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5 MANTLE-DERIVED GUYANAITE IN A Cr-OMPHACITITE XENOLITH FROM MOSES

6 ROCK DIATREME, UTAH

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22 Abstract

23 Guyanaite, naturally occurring β -CrOOH, has been identified in a xenolith of Cr-rich
24 omphacitite from the Moses Rock diatreme in the Navajo Volcanic Field of the southwestern
25 United States. It occurs as the dominant phase in small clusters of accessory minerals,
26 intergrown with kosmochlor-rich omphacite, zincian chromite, eskolaite and carmichaelite. The
27 assemblage is interpreted as the result of metasomatism of chromite-bearing serpentinite by slab-
28 derived fluids during subduction of the Farallon Plate in Laramide time. At the time of
29 entrainment of the xenolith, the rock was undergoing prograde metamorphism, with guyanaite
30 dehydrating to eskolaite plus water. This reaction, and the coeval dehydration of the inferred
31 accompanying host serpentinites (which would have been much more volumetrically
32 significant), provided water for hydration of the subcontinental upper mantle, contributing to
33 uplift of the Colorado Plateau. Recognition of guyanaite as a component of a subducted slab
34 supports recent proposals, based on laboratory experiments, that high-pressure polymorphs of
35 common crustal oxy-hydroxide minerals such as boehmite and goethite (i.e., high-pressure δ -
36 AlOOH and ϵ -FeOOH) can transport and store water into the upper mantle.

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38 Key words: guyanaite, upper mantle, xenolith, subduction, jade, kosmochlor, carmichaelite,
39 Colorado Plateau

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44 Introduction

45 Guyanaite, a polymorph of CrOOH, is a rare mineral, previously described from only
46 three locations. It is named for the type locality in Guyana where it occurs as a component of so-
47 called “merumite” pebbles in gold and diamond placer deposits in the Merume River (Milton
48 and Narain, 1969; Milton et al., 1976), intergrown with two other polymorphs of CrOOH
49 (bracewellite and grimaldiite), eskolaite (Cr₂O₃), mcconnellite (CrOOCu), chromian gahnite and
50 gold.

51 Here we describe guyanaite in a mantle-derived omphacitic clinopyroxenite xenolith
52 from the Moses Rock diatreme in the Navajo Volcanic Field in southeast Utah, USA (Watson,
53 1967). Its presence in an upper mantle setting is significant, as the synthetic equivalent, β-
54 CrOOH, has recently been shown to be stable to great depths in the mantle (pressures up to at
55 least 13.5 GPa; Jahn et al., 2012) and thus is a potentially significant repository for water in the
56 upper mantle.

57

58 Petrography

59 The sample we studied (#12-97-50) is a xenolith 6 cm in maximum dimension dominated
60 by pale emerald green clinopyroxene with small clots of dark accessory minerals (clots to 2 mm)
61 around which the clinopyroxene is more intensely green in hand sample and in thin section. Fig.
62 1 is a back-scatter electron (BSE) image of a portion of one of the clusters of accessory minerals.
63 The clusters are dominated by lamellar intergrowths of guyanaite and clinopyroxene. Stringers
64 of eskolaite traverse the guyanaite or occur at the guyanaite-clinopyroxene interfaces. Patches of
65 chromite are interspersed in some of the guyanaite-dominated clusters and consist of lamellar

66 intergrowths of two texturally different types of chromite, intergrown at the same scale as are the
67 guyanaite and clinopyroxene. In reflected light and BSE images one type of chromite has a
68 “spongy” texture and a darker BSE response due to lower average atomic number and the other
69 appears “clean” and brighter due to a higher average atomic number (Fig. 1). A few grains of
70 carmichaelite (a hydrous titanate mineral) occur in the clusters. Though similar in reflectivity
71 and BSE response to guyanaite, all carmichaelite grains larger than approximately 10 microns
72 have prominent cleavage (Fig. 1).

73

74 Mineral Compositions

75 Minerals were analysed at Queen’s University with a JEOL Superprobe, employing
76 standard wavelength dispersive methods and PAP corrections, using a combination of synthetic
77 and natural standards. Representative compositions given in Table 1 (average compositions and
78 standard deviations).

79 In this sample guyanaite, nominally CrOOH with 89.4 wt% Cr₂O₃, is inhomogeneous
80 (64.0 - 78.0 wt% Cr₂O₃) and contains substantial quantities of Fe₂O₃ (6.6 - 9.3 wt%) and TiO₂
81 (2.4 - 10.2 wt%) and smaller quantities of MgO (0.4 - 1.8 wt%) and Al₂O₃ (1.3 - 1.6 wt%) as the
82 main impurities. Cr₂O₃ content is negatively correlated with Fe₂O₃ and TiO₂.

83 Chromite is the only other accessory mineral in this rock that is significantly
84 inhomogeneous, as the two texturally distinct chromite varieties (“clean” and “spongy”) are also
85 compositionally distinct from one another, though homogeneous within each group. The darker
86 grains with the “spongy” texture (chromite I) have greater Al₂O₃ and lower Cr₂O₃
87 (approximately 5.8 and 55.8 wt%, respectively) than do the lighter, “clean” chromites (chromite

88 II, approximately 1.9 and 64.9 wt%, respectively). Chromite II is more reduced than chromite I
89 ($\text{Fe}^{2+}/\Sigma\text{Fe} = 0.91$ and 0.79 , respectively, calculated based on stoichiometry and charge balance).
90 Both types have significant zinc contents (ZnO in the range 5.5 - 5.7 wt% ZnO, equivalent to
91 approximately 15 mole % $\text{Zn}(\text{Al,Cr,Fe}^{3+})_2\text{O}_4$).

92 Carmichaelite is homogeneous, and dominated by TiO_2 (50.9 wt%) and Cr_2O_3 (29.3
93 wt%) with lesser Fe_2O_3 (9.3 wt%) and minor MgO (1.4 wt%) and Al_2O_3 (2.2 wt%) as significant
94 minor constituents.

95 Eskolaite is homogeneous, containing approximately 83.6 wt% Cr_2O_3 with substantial
96 Fe_2O_3 (8.1 wt%) and TiO_2 (6.3 wt%) and minor MgO (1.1 wt%) and Al_2O_3 (1.6 wt%).

97 In the main body of the rock, clinopyroxenes are virtually Cr-free omphacites with end-
98 member compositions of approximately 10-24 mole percent jadeite ($\text{NaAlSi}_2\text{O}_6$) and minor (7-
99 13%) acmite ($\text{NaFe}^{3+}\text{Si}_2\text{O}_6$). Within, and immediately adjacent to, clusters of accessory
100 minerals, the omphacitic pyroxenes are bright green and enriched in Cr (to 29 mole percent
101 kosmochlor - $\text{NaCrSi}_2\text{O}_6$). Table 1 includes analyses of omphacite with the highest Cr value,
102 and the two Cr-poor samples with the highest and lowest jadeite components.

