

26 **A new occurrence of yimengite-hawthorneite and crichtonite-group minerals in an**
27 **orthopyroxenite from kimberlite: Implications for mantle metasomatism**

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34 **ABSTRACT**

35 LILE-enriched chromium titanates of the magnetoplumbite ($AM_{12}O_{19}$) and crichtonite
36 ($ABC_{18}T_2O_{38}$) groups were recognized as abundant inclusions in orthopyroxene grains in a
37 mantle-derived xenolith from the Udachnaya-East kimberlite pipe, Daldyn field, Siberian craton.
38 The studied xenolith consists of three parts: an orthopyroxenite, a garnet clinopyroxenite, and a
39 garnet-orthopyroxene intermediate domain between the two. Within the host enstatite (Mg#
40 92.6) in the orthopyroxenitic part of the sample titanate inclusions are associated with Cr-spinel,
41 diopside, rutile, Mg-Cr-ilmenite, and pentlandite. Crichtonite-group minerals also occur as
42 lamellae inclusions in pyrope grains of the intermediate domain adjacent to the orthopyroxenite,
43 as well as in interstitial to enstatite oxide intergrowths together with Cr-spinel, rutile, and
44 ilmenite.

45 Yimengite-hawthorneite inclusions in enstatite contain (wt%) 3.72-8.04 BaO, 2.05-3.43
46 K_2O , and 0.06-0.48 CaO. Their composition is transitional between yimengite and hawthorneite
47 endmembers with most grains exhibiting K-dominant chemistry. A distinct feature of the studied
48 yimengite-hawthorneite minerals is a high content of Al_2O_3 (5.74-7.69 wt%). Crichtonite-group
49 minerals vary in compositions depending on the occurrence in the xenolith: inclusions in
50 enstatite are moderate-high in TiO_2 (62.9-67.1 wt%), moderately Cr-rich (12.6-14.0 wt% Cr_2O_3),
51 Ba- or K-specific in the A site, and contain low ZrO_2 (0.05-1.72 wt%), whereas inclusions in

52 pyrope are moderate in TiO₂ (61.7-63.3 wt% TiO₂), relatively low in Cr (8.98-9.62 wt% Cr₂O₃),
53 K-dominant in the A site, and are Zr-enriched (4.64-4.71 wt% ZrO₂). Crichtonite-group minerals
54 in polymineralic oxide intergrowths show highly diverse compositions even within individual
55 aggregates, where they are chemically dominated by Ba, Ca, and Sr.

56 *P-T* estimates indicate the orthopyroxenite to have equilibrated at ~800 °C and 35 kbar.
57 Preferentially oriented lamellae of enstatite-hosted Cr-spinel and diopside, as well as pyrope,
58 diopside, and Cr-spinel grains developed around enstatite crystals, are interpreted to have been
59 exsolved from the high-*T* Ca-Al-Cr-enriched orthopyroxene precursor. The observed textural
60 relationships between inclusions in enstatite and exotic titanate compositions imply that the
61 studied orthopyroxenite has undergone a metasomatic processing by a mobile percolating agent
62 afterwards; this highly evolved melt/fluid was enriched in Ba, K, HFSE, and other incompatible
63 elements. The infiltration of the metasomatizing liquid occurred through interstices and
64 vulnerable zones of enstatite grains and manifested in the crystallization of titanate inclusions. It
65 is assumed that Cr-spinel lamellae served as seeds for their nucleation and growth. The
66 prominent textural and chemical inhomogeneity of the interstitial oxide intergrowths is either a
67 consequence of the metasomatic oxide crystallization shortly prior the kimberlite magma
68 eruption, or arose from the intensive modification of pre-existing oxide clusters by the kimberlite
69 melt during the Udachnaya emplacement. Our new data provide implications for the
70 metasomatic treatment of orthopyroxenites in the subcontinental lithospheric mantle from the
71 view of exotic titanate occurrences.

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73 **Keywords:** yimengite, hawthorneite, magnetoplumbite-group minerals, crichtonite-group
74 minerals, Ti-oxide, xenolith, mantle metasomatism, Udachnaya kimberlite pipe

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Introduction

79 During recent decades, mantle-derived titanates have received increased attention due to
80 their capability to incorporate rare silicate-incompatible elements, which are important indicators
81 of mantle processes (Jones et al. 1982; Haggerty 1991; Kalfoun et al. 2002; Griffin et al. 2014).
82 Among the plethora of Ti-rich exotic oxides occurring in the subcontinental lithospheric mantle
83 (SCLM), **yimengite-hawthorneite series (YIHA)**, chromium-rich K- and Ba-specific endmembers
84 of the magnetoplumbite group, respectively) and crichtonite-group minerals (**CGM**) appear to be
85 the most indicative in upper mantle-derived rocks sampled by deep-sourced magmas. YIHA and
86 CGM readily accommodate large-ion lithophile elements (LILE: Ba, K, Sr) due to the presence
87 of 12-fold coordinated large cation site in their crystal structure; CGM of mantle origin are also
88 frequently enriched in Ca, some of the high field strength elements (HFSE: Zr, occasionally Nb),
89 and light rare earths (LREE: La, Ce). The occurrences of YIHA and CGM in metasomatized
90 associations, and their characteristic enrichment in incompatible constituents, have been
91 conventionally linked to metasomatic processes generated by fluids and melts (Haggerty 1983;
92 Wang et al. 1999; Konzett et al. 2013). These metasomatic events have taken place extensively
93 in the SCLM of ancient cratons throughout the geological history and are of paramount
94 significance in the refertilization of previously depleted protoliths (e.g. Frey and Green 1974;
95 Bailey 1982; Dawson 1984; Erlank et al. 1987; Harte et al. 1987; Pearson et al. 1995; O'Reilly
96 and Griffin 2013; Howarth et al. 2014).

