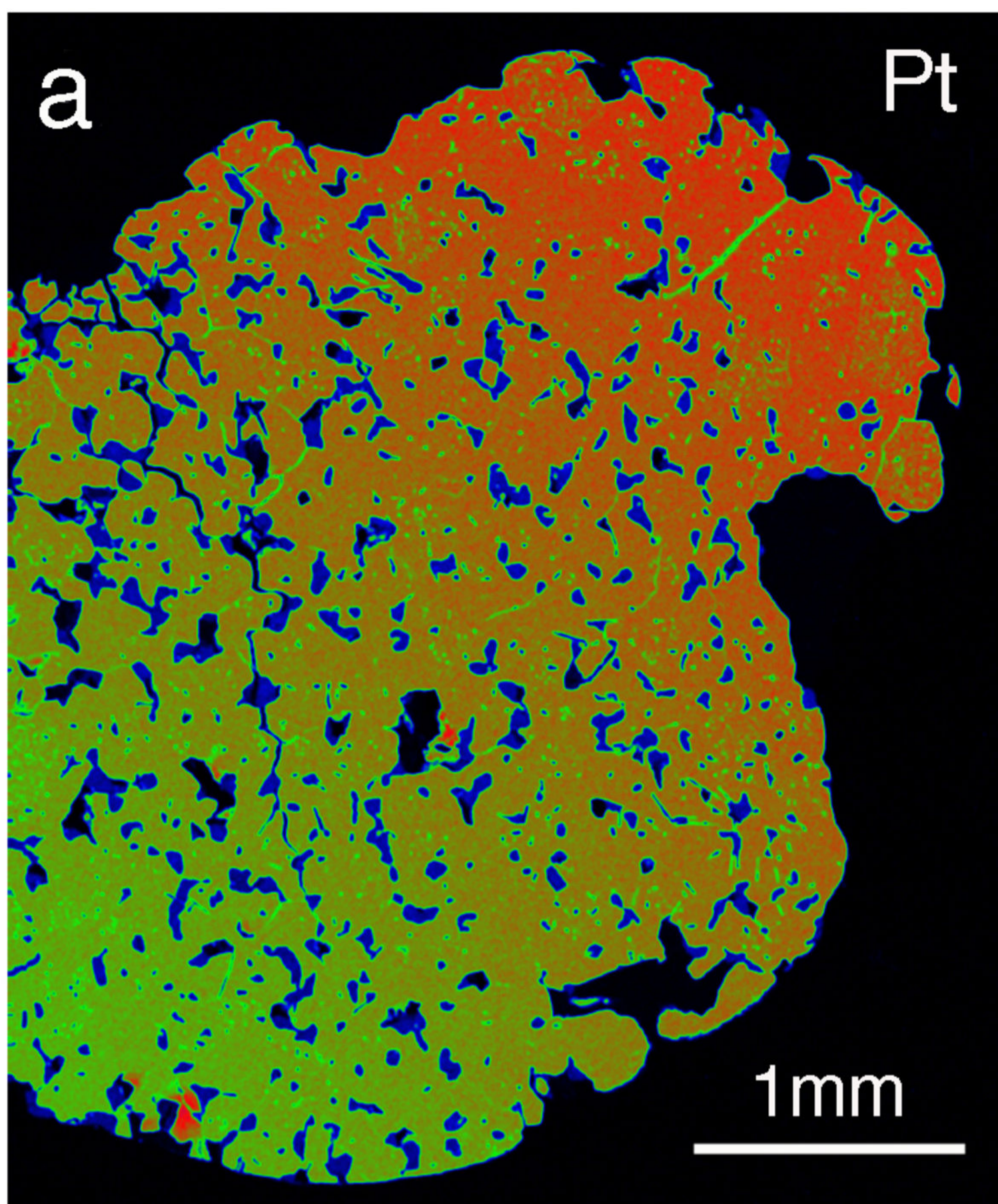
516 FIB-milled grain showing an increased number of grain boundaries, indicating the formation of
517 microcrystalline native Pt at the .Pt-Fe alloy surface.

518

519 **Figure 7.** (a) SEM micrograph of a FIB-sectioned Pt-Fe alloy with EBSD map showing the
520 twinned crystal orientation of the grain-center overlain; (b) detailed SEM micrographs and
521 EBSD map of the grain rim showing micro-crystalline secondary Pt; (c) Synchrotron μ XRF map
522 of Pt, Fe and Os (Red, Green, Blue), respectively, (d-f) showing the differences in Pt and Fe
523 from the center of the grain towards the rim; μ XRF map of Pt (max. 90.6 wt. %); μ XRF map of
524 Fe (max. 16.8 wt. %); μ XRF map of Os (max. 6.4 wt. %).







MIN  MAX

A color scale bar at the bottom of the figure, ranging from blue (MIN) to red (MAX), with green and yellow in between.