103

104 Micro X-ray Diffraction of Guyanaite and Associated Minerals

105 *In situ* micro X-ray diffraction (μXRD) of a polished thin section and of material from an
106 accessory mineral cluster extracted from the hand specimen was undertaken with a Bruker D8
107 Discover Micro X-ray diffractometer at Western University using cobalt radiation ($\text{Co } \alpha \lambda =$
108 1.79026 \AA), operated at 35 kV and 45 mA. The theta-theta geometry of this instrument allows
109 the sample to remain horizontal and stationary during data collection. A Göbel mirror parallel

110 optics system with a pinhole collimator snout produced a nominal beam of 100 μm . Target areas
111 were selected using a remote-controlled XYZ sample stage combined with a microscope and
112 laser system and a CCD camera for context images (e.g., Fig. 2a). Two-dimensional XRD data
113 (e.g., Fig. 2b) were collected using a Hi Star detector with General Area Detector Diffraction
114 System (GADDS) in omega scan mode. In this mode, the source and detector were
115 simultaneously rotated clockwise through 9-20 degrees to enable more lattice planes to satisfy
116 Bragg's Law in non-polycrystalline samples. Two 2D images were collected for each target and
117 integrated and merged to produce conventional intensity vs. 2θ plots for mineral identification by
118 comparison with the International Centre for Diffraction Data (ICDD) database (via Bruker's
119 DiffractPLUS EVA evaluation software).

120 The μXRD data for the clusters of accessory minerals confirm the presence of guyanaite,
121 kosmochlor and chromite plus minor eskolaite and/or carmichaelite (Fig. 2c). Unambiguous
122 identification of the phases is difficult due to the polymineralic nature and fine grain size of the
123 clusters and the considerable overlap of diffraction lines for the various phases (e.g., Fig. 2c).
124 The data best support identification of guyanaite as the CrOOH polymorph present as the lines
125 for guyanaite are a better match for the unknown than are those of bracewellite and grimaldiite
126 (Fig. 2d).

127 Textural information from the 2D GADDS images (Fig. 2b) show that guyanaite and the
128 kosmochlor-rich omphacite have similar grain sizes. They are relatively coarse-grained
129 crystallites (the data are bright spots as opposed to complete powder rings - see Flemming,
130 2007). The streaky nature of the bright spots is probably an orientation effect due to the
131 intergrown nature of the kosmochlor-rich omphacite and guyanaite.

132 Because of the relatively coarse-grained nature of the crystallites, not all of the expected
133 diffraction lines were obtained from any one location, as, even using omega scan mode, not all
134 lattice planes satisfied the diffraction condition. This added additional ambiguity to phase
135 identification. A stack plot of four targets in various orientations accounts for most of the
136 diffraction pattern for guyanaite (Fig. 2c. and 2d.).

137
138 Discussion

139 Guyanaite, identified here by its composition and crystal structure, has only been
140 described previously from three occurrences, all in crustal rocks. The occurrence in “merumite”
141 pebbles (a complex intergrowth of guyanaite, bracewellite, grimaldiite, eskolaite and other
142 minerals) in Guyana was described as having a hydrothermal origin with a possible protolith of
143 volcanic tuff (Milton and Narain, 1969; Milton et al., 1976). Guyanaite from the Outokumpu
144 massive sulfide deposit in Finland is a hydrous alteration product of eskolaite (Vourelainen et al.,
145 1968), apparently also of late-stage hydrothermal origin. Guyanaite was also mentioned as being
146 a component of lateritic alteration at the Omai mine in Guyana (Voicu and Bardot, 2002).

147 The guyanaite in this study is from a significantly different geologic setting. The
148 omphacite xenolith in which it occurs is part of a suite of ultramafic xenoliths that includes
149 low-temperature metamorphic rocks such as lawsonite- and phengite-bearing eclogites, Cr-
150 pyrope xenocrysts with inclusions of hydrous minerals as well as hydrated peridotites and
151 pyroxenites containing minerals such as magnesian chlorite, antigorite and pargasite. All of
152 these rock types are clearly of mantle origin (e.g., McGetchin and Silver, 1972; Helmstaedt and
153 Doig, 1975; Smith, 1979, 1995). Xenoliths of omphacite rocks and jadeite clinopyroxenites
154 were interpreted by Helmstaedt and Schulze (1988) as having origins similar to those of jadeite

155 bodies associated with serpentinites in crustal settings.

156 As in such jadeitite bodies (“jade”), this sample is essentially monomineralic sodic
157 clinopyroxene (though not as jadeite-rich as classical jades, which typically have >90mole%
158 jadeite component in the pyroxene - Harlow and Sorensen, 2005). Enrichment of clinopyroxene
159 in the kosmochlor component adjacent to the clusters of Cr-rich minerals in our sample is also
160 similar to that occurring around chromite grains in the famous green jades of Myanmar (e.g.,
161 Yang, 1984; Shi et al., 2005). In addition, lawsonite eclogites are associated with some jadeite
162 bodies (e.g., in Guatemala - Tsujimori et al., 2006). A significant difference is that the Navajo
163 omphacitites do not contain secondary minerals such as albite and amphibole that are
164 characteristic of retrograde alteration processes that occur during transport of crustal occurrences
165 of jadeitite from their depths of formation in the mantle to Earth’s surface (e.g., Harlow and
166 Sorensen, 2005).

167 The origin of jade bodies in paleo-subduction zone settings (e.g., Myanmar, Guatemala,
168 California) is thought to be due to metasomatic replacement of chromite-bearing serpentinites in
169 the mantle wedge above active subduction zones, or in bodies of serpentinitized peridotite of
170 oceanic lithosphere origin dragged down the subduction zone, by fluids rich in Na, Al and Si
171 derived from prograde dehydration reactions in associated subducted slabs (e.g., Harlow and
172 Sorensen, 2005; Shi et al., 2005; Tsujimori and Harlow, 2012). Either scenario may apply to the
173 sample in this study, as serpentinitized peridotites from both environments have been proposed to
174 exist in the Navajo mantle xenolith suite (Smith, 2010).

175 A serpentinite protolith for the omphacitite in our study is consistent with the presence of
176 the chromite-bearing accessory mineral clusters dominated by Cr-rich minerals, but the

177 evolutionary path from chromite to various Cr-rich minerals in the clusters is complex. The
178 peculiar texture of the lamellar intergrowths of guyanaite and kosmochlor-rich clinopyroxene
179 (Fig. 1) is reminiscent of altered spinel group minerals that have undergone exsolution and
180 oxidation resulting in skeletal intergrowths of relict oxides and alteration products (e.g.,
181 Haggerty, 1991). We interpret the accessory mineral clusters as altered Cr-rich spinels that have
182 experienced a similar history, followed by metasomatism by fluids rich in Na, Al and Si. This
183 metasomatism (the “jade-forming” process) ultimately resulted in replacement of the Al-rich
184 chromite lamellae by omphacite and the Cr-rich lamellae by guyanaite. The lamellar
185 intergrowths of two distinctly different chromites in the clusters (Fig. 1) are apparently relicts of
186 an intermediate exsolution stage between fresh chromite and the guyanaite-kosmochlor
187 intergrowths.