97 The Middle Paleozoic kimberlite pipe Udachnaya-East (Daldyn field, Daldyn-Alakit
98 diamondiferous district, Siberian craton) is the worldwide renowned primary diamond mine,
99 which carries exceptional well-preserved xenoliths of deep-seated mantle rocks. The geological
100 setting of the Udachnaya-East pipe, types of kimberlites and their petrography have been
101 comprehensively described elsewhere (e.g. Kamenetsky et al. 2014; Abersteiner et al. 2018).
102 Long-term studies of the Udachnaya mantle column made up of granular and sheared peridotites
103 with a minor proportion of eclogites, pyroxenites and other rock types have revealed extensive

104 evidence of a metasomatic re-enrichment during the prolonged evolution of the Siberian craton
105 (Boyd et al. 1997; Shimizu et al. 1997; Ionov et al. 2010; Goncharov et al. 2012; Doucet et al.
106 2013). In particular, several reports emphasized the multi-stage nature of refertilization processes
107 in the Udachnaya SCLM (e.g. Pearson et al. 1995; Solov'eva et al. 2012; Agashev et al. 2013;
108 Howarth et al. 2014). The metasomatism manifested in a change of whole-rock chemistry and
109 elemental distributions within rock-forming minerals (cryptic metasomatism; Dawson 1984), as
110 well as in a crystallization of new minerals which appearance is superimposed on primary
111 mineral assemblages (modal metasomatism; Harte 1983). YIHA and CGM are representative
112 small-volume products of a modal metasomatism, with their occurrence in a rock sample being a
113 useful signature reflecting the addition of a series of trace elements considered incompatible in
114 primitive silicate melts. Surprisingly, the literature data concerning titanates of the
115 magnetoplumbite and crichtonite groups are almost completely lacking in case of the Udachnaya
116 lithospheric column despite a few examples of CGM inclusions in pyrope crystals (Alifirova et
117 al. 2012). The present paper aims to document the first occurrence of YIHA and CGM in a
118 mantle orthopyroxene, as well as in other associated assemblages, and to provide inferences
119 concerning the titanates origin in order to further understand the processes responsible for the
120 reworking of mantle lithologies beneath the Daldyn kimberlite field.

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122 **Previous studies**

123 Pioneer works have shown YIHA and CGM to be minor but widespread constituents of
124 metasomatized peridotite xenoliths carried out by kimberlite magmas in South Africa (Haggerty
125 1975, 1983, 1988, 1989; Jones et al. 1982; Haggerty et al. 1983, 1989; Erlank et al. 1987; Grey
126 et al. 1987, Jones 1989), China (Dong et al. 1984; Zhou et al. 1984), and Venezuela (Nixon and
127 Condliffe 1989). Later reports enhanced the data concerning YIHA and CGM in peridotite
128 xenoliths from on-cratonic kimberlites and kimberlite-like rocks (Kiviets et al. 1998; Konzett et
129 al. 2000, 2013; Almeida et al. 2014; Giuliani et al. 2014, 2018; Griffin et al. 2014) and also

130 documented the occurrences of Ca-rich CGM in mantle xenoliths derived by alkali basaltic
131 magmas within off-craton settings (Ionov et al. 1999; Grégoire et al. 2000; Kalfoun et al. 2002;
132 Litasov et al. 2006). Special attention has been given to CGM inclusions in chromium pyropes
133 (see compilation in Rezvukhin et al. 2018). A brief reference was made to the presence of CGM
134 inclusions in a mantle clinopyroxene from the Letseng-la-Terae kimberlite in Lesotho (Mair et
135 al. 2010). Giuliani et al. (2014, 2018) reported CGM grains enclosed in phlogopite.
136 Magnetoplumbite- and crichtonite-type minerals were recognized as inclusions in diamond
137 testifying their deep mantle origin including the diamond stability field (Sobolev et al. 1988,
138 1997; Leost et al. 2003; Bulanova et al. 2004). The *P-T* stability of YIHA and CGM under the
139 upper mantle conditions and deeper has been experimentally proved by Foley et al. (1994) and
140 Konzett et al. (2005). Isotopic studies of the exotic titanates and recent advances in
141 geochronological techniques have made it possible to provide constraints on the timing of mantle
142 metasomatism (Bulanova et al. 2004; Giuliani et al. 2014, 2018; Griffin et al. 2014).