188 The relatively large size of the clusters of accessory minerals (to 2 mm) is inconsistent
189 with the protolith of this sample having been a basalt, as was suggested for the
190 phengite/lawsonite-bearing eclogites from these diatremes, in which the pyroxene is also
191 omphacite (e.g., Helmstaedt and Doig, 1975). Chromites in basalts are typically only tens to
192 hundreds of microns in size. The inferred parent spinels to the guyanaite-dominated
193 intergrowths (mm scale) are thus interpreted as phases in serpentinized peridotite in which spinel
194 grains are typically coarser. As spinel-group minerals in serpentinites have higher Zn contents
195 than do primary spinels in fresh peridotites (e.g., Sack and Ghiorso, 1991), the high Zn content
196 of the chromites in our sample is (15 mole% $\text{Zn(Al,Cr,Fe}^{3+})_2\text{O}_4$ component) consistent with a
197 serpentinite protolith for this rock, as opposed to direct conversion of peridotite to omphacite
198 by metasomatism.

199 Although constraints on the conditions of formation of the guyanaite in this sample are
200 few, the equilibration conditions of various other members of the xenolith suite have been
201 estimated using a variety of methods. Estimated pressures of equilibration are in the
202 approximate range 1.5-3.6 GPa and temperatures are in the range 410-800°C (e.g., Helmstaedt
203 and Schulze, 1988; Smith, 1995, 2010, 2013; Wang et al., 1999; Smith et al., 2004).

204 The textural relationship between the guyanaite and eskolaite (eskolaite is present as thin
205 rims and small stringers within the dominant guyanaite - Fig. 1) is interpreted as indicating that
206 at the time of entrainment as a xenolith, the rock was undergoing prograde metamorphism and
207 guyanaite was in the process of breaking down (dehydrating) to eskolaite plus water. The
208 conditions of guyanaite stability relative to eskolaite + water determined by synthesis
209 experiments (Jahn et al., 2012) can be applied to constrain the conditions of formation of the
210 guyanaite-eskolaite intergrowths (bearing in mind that the experimental data are for end-member
211 CrOOH and the guyanaite in our sample contains considerable Ti and Fe - Table 1). Both data
212 sets (the equilibration conditions for other xenoliths and the data of Jahn et al., 2012) are shown
213 in Fig. 3, as are the estimated equilibration conditions for three phengite-bearing eclogites
214 (Smith et al., 2004). We suggest that a reasonable estimate of conditions of the beginning of the
215 breakdown of guyanaite to eskolaite in this sample is in the range 650-800°C, 2.5-3.5 GPa.

216 The discovery of eskolaite intergrown with diamond (Logvinova et al., 2008) confirms
217 that eskolaite is also stable to great pressures. There may be a genetic link between the eskolaite
218 formed by prograde metamorphism of guyanaite in our sample and eskolaite associated with
219 diamond.

220 Carmichaelite, present as a minor constituent of the accessory mineral clusters, has been

221 described previously only as inclusions in Cr-pyrope xenocrysts from the nearby Garnet Ridge
222 diatreme (Wang et al., 1999, 2000), and no data exist that bear on its stability field. Together
223 with other hydrous minerals included in Cr-pyrope xenocrysts (e.g., amphibole, chlorite,
224 titanoclinohumite), it was interpreted as having formed from fluids derived from Proterozoic
225 subduction (e.g., Hunter and Smith, 1981; Smith, 1987; Wang et al., 1999, 2000), with the
226 products encapsulated in garnets in peridotite during prograde metamorphism of subducted
227 oceanic lithosphere and incorporated into the sub-cratonic Colorado Plateau lithospheric mantle.
228 The presence of strong gradients in Fe/Mg ratios in olivine grains also encapsulated in some of
229 the pyrope xenocrysts was interpreted as due to slow cooling of these minerals, consistent with
230 the interpretation that the encapsulated minerals were formed in the Proterozoic. In a re-
231 evaluation of the Cr-pyrope xenocrysts, based on comparison between their olivine inclusions
232 and olivines in hydrous peridotites, Smith (2010) expressed reservations about their Proterozoic
233 heritage. We interpret the carmichaelite in our sample as having been a stable member of the
234 accessory mineral assemblage in the omphacitite in the open system of the upper mantle, actively
235 undergoing prograde metamorphism at the time of entrainment.

236 These two types of occurrences of carmichaelite are not easily explained by a single
237 mode of formation, as should probably be expected given that they are the only two occurrences
238 of this mineral, and both are in xenoliths from the same volcanic field. In contrast to the model
239 of carmichaelite formation in the Proterozoic, we interpret the carmichaelite/guyanaite xenolith
240 as related to subduction of the Farallon Plate, the origin suggested by Helmstaedt and Doig,
241 (1975) for the Navajo phengite- and lawsonite-bearing eclogites. It may have been a component
242 of the oceanic Farallon slab itself, or may have been part of the serpentized mantle wedge

243 overlying the subducted plate, as suggested for other xenoliths in the Navajo suite (Helmstaedt
244 and Schulze, 1991; Smith, 2010). The textural relationship of the guyanaite and eskolaite is
245 suggestive of dehydration of the guyanaite to eskolaite + water as an ongoing processes at the
246 time of entrainment of the xenolith into the diatreme. At the time of eruption, this reaction was
247 “live”, and indicative of prograde metamorphism during heating and increase in pressure that
248 would accompany descent of the Farallon slab (and accompanying fragments of the wedge) into
249 the sub-Colorado Plateau mantle lithosphere. If our interpretation is valid (also see Usui et al.,
250 2003), either the significance of the carmichaelite-bearing pyropes described by Wang et al.
251 (1999, 2000) should be reconsidered, or the only two known occurrences of carmichaelite have
252 distinctly different origins.

253 Both guyanaite and carmichaelite are hydrous minerals and thus potentially important
254 repositories for water in the upper mantle, as well as vehicles for transporting water during
255 subduction, potentially deep into the mantle. They are, however, rare minerals, and their
256 importance in these processes is unclear. In crustal occurrences of jade, host serpentinites are
257 much more volumetrically significant, and we suggest that large volumes of serpentinite was
258 transported along with the omphacitites and also dehydrated. We concur with Smith (2010) who
259 documented prograde metamorphism of antigorite-bearing meta-serpentinites and suggested that
260 water produced by the dehydration of serpentine hydrated the sub-Plateau mantle lithosphere,
261 contributing to uplift of the Colorado Plateau (also see Humphreys et al., 2003).

262

263 Implications

264 Most of the material in the oceanic crust and upper mantle that is subducted into the

265 mantle at convergent margins disappears from the geologic record. Notable exceptions include
266 slab-derived components of arc magmas (including volatiles) and the intact examples of rocks in
267 high-pressure and ultrahigh-pressure (UHP) metamorphic terranes (e.g., Ernst and Liou, 2008).
268 The ultramafic xenoliths in the diatremes of the Navajo Volcanic Field of the south-western
269 United States appear to be an exception to this situation. The xenoliths of low-temperature
270 eclogite (some of which contain lawsonite and/or phengite) and related rocks have been
271 interpreted as fragments of the subducted Farallon Plate that were plucked from the flat
272 subduction zone in Laramide time (e.g., Helmstaedt and Doig, 1975; Helmstaedt and Schulze,
273 1988) and returned to Earth's surface without experiencing the alteration and retrograde
274 metamorphism that is so pervasive in equivalent high-pressure metamorphic rocks preserved at
275 the sites of former convergent margins (e.g., the Franciscan Formation of California).

276 With its many similarities to jadeite bodies in serpentinites from convergent boundaries
277 in the crust, the guyanaite-bearing jadeite-rich pyroxenite strengthens this connection. The
278 evidence for the prograde reaction $\text{guyanaite} = \text{eskolaite} + \text{water}$ supports the interpretation that
279 the zonation in the garnets of the Navajo eclogite xenoliths is evidence of prograde
280 metamorphism, as would be expected during subduction of the Farallon Plate (e.g., Helmstaedt
281 and Schulze, 1988), although others disagree with this interpretation (e.g., Smith and Zeintek,
282 1979). The evidence of a prograde dehydration reaction also supports the suggestion that some
283 of the Navajo hydrous peridotite xenoliths are also prograde metamorphic rocks and the water
284 released on dehydration reactions in these rocks caused hydration and expansion of the
285 subcontinental mantle lithosphere, contributing to the uplift of the Colorado Plateau (Humphreys
286 et al., 2003; Smith, 2010).

287 The recognition of guyanaite in a mantle setting is perhaps even more important from a
288 global perspective. Low-temperature/pressure oxy-hydroxide minerals such as goethite
289 (FeOOH) and boehmite/diaspore (AlOOH) have recently been shown to have high-pressure
290 polymorphs (e.g., Sano-Furukawa et al., 2009 and references therein) and it has been suggested
291 that such phases, with stability to extraordinarily high pressures (e.g., Sano-Furukawa et al.,
292 2009 demonstrated stability of δ -AlOOH to 34.9 GPa), may transport water deep into the upper
293 mantle. Although guyanaite is rare (we report the fourth occurrence of this mineral), we have
294 shown that it actually exists in mantle rocks, substantiating theories based on experiments (Jahn
295 et al., 2012). The oxy-hydroxides of Al and Fe, which are much more abundant in low-pressure
296 crustal rocks than are the polymorphs of CrOOH, could certainly be important in transporting
297 water to great depths in their ultrahigh-pressure equivalents, and may yet be identified in UHP
298 rocks.

299

300

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306

307 References

308 Bohlen, S. R., and Boettcher, A.L. (1982) The quartz-coesite transformation: A precise

- 309 determination and the effects of other components. *Journal of Geophysical Research*, 87,
310 7073–7078.
- 311 Chatterjee, N. D., Johannes, W., and Leistner, H. (1984) The system CaO-Al₂O₃-SiO₂-H₂O:
312 New phase equilibria data, some calculated phase relations, and their petrological
313 applications. *Contributions to Mineralogy and Petrology*, 88, 1–13.
- 314 Ernst, W.G., and Liou, J.G. (2008) High- and ultrahigh-pressure metamorphism: Past results and
315 future prospects. *American Mineralogist*, 83, 1771-1796.
- 316 Flemming, L. (2007) Micro X-ray Diffraction (μ XRD): A versatile technique for
317 characterization of Earth and planetary materials. *Canadian Journal of Earth Sciences*,
318 44, 1333-1346.
- 319 Haggerty, S.E. (1991) Oxide textures - A mini-atlas. In *Mineralogical Society of*
320 *America Reviews in Mineralogy*, 25, 129-219.
- 321 Harlow, G.E., and Sorensen, S.S. (2005) Jade (nephrite and jadeitite) and serpentinite:
322 metasomatic connections. *International Geology Review*, 47, 113–146.
- 323 Helmstaedt, H., and R. Doig (1975) Eclogite nodules from kimberlite pipes of the Colorado
324 Plateau -- Samples of subducted Franciscan-type oceanic lithosphere. *Physics and*
325 *Chemistry of the Earth*, 9, 95–111.
- 326 Helmstaedt, H., and Schulze, D.J. (1979) Garnet clinopyroxenite - chlorite eclogite transition in
327 a xenolith from Moses Rock: further evidence for metamorphosed ophiolites under
328 the Colorado Plateau. In: F.R. Boyd and H.O.A. Meyer, eds., *The Mantle Sample:*
329 *Inclusions in Kimberlite and Other Volcanics*, p. 357–365, AGU, Washington, D.C.
- 330 Helmstaedt, H., and Schulze, D.J. (1988) Eclogite-facies ultramafic xenoliths from Colorado

- 331 Plateau diatreme breccias: Comparison with eclogites in crustal environments, evaluation
332 of the subduction hypothesis, and implications for eclogite xenoliths from
333 diamondiferous kimberlites. In: D.C. Smith, ed., *Eclogites and Eclogite-facies Rocks*, p.
334 387-450, Elsevier, New York.
- 335 Helmstaedt, H. H., and Schulze, D.J. (1991) Early to mid-Tertiary inverted metamorphic
336 gradient under the Colorado Plateau: Evidence from eclogite xenoliths in ultramafic
337 microbreccias, Navajo volcanic field. *Journal of Geophysical Research*, 96, 13225–
338 13235.
- 339 Humphreys, E., Hessler, E., Dueker, K., Farmer, G.L., Erslev, E., and Atwater, T. (2003) How
340 Laramide-age hydration of North American lithosphere by the Farallon slab controlled
341 subsequent activity in the western United States. *International Geology Review*, 45, 575-
342 595.
- 343 Hunter, W. C., and Smith, D. (1981) Garnet peridotite from Colorado Plateau ultramafic
344 diatremes: Hydrates, carbonates, and comparative geothermometry. *Contributions to*
345 *Mineralogy and Petrology*, 76, 312-320.
- 346 Jahn, S., Wunder, B., Koch-Muller, M., Tarrieu, L., and Pohle, M. (2012) Pressure-induced
347 hydrogen bond symmetrisation in gyaunaite, β -CrOOH: Evidence from spectroscopy and
348 ab initio simulations. *European Journal of Mineralogy*, 24, 839-850.
- 349 Logvinova, A.M, Wirth, R., Sobolev, N.V., Seryotkin, Y.V., Yefimova, E.S., Floss, C., and
350 Taylor, L.A. (2008) Eskolaite associated with diamond from the Udachnaya kimberlite
351 pipe, Yakutia, Russia. *American Mineralogist*, 93, 685-690.
- 352 McGetchin, T. R., and Silver, L.T. (1970) Compositional relations in minerals from kimberlite

- 353 and related rocks in the Moses Rock Dike, San Juan County, Utah. American
354 Mineralogist, 55,1738–1771.
- 355 Milton, C., and Narain, S. (1969) Merumite occurrence in Guyana. Economic Geology, 64, 910–
356 914.
- 357 Milton, C., Appleman, D.E., Appleman, M.H., Chao, E.C.T., Cuttitta, F., Dinnin, E.J., Dwornik,
358 B.L., Ingram, B.L., and Rose Jr., H.J. (1976) Merumite, a complex assemblage of
359 chromium minerals from Guyana. United States Geological Survey Professional Paper,
360 887, 1–29.
- 361 Sack, R.O., and Ghiorso, M.S. (1991) Chromite as a petrogenetic indicator. In Mineralogical
362 Society of American Reviews in Mineralogy 25, pp. 323-353.
- 363 Sano-Furukawa, A., Kagi, H., Nagai, T., Nakano, S., Fukura, S., Ushijima, D., Iizuka, R.,
364 Ohtani, E., and Yagi, T. (2009) Change in compressibility of δ -AlOOH and δ -AlOOD at
365 high-pressure: A study of isotope effect and hydrogen bond symmetrization. American
366 Mineralogist, 94, 1255-1261.
- 367 Shi, G.H., Stockhert, B., and Cui, W.Y. (2005) Kosmochlor and chromian jadeite aggregates
368 from the Myanmar jadeitite area. Mineralogical Magazine, 69, 1059-1075.
- 369 Smith, D. (1979) Hydrous minerals and carbonates in peridotite inclusions from the Green Knobs
370 and Buell Park kimberlitic diatremes on the Colorado Plateau. In: F.R. Boyd and H.O.A.
371 Meyer, eds., The Mantle Sample: Inclusions in Kimberlite and Other Volcanics, p. 345–
372 356, AGU, Washington, D.C.
- 373 Smith, D. (1995) Chlorite-rich ultramafic reaction zones in Colorado Plateau xenoliths:
374 Recorders of sub-Moho hydration. Contributions to Mineralogy and Petrology, 121, 185–