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Methods

145 Analytical procedures were carried out in Sobolev Institute of Geology and Mineralogy
146 (Analytical Center for multi-elemental and isotope research, Siberian Branch of the Russian
147 Academy of Sciences), Novosibirsk, Russia. Back-scattered electron (BSE) images and
148 preliminary qualitative analyses of minerals were acquired using a Tescan MIRA 3 LMU
149 scanning electron microscope equipped with an INCA Energy 450 XMax 80 (Oxford
150 Instruments) energy-dispersive system (EDS), as well as a JEOL JXA-8230 microanalyzer
151 employed in a qualitative mode. Quantitative wavelength-dispersive (WDS) analyses were
152 conducted using a JEOL JXA-8100 electron microprobe (EMP) instrument. EMP analyses of
153 silicates, rutile, ilmenite, and spinel were performed with an acceleration voltage of 20 kV, 20
154 nA beam current, and counting times of 10 s for peaks and mostly 5 s for each side of the
155 background (Lavrent'ev et al. 2015); during EMP analyses of YIHA and CGM a beam current of

156 100 nA was employed in order to increase precision in determining minor elements. A particular
157 emphasis was given to peak overlap corrections e.g. for Ti and V, Ti and Ba, Ti and Ce, Ba and
158 Ce. Silicon was included in the set of analyzed elements for all types of oxide inclusions in order
159 to trace the possible contamination by the host silicates. Raw analytical data were processed
160 using ZAF and CITZAF fully automated routines. Detection limits vary within 0.01–0.05 wt%
161 oxide. Wavelength-dispersive X-ray map of elemental abundances in the representative oxide
162 intergrowth was conducted over ~16 hours on a 300×265 μm area with 20 kV, 30 nA, pixel size
163 0.8×0.8 μm, and dwell time of 100 ms.

164 Estimation of lamellae volume percentages in the host orthopyroxene crystals and mineral
165 modes in the rock, as well as reintegration of pre-exsolved orthopyroxene composition were
166 carried out according to the approach described in (Alifirova et al. 2015).

167

168 **Results**

169 **Sample petrography**

170 Sample UV-13-233 is a 5×7×8 cm fragment of the entire xenolith enclosed in the host
171 kimberlite. It was picked from volcanoclastic sedimentary xenolith-poor (5–15 vol%) partially
172 serpentinized kimberlite unit (Abersteiner et al. 2018; Mikhalenko et al. 2018) in the central part
173 of the Udachnaya-East open-pit mine at the depth interval 620-640 m. The xenolith is of unique
174 nature and consists of three distinct zones: an orthopyroxenite, a low-chromium garnet
175 clinopyroxenite, and a wide (up to 3 cm) intermediate garnet-orthopyroxene assemblage in
176 between. We have focused our research on the orthopyroxenite part of the sample and the
177 fragment of the garnet-rich intermediate domain right beside the orthopyroxenite (Fig. 1), since
178 only here the exotic titanates have been recognized. The orthopyroxenite exhibits coarse-grained
179 texture and consists mostly of large (1-10 mm) orthopyroxene grains estimated to occupy ~97.8
180 vol% of the bulk rock with a small volume proportion of vein-like (“necklace”) garnet (~0.9
181 vol%), clinopyroxene (0.2-1.5 mm in size; ~1.1 vol%), and Cr-spinel (0.2-1.0 mm in size; ~0.2

182 vol%), as well as minor phlogopite, amphibole, olivine, apatite, sulfides, Ti-bearing oxides, and
183 secondary hydrothermal minerals filling interstitial space between rock-forming minerals (Figs.
184 1 and 2).

185 Orthopyroxene is enstatite with moderate amounts of CaO (0.26 ± 0.02 wt%) and Al_2O_3
186 (0.80 ± 0.04 wt%) and high Mg# (92.6; Opx1 in Table 1). Enstatite crystals enclose numerous Cr-
187 spinel and clinopyroxene inclusions (Figs. 2-4), which can be classified into two types according
188 to their grain size and morphology: preferentially oriented lamellae and needles 0.1-5 μm wide
189 and 10-1000 μm long (Type 1) and anhedral expanded (up to 100 μm in width) grains of
190 irregular shapes and rough outlines, commonly found as intergrowths with Ti-rich oxide
191 minerals (Type 2) (e.g. Figs. 2a, 2b, 3). On average, Cr-spinel occupies ~ 0.3 vol% of the host
192 enstatite, while clinopyroxene consumes ~ 1.1 vol%. All the clinopyroxene which constitutes
193 Type 1 and Type 2 inclusions, as well as grains interstitial to enstatite (Cpx1, Cpx2, and Cpx3,
194 respectively, in Table 1), is sodic Cr-diopside with roughly uniform composition throughout the
195 orthopyroxenite. However, Cpx2 is noticeably higher in Na (3.00 wt% Na_2O) than Cpx1 (2.68
196 wt% Na_2O) and Cpx3 (2.65 wt% Na_2O). Vein-like garnet developed around enstatite grains
197 (Figs. 2d-2f) and garnet of the intermediate domain close to the margin with the orthopyroxenite
198 (Fig. 1) are classified as chromium pyropes (Grt1 and Grt2, respectively, in Table 1). As a rule,
199 vein-like garnet is intensively replaced by phlogopite.