- 375 200.
- 376 Smith, D (1987) Genesis of carbonate in pyrope from ultramafic diatremes on the Colorado
377 Plateau, southwestern United States. *Contributions to Mineralogy and Petrology*, 97, 389-
378 396.
- 379 Smith, D. (2010) Antigorite peridotite, metaserpentinite, and other inclusions within diatremes
380 on the Colorado Plateau, SW USA: Implications for the mantle wedge during low angle
381 subduction. *Journal of Petrology*, 51, 1355–1379.
- 382 Smith, D. (2013) Olivine thermometry and source constraints for mantle fragments in the Navajo
383 Volcanic Field, Colorado Plateau, southwest United States: Implications for the mantle
384 wedge. *Geochemistry, Geophysics, Geosystems*, 14 (3), doi:10.1002/ggge.20065
- 385 Smith, D., and Zeintek, M. (1979) Mineral chemistry and zoning in eclogite inclusions from the
386 Colorado Plateau. *Contributions to Mineralogy and Petrology*, 69, 119-131.
- 387 Smith, D., Connelly, J.N., Manser, K., Moser, D.E., Housh, T.B., McDowell, F.W., and Mack,
388 L.E. (2004) Evolution of Navajo eclogites and hydration of the mantle wedge below the
389 Colorado Plateau, southwestern United States. *Geochemistry Geophysics Geosystems*, 5,
390 doi:10.1029/2003GC000675.
- 391 Tsujimori, T., and Harlow, G. (2012) Petrogenetic relationships between jadeitite and associated
392 high-pressure and low-temperature metamorphic rocks in worldwide jadeitite localities:
393 A review. *European Journal of Mineralogy*, 24, 371-390.
- 394 Tsujimori, T., Sisson, V.B., Liou, J.G., Harlow, G.E., and Sorensen, S.S. (2006) Petrologic
395 characterization of Guatemalan lawsonite eclogite: Eclogitization of subducted oceanic
396 crust in a cold subduction zone. in B.R. Hacker, W.C. McClelland, J.G. Liou, eds.,

- 397 Ultrahigh-pressure metamorphism: Deep continental subduction, Geological Society of
398 America Special Paper, 403, 147–168.
- 399 Usui, T., Nakamura, E., Kobayashi, K., Maruyama, S., and Helmstaedt, H.H. (2003) Fate of the
400 subducted Farallon plate inferred from eclogite xenoliths in the Colorado Plateau.
401 *Geology*, 31, 589-592.
- 402 Voicu, G., and Bardot, M. (2002) Geochemical behavior under tropical weathering of the
403 Barama-Mazaruni greenstone belt at Omai gold mine, Guiana. *Applied Geochemistry*,
404 17, 321-336.
- 405 Vuorelainen, Y., Hakli, T.A., and Kataja, M. (1968) A hydrated oxide of chromium as a
406 pseudomorph after eskolaite, Outokumpu, Finland. *Bulletin of the Geological Society of*
407 *Finland*, 40, 125–129.
- 408 Wang, L., Essene, E.J., and Zhang, Y. (1999) Mineral inclusions in pyrope crystals from Garnet
409 Ridge, Arizona, USA: Implications for processes in the upper mantle.
410 *Contributions to Mineralogy and Petrology*, 135, 164–178.
- 411 Wang, L., Rouse, R. C., Essene, E. J., Peacor, D. R., and Zhang, Y. (2000) Carmichaelite, a new
412 hydroxyl-bearing titanate from Garnet Ridge, Arizona. *American Mineralogist* 85, 792-
413 800.
- 414 Watson, K.D. (1967) Kimberlite pipes of northeastern Arizona. In: P.J. Wyllie, ed., *Ultramafic*
415 *and Related Rocks*, p. 261-269, Wylie, New York.
- 416 Yang, C.M.O. (1984) A terrestrial source of ureyite. *American Mineralogist*, 69, 1180-1183.
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420 Figure Captions

421 Figure 1. Backscatter secondary electron image of a portion of a cluster of accessory
422 minerals in sample 12-90-50. Phases labelled are guyanaite (guy), eskolaite (es), carmichaelite
423 (carm) and chromite (cht). These phases are set in a matrix of omphacite that appears very dark
424 grey in this image. The scale bar represents 20 microns.

425 Figure 2. *In situ* μ XRD for accessory minerals from clusters in sample 12-90-50. a)
426 context image of polished thin section with target locations of the four μ XRD patterns in c and d.
427 The red box represents the area of the BSE image in Fig. 1, b) two-dimensional GADDS images
428 of raw μ XRD data; the bright spots indicate larger crystallites and streaks indicate slight
429 dispersion of crystallite orientation likely due to intergrowth of kosmochlor (kos) and guyanaite
430 (guy). The absence of complete Debye rings indicates that these crystallites do not occur in a
431 random distribution but in oriented mineral clusters; c) stack plot of conventional intensity vs. 2θ
432 diffraction patterns for four target locations (areas 1, 2, 5, 7). The best matching mineral phases
433 from the ICDD database are shown as coloured sticks below the patterns; d) stack plot of the
434 same four patterns (areas 1, 2, 5, 7) compared with ICDD patterns for the CrOOH polymorphs
435 guyanaite, bracewellite and grimaldiite. The DIF pattern of carmichaelite in c) was constructed
436 from the data in Wang et al. (2000). (Omega scan collection conditions: Frame 1 - $\theta_1 = 14.5^\circ$, θ_2
437 = 18.0° , omega = 9, time = 60 minutes; Frame 2 - $\theta_1 = 31.5^\circ$, $\theta_2 = 40.0^\circ$, omega = 20, time = 60
438 minutes).

439 Figure 3. Field of likely equilibration conditions of guyanaite-bearing xenolith (rounded
440 rectangle with dark shading). Black dots are estimated equilibration conditions of three phengite

441 eclogites from Smith et al. (2004). Stability field of guyanaite relative to eskolaite + water
442 (region with light shading represents uncertainty) is from Jahn et al. (2012). The quartz (Qz) -
443 coesite (Coes) transition and the reaction lawsonite = zoisite (Zo) + kyanite (Ky) + quartz (Qz) +
444 H₂O are from Bohlen and Boettcher (1982) and Chatterjee et al. (1984), respectively.
445

Table 1. Electron microprobe analyses of minerals in sample 12-97-50, weight percent oxide.

	guyanaite (9) ^a		chromite I (12)		chromite II (11)	
	s.d. ^b		s.d.		s.d.	
SiO ₂	0.05	0.01	0.07	0.04	0.04	0.02
Al ₂ O ₃	1.44	0.14	5.84	0.57	1.93	0.36
TiO ₂	5.46	2.63	0.17	0.05	0.10	0.05
Cr ₂ O ₃	72.74	4.45	55.78	0.79	64.93	1.00
V ₂ O ₃	0.12	0.04	0.14	0.03	0.05	
Nb ₂ O ₅	0.01	0.01	0.02	0.02	0.01	
Fe ₂ O ₃ ^d	7.75	0.88	7.05	0.66	2.53	0.51
FeO	nd ^e		24.36	0.21	24.63	0.17
MnO	0.09	0.02	0.26	0.04	0.26	0.05
MgO	1.00	0.51	2.06	0.07	1.82	0.06
NiO	0.30	0.16	0.13	0.03	0.06	0.02
ZnO	0.02	0.02	5.71	0.27	5.46	0.20
CaO	0.11	0.03	0.04	0.02	0.05	0.02
Na ₂ O	nd		nd		nd	
K ₂ O	nd		nd		nd	
Total	89.09		100.99		101.64	
formulae normalized to n cations	n =	1	3		3	
	Si ⁴⁺	0.001	0.002		0.001	
	Al ³⁺	0.024	0.244		0.082	
	Ti ⁴⁺	0.058	0.005		0.003	
	Cr ³⁺	0.808	1.562		1.847	
	V ³⁺	0.001	0.004		0.001	
	Nb ⁵⁺	0.000	0.000		0.000	
	Fe ³⁺	0.082	0.190		0.069	
	Fe ²⁺	nd	0.722		0.742	
	Mn ²⁺	0.001	0.008		0.008	
	Mg ²⁺	0.021	0.109		0.098	

Ni ²⁺	0.003	0.004	0.002
Zn ²⁺	0.000	0.149	0.145
Ca ²⁺	0.002	0.002	0.002
Na ⁺	nd	nd	nd
K ⁺	nd	nd	nd
Total	1.000	3.000	3.000
Fe ²⁺ /(Fe ²⁺ +Fe ³⁺) (molar)		0.792	0.914
Fe ³⁺ :Cr:Al (molar)		0.095:0.783:0.122	0.034:0.924:0.082

^a Values in parentheses indicate number of analyses used in average

^b Standard deviation

^c Abbreviations: jd - jadeite component, ko - kosmochlor component, ac - acmite component

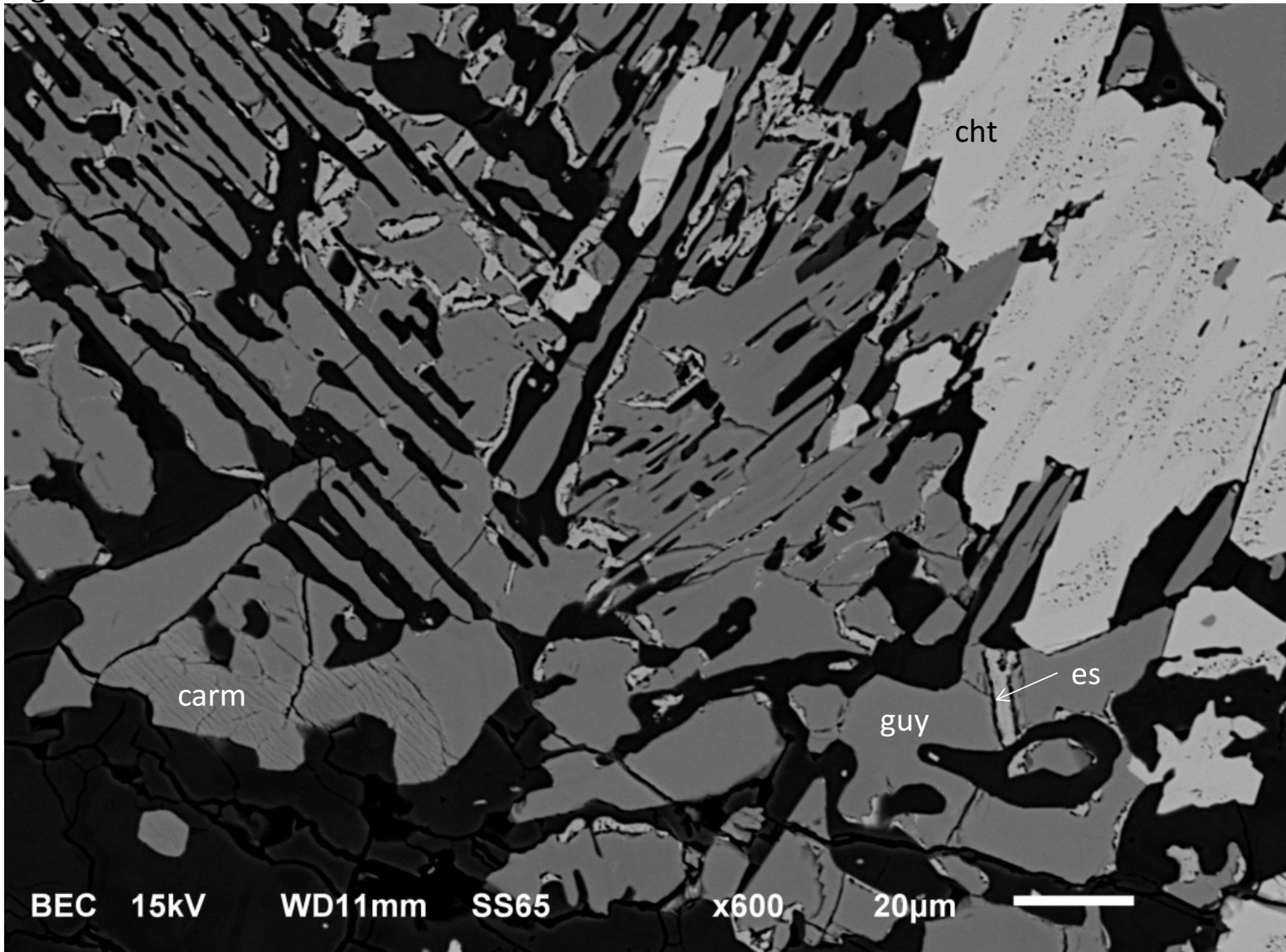
^d Fe reported as Fe³⁺ for guyanaite, carmichaelite and eskolaite. Fe²⁺ and Fe³⁺ calculated by charge balance for chromite and omphacite