200 Within the host enstatite crystals, YIHA and CGM comprise inclusions with a size up to
201 100 μm . Here YIHA grains demonstrate strong spatial association with Type 2 Cr-spinel
202 inclusions and form abundant intergrowths with them (Figs. 3b-3e), although individual YIHA
203 grains are also occasionally present (Fig. 3a). Intergrowths of CGM with Type 2 Cr-spinel
204 appear to be less frequent compared to the YIHA + Cr-spinel \pm clinopyroxene assemblages.
205 However, it should be taken into account that CGM and Cr-spinel grains in enstatite have
206 roughly similar mean atomic values, making them visually almost indistinguishable in BSE
207 images (e.g. Fig. 3i). The distribution of YIHA, CGM, and Type 2 Cr-spinel/clinopyroxene

208 inside enstatite crystals is highly heterogeneous, with no regular pattern observed. Nevertheless,
209 it is particularly notable that inclusions of YIHA and CGM in all instances follow the general
210 orientation designated by Type 1 Cr-spinel and clinopyroxene lamellae (Fig. 2). Cr-rutile, Mg-
211 Cr-ilmenite, and pentlandite occur as associated phases in polyminerally intergrowths with the
212 exotic titanates (Figs. 3b, 3d, 3e), less frequently as individual inclusions.

213 YIHA grains have been recognized only in orthopyroxene, while CGM ones, in addition to
214 those enclosed in enstatite, have also been documented in Cr-pyroxene crystals in the intermediate
215 domain close to the orthopyroxenitic part of the xenolith (Fig. 4c, 4d), as well as in complex
216 oxide intergrowths which sporadically occur as isolated blebs in intergranular space of the
217 orthopyroxenite (Figs. 2c, 2f). These clusters are composed of Ti-rich oxide minerals i.e. rutile,
218 CGM, titaniferous Cr-spinel, occasionally ilmenite, and show pronounced inhomogeneity in
219 terms of both modal mineral proportions and compositions of individual minerals. Element
220 abundances in one of such oxide aggregates have been mapped by means of EMP technique
221 (Fig. 5).

222 The bulk xenolith is remarkably fresh, showing signs of alteration only on a micro-scale.
223 These include signs of the selective orthopyroxene dissolution during the late-stage impregnation
224 of kimberlite-related melt, as is evident from the occurrence of complex polyminerally inclusions
225 assumed to represent the crystallization products of the melt droplets. These inclusions vary in
226 size and distribution between marginal and central parts of the orthopyroxenite, being large (up
227 to 2 mm in maximum dimension) and widespread within the former and smaller (20-250 μm)
228 and scarce within the latter. The droplets are composed of olivine, phlogopite, apatite, calcite,
229 spinel, perovskite, Ca-Na-K amphibole (pargasite), Fe-Ni-sulfides, and djerfisherite. A series of
230 late-stage low- T hydrothermal minerals (serpentine, dolomite, barite, hydroxides and
231 hydroxohalides of Fe) occur in volumetrically small proportions in the melt inclusions and rock
232 interstices.

233

234 **Composition of yimengite-hawthorneite series**

235 YIHA minerals belong to the magnetoplumbite group with the generalized crystal-
236 chemical formula $AM_{12}O_{19}$, where major cations are: $^{XII}A = K, Ba, Sr, Ca, Na, La, Ce, Pb$; $M =$
237 $Ti, Fe, Cr, Al, V, Nb, Mn$. Selected compositions of YIHA inclusions in enstatite are shown in
238 Table 2. YIHA grains contain (all wt%) 22.7-28.1 TiO_2 , 31.1-34.6 Cr_2O_3 , 17.1-18.8 FeO_{total} ,
239 5.33-6.45 MgO , 5.74-7.69 Al_2O_3 , 0.28-0.47 V_2O_3 . BaO varies from 3.72 to 8.04, K_2O ranges
240 from 2.05 to 3.43, and CaO lies within 0.06-0.48. Other components ($SiO_2, Na_2O, MnO, NiO,$
241 HfO_2) do not exceed 0.3 wt%, while concentrations of $La, Ce, Sr, Nb, Y,$ and Zr oxides are
242 commonly below EMP detection limit.

243 The simplified empirical formula for the studied YIHA inclusions in enstatite, normalized
244 to 19 O atoms, is $(Ba, K)_{\Sigma=1}(Ti_3Cr_4Fe^{2+}_xFe^{3+}_{(2.5-x)}Mg_{1.5}Al)_{\Sigma=12}O_{19}$, where x is estimated to vary
245 from 1.0 to 1.3. Potassium in YIHA grains occupies 0.43-0.70 atoms per formula unit (a.p.f.u.),
246 while barium is between 0.23 and 0.52 a.p.f.u; in seventeen of the twenty one analyzed grains
247 (~80%) K predominates over Ba in the A site. In $Ba - K - Ca+Na+Sr+LREE$ axes the A-site
248 occupancy in mantle-derived magnetoplumbite-type phases is demonstrated (Fig. 6). Here YIHA
249 grains define a distinct compositional field compared to other reported compositions of
250 magnetoplumbite-group minerals from South Africa (Haggerty et al. 1989), China (Dong et al.
251 1984; Zhao 1991; Lu and Chou 1994; Zhou et al. 1996; Lu et al. 2007), Venezuela (Nixon and
252 Condliffe 1989), Zimbabwe (Bulanova et al. 2004), and Siberia (Sobolev et al. 1997).