^e nd - not determined

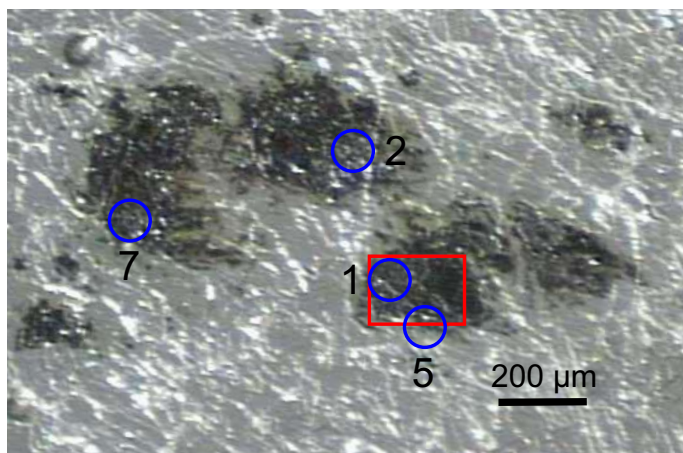
carmichaelite (5)		eskolaite (4)		Omphacite	Omphacite	Omphacite
s.d.		s.d.		highest ko ^c (1)	highest jd (1)	lowest jd (1)
0.10	0.06	0.12	0.05	54.63	56.21	55.55
1.23	0.03	1.56	0.02	3.18	5.56	2.41
50.94	0.17	6.31	0.35	0.03	0.02	0.01
29.27	0.66	83.59	0.60	10.01	0.08	0.07
0.20	0.03	0.13	0.04	nd	nd	nd
0.04	0.01	0.02	0.01	nd	nd	nd
9.30	0.17	8.09	0.10	2.60	2.49	2.45
nd		nd		2.19	3.75	3.20
0.03	0.01	0.14	0.03	0.04	0.04	0.04
1.40	0.06	1.05	0.08	8.79	11.36	13.92
0.16	0.04	0.38	0.03	0.10	0.12	0.14
0.03	0.04	0.03	0.04	nd	nd	nd
0.26	0.10	0.17	0.04	13.07	16.66	20.47
nd		nd		6.60	4.68	2.59
nd		nd		0.00	0.01	0.00
92.95		101.58		101.25	100.98	100.85
1		2		4	4	4
0.001		0.003		1.984	2.010	2.005
0.020		0.045		0.136	0.235	0.102
0.521		0.117		0.001	0.001	0.000
0.315		1.628		0.287	0.002	0.002
0.002		0.003		nd	nd	nd
0.000		0.000		nd	nd	nd
0.106		0.150		0.071	0.067	0.067
nd		nd		0.066	0.112	0.096
0.000		0.003		0.001	0.001	0.001
0.028		0.039		0.476	0.606	0.749

	0.002		0.008		0.003	0.003	0.004
	0.000		0.001	nd	nd	nd	
	0.004		0.005		0.509	0.638	0.791
nd		nd			0.465	0.324	0.182
nd		nd			0.000	0.000	0.000
	1.000		1.000		4.000	4.000	4.000
				jd 14	jd 23	jd 10	
				ko 29	ko 0	ko 0	
				ac 7	ac 7	ac 7	

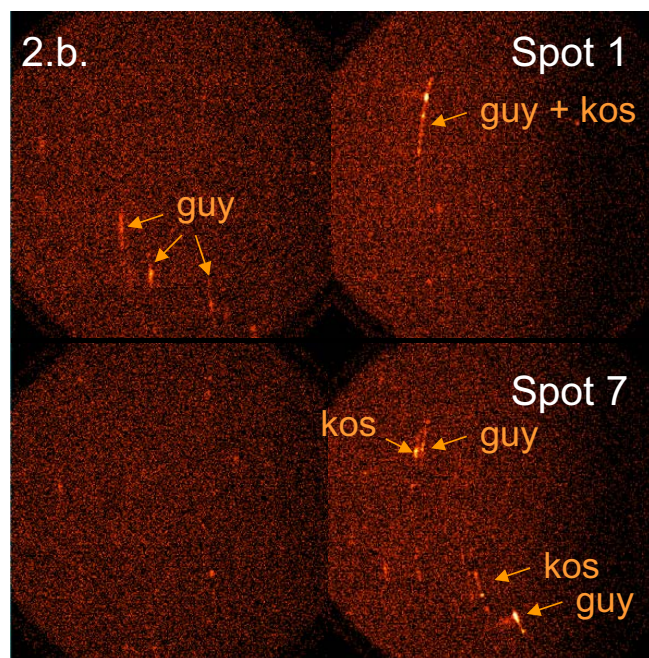
Fig 1



2.a.



2.b.



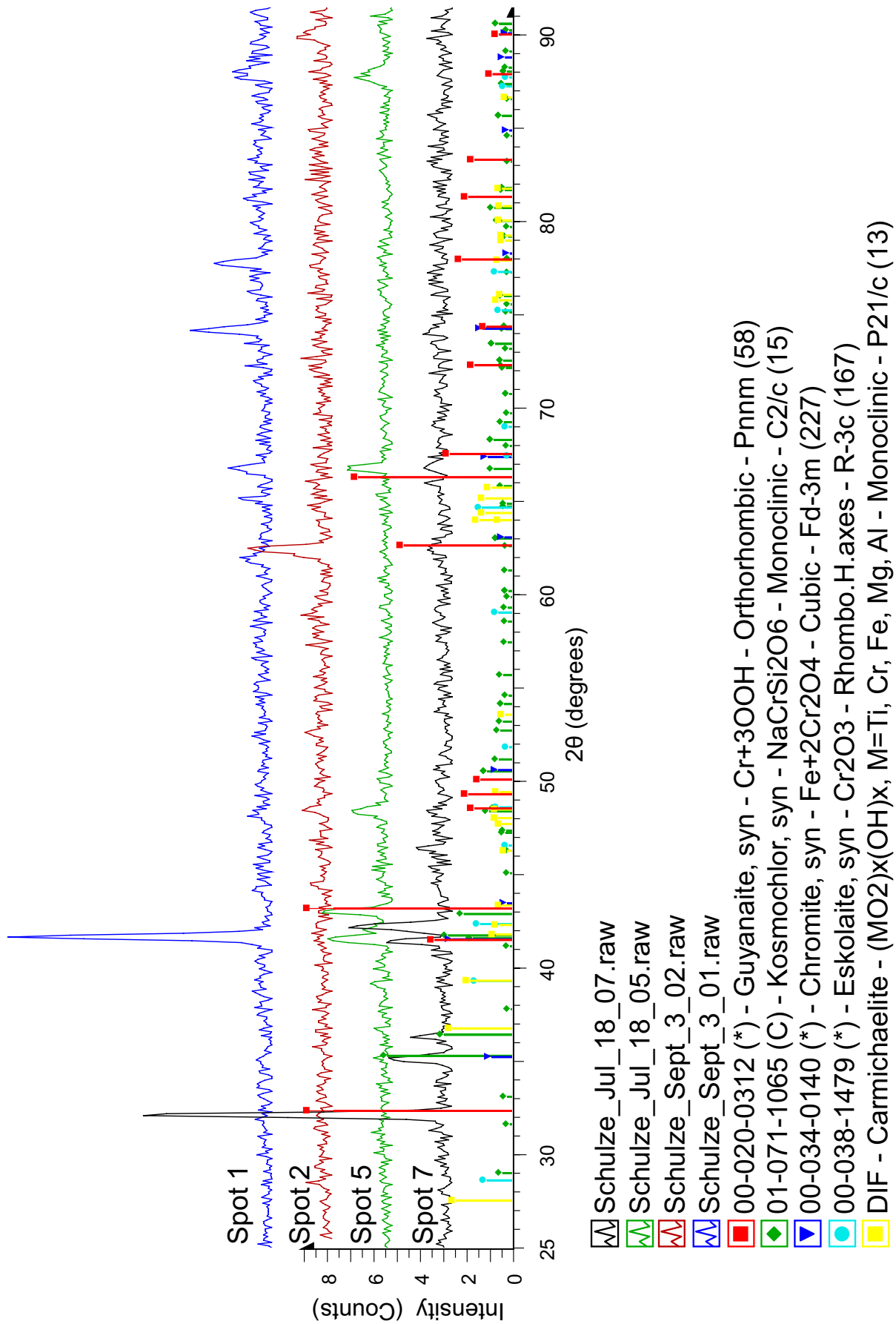


Fig 2.c.