253

254 **Composition of crichtonite-group minerals**

255 CGM are complex oxides with the general crystal-chemical formula $^{XII}A^{VI}B^{VI}C_{18}^{IV}T_2\Phi_{38}$,
256 where major cations are: $^{XII}A = \underline{K}, \underline{Ba}, \underline{Sr}, \underline{Ca}, \underline{Na}, \underline{La}, \underline{Ce}, \underline{Pb}$; $^{VI}B = \underline{Mn}, \underline{Y}, \underline{U}, \underline{Fe}, \underline{Zr}, \underline{Sc}$; $^{VI}C_{18}$
257 $= \underline{Ti}, Fe, Cr, Al, \underline{V}, Nb, Mn$; $^{IV}T_2 = \underline{Fe}, \underline{Mg}, \underline{Zn}, Mn$; $\Phi = O, (OH), F$ (cations known to dominate
258 in natural samples are underlined and coordination numbers are shown by Roman numerals).
259 Compositions of CGM are highly variable depending on the occurrence in the xenolith (Table 3).

260 CGM inclusions in enstatite are moderate to high in Ti (62.9-67.1 wt% TiO₂), moderately Cr-
261 rich (12.6-14.0 wt% Cr₂O₃), Ba- or K-specific in the A site, and contain low ZrO₂ (0.05-1.72
262 wt%). The studied CGM inclusions in pyrope grains are moderate in Ti (61.7-63.3 wt% TiO₂),
263 low in Cr (8.98-9.62 wt% Cr₂O₃), K-dominant in the A site and are relatively Zr-rich (4.64-4.71
264 ZrO₂). CGM in interstitial inhomogeneous oxide intergrowths exhibit wide chemical variations
265 even within individual cluster (Fig. 5, Table 3). Here CGM have very contrasting concentrations
266 of TiO₂ (55.1-67.9 wt%), Cr₂O₃ (12.0-20.4 wt%), and ZrO₂ (0.57-4.41 wt%); these grains are
267 mostly Ca- and Ba-characteristic in the A site, and single analysis (№ 13) shows the prevalence
268 of Sr (Table 3). Note that REE enrichment (up to 2.24 La₂O₃ + Ce₂O₃) is observed uniquely in
269 CGM grains within the oxide aggregates. The studied CGM in the rock are generally high in
270 Al₂O₃ (1.30-1.97 wt%) and low in Nb₂O₅ (around or less than EMP detection limit). However,
271 one analyzed spot (№ 12, Table 3) in the oxide intergrowth displays low Al (0.21 wt% Al₂O₃)
272 and elevated Nb (0.43 wt% Nb₂O₅) further highlighting the prominent compositional
273 heterogeneity of minerals within the interstitial oxide clusters.

274

275 **Composition of associated oxides (Cr-spinel, rutile, ilmenite)**

276 Chemical compositions of the studied oxide minerals in terms of major elements are
277 displayed in Fig. 7. Like CGM, Cr-spinel varies in chemistry depending on the occurrence in the
278 sample. Thin Cr-spinel lamellae in enstatite (Type 1 inclusions; Spl1 in Table 4) are virtually
279 homogeneous in composition, which correspond to a common upper mantle-derived
280 magnesiochromite-chromite with Mg# = $100 \times \text{Mg}/(\text{Mg}+\text{Fe}) = 53.0$ and Cr# = $100 \times \text{Cr}/(\text{Cr}+\text{Al})$
281 = 68.8. Note that Type 1 Cr-spinel is the most aluminous spinel variety among those occurring in
282 the orthopyroxenite, whilst containing the lowest Fe and Ti (Fig. 7). Type 2 Cr-spinel inclusions
283 in enstatite (Spl2) exhibit significantly wider ranges of constituent elements with increasing
284 levels of Fe and Ti. Major-element concentrations in Type 2 Cr-spinel inclusions vary as follows
285 (wt%): 10.5-13.1 MgO, 20.1-23.6 FeO_{total}, 9.8-14.8 Al₂O₃, 48.6-53.7 Cr₂O₃, 1.11-4.27 TiO₂.

286 Large (0.2-1.0 mm) individual Cr-spinel grains interstitial to enstatite (Spl3) are chemically
287 reminiscent of Type 1 Cr-spinel inclusions in enstatite, whereas Cr-spinel associated with Ti-rich
288 oxides in interstitial oxide intergrowths (Spl4) is titaniferous chromite covering the following
289 compositional range: 9.9-11.7 MgO, 21.6-26.4 FeO_{total}, 6.52-9.77 wt% Al₂O₃, 47.5-55.3 Cr₂O₃,
290 1.93-7.19 TiO₂. Small (< 50-70 μm) grains of spinel scattered in interstitial space of the rock are
291 of highly diverse compositions, from the early generation titaniferous chromite-
292 magnesiochromite to varieties enriched in Fe³⁺, Al, and Mn that are clearly secondary in origin.

293 Rutile inclusions in enstatite associated with other Ti-rich oxides and Type 2 Cr-spinel are
294 Cr-bearing (1.54-1.91 wt% Cr₂O₃), though contain low Zr and Nb. Rutile in interstitial oxide
295 intergrowths is generally low in HFSE as well and contains mainly Cr₂O₃ (2.62-3.36 wt%), but is
296 enriched in HFSE in particular parts of a cluster. For instance, at the edge of the mapped oxide
297 aggregate, rutile has high concentrations of Nb (up to 4.26 wt% Nb₂O₅) and/or Zr (up to 0.77
298 wt% ZrO₂) (Fig. 5, Table 4).

299 Ilmenite inclusions in enstatite incorporate a high proportion of a geikielite component
300 (about 40-50 mol%). These contain 54.2-55.5 wt% TiO₂, 24.4-27.4 wt% FeO_{total}, 12.4-14.8 wt%
301 MgO, and 3.93-4.96 wt% Cr₂O₃. A composition of ilmenite in oxide intergrowths basically
302 covers the same range, although, similar to rutile and CGM, ilmenite here shows local
303 enrichment in Nb (up to 0.40 wt% Nb₂O₅).

304

305

Discussion

306

Comparison of titanate compositions with reported data

308 The studied YIHA grains are compositionally interjacent between yimengite and
309 hawthorneite with an overall tendency towards K-dominant compositions. According to the
310 available literature data, mantle-derived magnetoplumbite-type titanates are predominantly K-
311 rich worldwide (Fig. 6). Extremely Ba-rich hawthorneite (~ 13 wt% BaO, 0.9 Ba cations per 19

312 oxygens) was described only in a metasomatized harzburgite xenolith from the Bultfontein
313 kimberlite mine (South Africa) as a holotype mineral (Grey et al. 1987; Haggerty et al. 1989).
314 Another Ba-characteristic magnetoplumbite-group mineral of probable deep-seated mantle origin
315 is haggertyite, ideally $\text{Ba}(\text{Ti}_5\text{Fe}_4^{2+}\text{Fe}_2^{3+}\text{Mg})\text{O}_{19}$, recognized in the Prairie Creek lamproite, USA
316 (Grey et al. 1998; Velde 2000). Haggertyite, however, is a relatively low-Cr mineral (mostly <5
317 wt% Cr_2O_3) with highly specific conditions of growth, attributed to the reaction between
318 lamproite melt and enclosed mafic xenoliths (Velde 2000). The proportion of calcium
319 endmember in the studied YIHA grains is low (Fig. 6). Ca-characteristic minerals supposed to
320 belong to the magnetoplumbite group were reported in a kimberlite from the Shandong province
321 in China (Lu et al. 2007), where holotypic yimengite has been also recognized (Dong et al.
322 1984). However, these Ca-enriched minerals have unusual crystal chemistry with lower A-site
323 occupancy and higher concentration of smaller cations compared to the reported
324 magnetoplumbite-type titanates. The prominent feature of the YIHA minerals studied here,
325 which distinguishes them from the majority of described mantle-derived magnetoplumbite-group
326 species, is a high content of Al_2O_3 (5.74-7.69 wt%); yimengite with similar high concentration of
327 Al was documented only as inclusions in diamond from the Sese kimberlite, Zimbabwe
328 (Bulanova et al. 2004). The only magnetoplumbite-group mineral reported so far in the
329 lithospheric mantle of the Siberian craton is the chromium-rich (48.8 wt% Cr_2O_3) exceptionally
330 high-Sr (4.00 wt% SrO) yimengite inclusion in diamond from the Sputnik kimberlite pipe, Mirny
331 field (Sobolev et al. 1997).

332 Ba- and K-rich CGM inclusions in enstatite chemically resemble **lindsleyite-mathiasite**
333 minerals (**LIMA**, solid solution of Zr-enriched Ba- and K-characteristic CGM, respectively),
334 reported in metasomatized peridotite xenoliths from South African and Chinese kimberlites (e.g.
335 Jones et al. 1982; Haggerty et al. 1983; Haggerty 1991; Lu and Zhou 1994; Zhou et al. 1996;
336 Konzett et al. 2000, 2013; Griffin et al. 2014; Giuliani et al. 2014, 2018). However, CGM
337 inclusions in enstatite studied here are higher in TiO_2 and Al_2O_3 than described LIMA minerals,

338 with the latter containing 52-62 wt% TiO₂ and < 1 wt% Al₂O₃. In addition, the contents of ZrO₂
339 below 1 wt% in many studied CGM inclusions in orthopyroxene are uncommon to most mantle-
340 derived CGM, since inclusions in Cr-pyrope generally contain 1-5 wt% ZrO₂ worldwide, while
341 LIMA minerals from South African kimberlites show even higher ZrO₂ at 2-7 wt% (see
342 compilations in Haggerty et al. 1991; Rezvukhin et al. 2018). K-dominant composition of the
343 pyrope-hosted CGM is also unique, since K-characteristic CGM has not been reported
344 previously as an inclusion in mantle garnet. The rarity of such kind of chemistry may be related
345 to the distinct conditions of CGM crystallization. Comparatively high K concentrations in CGM
346 as inclusions in pyrope have been perhaps inherited from the K-Ba-rich titanate mineralization
347 occurring in the orthopyroxenite part of the sample, to which pyrope with CGM inclusions is
348 spatially adjoint.

349 Within the group, CGM have been classified earlier on the basis of a predominant large
350 cation in the A site. According to the currently used nomenclature (Orlandi et al. 1997),
351 prevailing cations in four types of structural sites are invoked to constrain the mineral species. In
352 this respect, the studied orthopyroxenite hosts a diversity of mineral species of the crichtonite
353 group, which are lindsleyite, mathiasite, loweringite, as well as their Zr-poor Fe-dominant in the
354 B site analogues (not approved yet as individual mineral species). Of particular interest is also an
355 uncommon Sr-characteristic mantle-derived variety (Table 3, №13) reported previously mostly
356 as inclusions in pyrope xenocrysts (Wang et al. 1999; Zibera et al. 2013; Rezvukhin et al. 2018)
357 and as rare findings associated with LIMA in metasomatized peridotite xenoliths from South
358 African kimberlites (e.g. Haggerty et al. 1983).