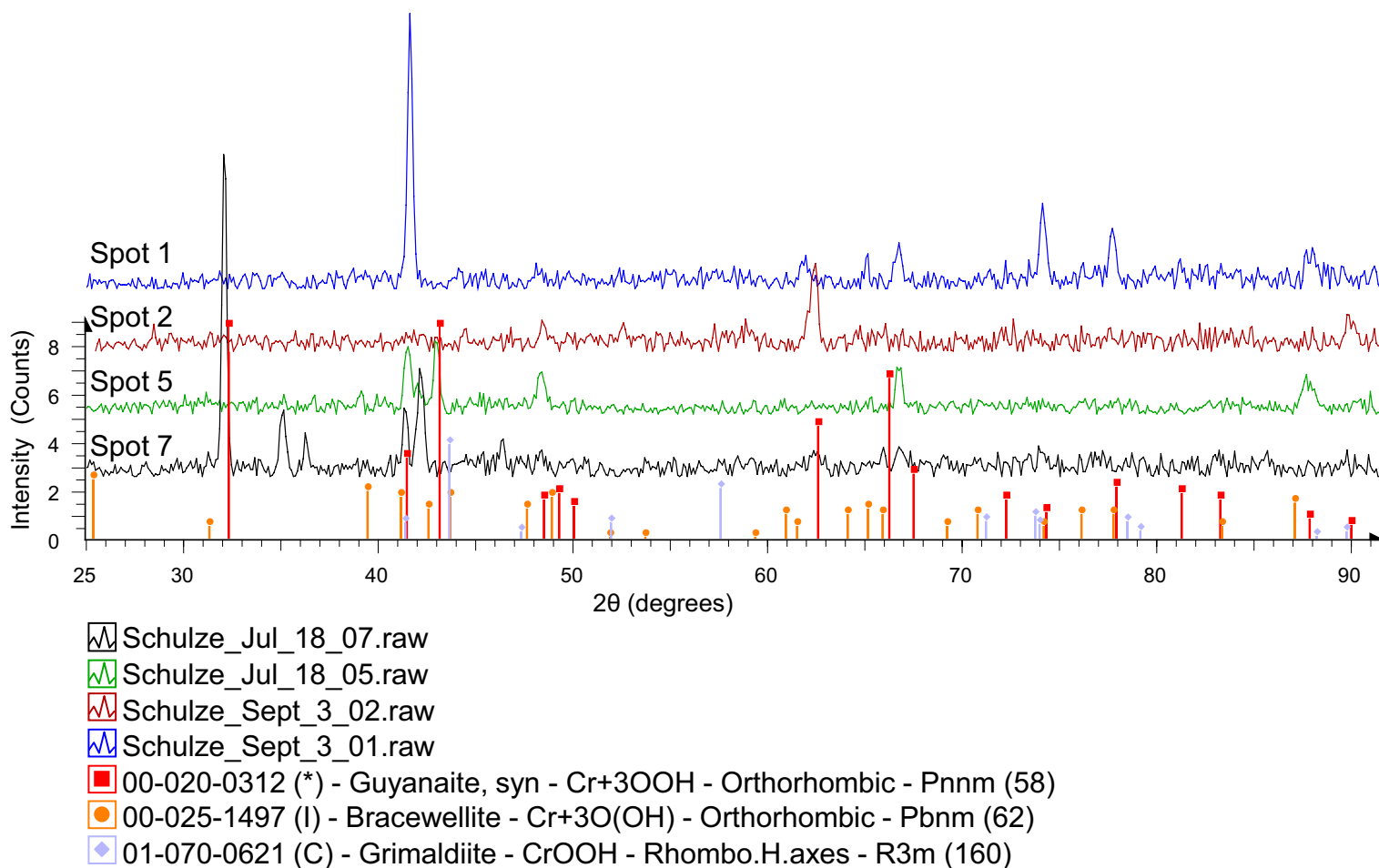


Fig 2.d.

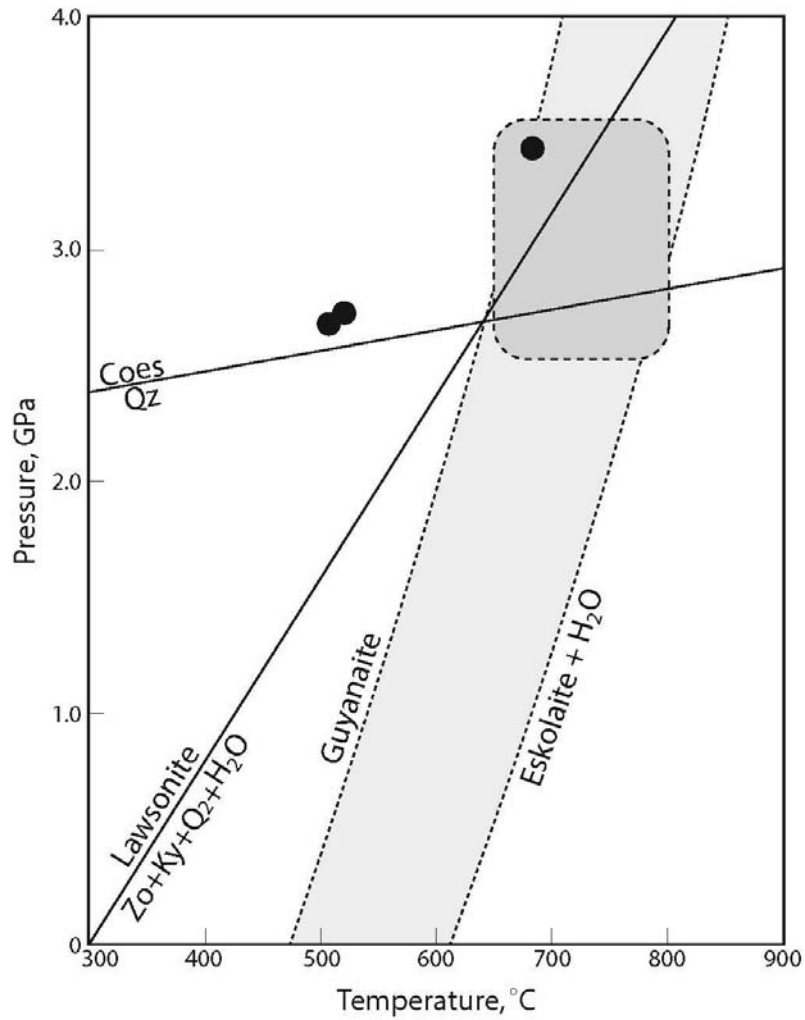


Fig. 3