359

360 ***P-T* constraints**

361 Estimation of the orthopyroxenite *P-T* equilibration parameters has been performed
362 following the recommendations in (Nimis and Grütter 2010). We have applied the compositions
363 of enstatite (Opx1), enstatite-hosted diopside (Cpx1), and vein-like pyrope (Grt1) listed in Table

364 I to proceed with calculations. Orthopyroxene-garnet barometer of Nickel and Green (1985)
365 yielded pressure value of 35 kbar, whilst two-pyroxene thermometer of Taylor (1998) gave
366 temperature estimate of ~810 °C. Following Nimis and Grutter (2010), this combination of
367 thermobarometric equations is assumed to provide the most reliable *P-T* conditions for samples
368 bearing garnet and two pyroxenes, although the correctness of estimates is defined by the
369 precision of EMP analyses and accuracy of ferric iron calculations. We have also used Ca-in-
370 orthopyroxene thermometer of Brey and Köhler (1990) and orthopyroxene-garnet thermometer
371 of Nimis and Grutter (2010), which yielded similar temperature values of ~810 and ~780 °C,
372 respectively. Single-pyroxene thermobarometry of Nimis and Taylor (2000) provided coinciding
373 estimates of 33 kbar and ~800 °C. The obtained *P-T* estimates clearly support the well-
374 equilibrated character of the silicate assemblage yielded by the intergranular partitioning of
375 major elements, as well as show all subsequent impacts to have little or negligible effect on the
376 utilized major-elements relationships.

377

378 **On the origin of yimengite-hawthorneite and crichtonite-group minerals in the** 379 **orthopyroxenite**

380 The uniform distribution and shape preferred orientation of thin Cr-spinel and
381 clinopyroxene lamellae (Type 1 inclusions) in the volume of the host enstatite suggests these
382 minerals to have been exsolved from the primary high-*T* Ca-Al-Cr-enriched orthopyroxene
383 precursor (Opx2 in Table 1). Oriented lamellae of Cr-spinel and clinopyroxene interpreted to be
384 of exsolution origin from the host orthopyroxene have been reported previously (e.g. Spengler et
385 al. 2012). As for vein-like pyrope, diopside, and Cr-spinel interstitial to enstatite, they appear to
386 have been formed via the same genetic scenario as well (i.e. being the products of the subsolidus
387 exsolution from the orthopyroxene host with the assumed composition Opx3 in Table 1). The
388 possibility of the isochemical exsolution through the formation of garnet “necklaces” and
389 diopside grains around orthopyroxene has been thoroughly reviewed by Gibson (2017).

390 By contrast, the origin of YIHA and CGM by exsolution from orthopyroxene is
391 improbable, since orthopyroxene is an unlikely candidate to store such amounts of elements
392 incompatible to mantle silicates (like LILE, HFSE, REE), which are necessary for the formation
393 of the studied exotic oxide assemblages. For instance, the chemistry of precursor orthopyroxene
394 would demand for LILE concentrations much higher than is known for worldwide natural
395 occurrences. In order to exsolve 0.1 vol% of YIHA incorporating 3.37 wt% K₂O from
396 orthopyroxene, the latter would need to contain no less than 40 ppm of potassium. Producing the
397 same volume of YIHA with 7.8 wt% of BaO would require about 90 ppm of barium. These
398 estimates are at odds with respect to the data available on mantle-derived orthopyroxene, with
399 the latter typically containing no more than a few ppm of Ba and K (Grégoire et al. 2003; Scott
400 et al. 2016).

401 Further arguments could be provided in favor of the non-cognate origin of the studied
402 titanates and exsolved minerals. Inclusions of Cr-spinel and clinopyroxene in enstatite
403 demonstrate two contrasting types of morphology, with Type 1 varieties being regularly spaced
404 and preferentially oriented and Type 2 species showing drastically different morphological
405 features and uneven distribution within the host enstatite. Similar to Type 2 Cr-spinel and
406 clinopyroxene, the distribution of titanate inclusions in enstatite is non-uniform. In many
407 instances the clear evidence has been found that the titanate distribution is controlled by zones of
408 weakness (like fractures) within the host enstatite crystals (Figs. 2c, 2d). Type 2 Cr-spinel and
409 clinopyroxene typically occur in polymineralic assemblages with YIHA and CGM, where all
410 constituent minerals demonstrate anhedral morphology. As opposed to Type 1 Cr-spinel lamellae
411 characterized in the rock by a fairly homogeneous composition, Type 2 Cr-spinel inclusions have
412 wider ranges of major-element abundances with apparent enrichment in Fe and Ti. All the
413 observations outlined above argue against the single-stage formation of mineral inclusions within
414 enstatite.

415 Hence, to our mind, after the cooling and exsolution processes had taken place, the
416 xenolith experienced the influence of a mobile incompatible element-charged metasomatic agent,
417 which caused the superimposed precipitation of the Ti-rich oxide mineralization. The
418 metasomatizing liquid percolated basically through interstitial space, but also affected
419 orthopyroxene grains, impregnating by small-volume portions in directions corresponding to the
420 most vulnerable zones of enstatite crystals (such as fractures, cleavage planes, and inclusion-rich
421 domains). Textural evidence suggest that the metasomatic front has induced the following
422 essential consequences: 1) the local treatment and recrystallization of some of the Cr-spinel and
423 clinopyroxene lamellae resulted in their coarsening and morphological transformation to
424 irregularly-shaped (i.e. coalescence of fine Type 1 lamellae into bigger Type 2 grains), 2) the
425 nucleation and growth of YIHA and CGM along with other Ti-bearing oxides (rutile, ilmenite,
426 and recrystallized Ti-enriched spinel) and pentlandite within the host enstatite, and 3) the
427 formation of interstitial Ti-oxide clusters. Phlogopite and amphibole, which are abundant in
428 intergranular space of the orthopyroxenite, may have been coeval with the Ti-metasomatism in
429 question. However, these do not occur together with YIHA and CGM within enstatite and
430 therefore are likely related to kimberlite melt which subsequently infiltrated the sample during
431 the Udachnaya magma eruption (e.g. Sharygin et al. 2012; Golovin et al. 2018).

432 The characteristic feature of mantle-derived YIHA and CGM is the enrichment in Cr and
433 Mg (Nixon and Condliffe 1989; Haggerty 1991; Rezvukhin et al. 2018). In other reported
434 occurrences the exotic titanates often showed close spatial relation to Cr-spinel, occurring as
435 rims on, or intergrowths with, magnesian chromite, denoting the YIHA and CGM to be the
436 alteration products of the latter (Jones et al. 1982; Dong et al. 1984; Haggerty et al. 1989; Nixon
437 and Condliffe 1989; Haggerty 1991; Bulanova et al. 2004). From the crystal structure point of
438 view, magnetoplumbite-group minerals are partly composed of spinel-type structural slabs; thus,
439 their pronounced spatial and genetic relationship to spinel in natural associations is not
440 surprising. In case of hawthorneite, it has been shown that Cr and Mg in spinel are replaced by

441 Ti and Ba which results in the formation of BaTiO₃ hexagonal segments in the spinel structure
442 (Grey et al. 1987; Haggerty et al. 1989). Based on the envisaged textural relationships, it seems
443 that at least a part of YIHA and CGM inclusions in enstatite crystallized on Type 1 Cr-spinel
444 lamellae, with the latter serving as substrates for the titanate nucleation. A strict matching
445 between the orientation of titanate inclusions and Type 1 Cr-spinel (and clinopyroxene) lamellae
446 in each enstatite grain (Fig. 2) is the evidence in favor of the proposed genetic mechanism. Given
447 the small size of Cr-spinel lamellae, most of these original seeds have been probably fully
448 consumed during the reaction.

449 The important genetic issue is the origin of inhomogeneous CGM-bearing oxide
450 intergrowths which are scattered in intergranular space between enstatite crystals. As is evident
451 from the EMP elemental mapping (Fig. 5), such blebs show dramatic small-scale variations in
452 major and trace element chemistry, even within individual mineral areas. The interpretation of
453 prominent textural and compositional heterogeneity within interstitial oxide intergrowths may be
454 two-fold. Since the equilibration process has not been finished, the observed inhomogeneity
455 either constrains the genesis of interstitial CGM and other associated Ti-bearing oxide minerals
456 to relatively short (<< several Ma) time spans before the Udachnaya magma eruption or,
457 alternatively, reflects the overprinting impact of an additional fluid/melt, which percolated along
458 interstitial space of the rock and altered the primary (pre-existing) oxide segregation.
459 Considering the occurrence of melt inclusions in enstatite that are composed of typical
460 kimberlitic minerals (see section “Sample petrography”) and time constraints, the feasible agent
461 for the possible alteration of the oxide aggregates may have been a kimberlite melt.

462

463

Implications

464 The present study reports the first finding of yimengite-hawthorneite solid solution series
465 and crichtonite-group minerals as inclusions in orthopyroxene from a mantle xenolith and
466 regards these minerals to have more widespread occurrences than it has been known so far. The

467 obtained results are consistent with the previous observations that metasomatic processing of
468 mantle rocks may find ubiquitous manifestations on an inclusion and/or interstice scale, thus
469 even modal metasomatism can be subtle and stealthy. Nevertheless, these micro-scale
470 occurrences might offer important petrological implications to the migration of highly
471 fractionated LILE-transporting melts and fluids in the SCLM, as well as to the clues for the
472 mobility of carried incompatible elements within different media. YIHA and LIMA minerals are
473 only minor constituents of peridotite xenoliths sampled by South African and Chinese
474 kimberlites, but clearly reflect the effect of deep-sourced Ba-K-rich fluids that operated in the
475 SCLM beneath the Kaapvaal and North China cratons. In respect to the South African
476 occurrences, LIMA phases mark the most advanced stage of the progressive metasomatism from
477 garnet-phlogopite peridotites (GPP) through phlogopite peridotites (PP) to phlogopite-K-
478 richterite peridotites (PKP), being frequently associated with the latter (Erlank et al. 1987).
479 Titanate inclusion studies showed the significance of agents rich in Ba, K, Sr, Zr, and REE in the
480 formation of mantle minerals such as pyrope (Wang et al. 1999, 2000; Rezvukhin et al. 2018)
481 and diamond (Sobolev et al. 1997; Leost et al. 2003; Bulanova et al. 2004). Inclusions of YIHA
482 and CGM in orthopyroxene studied here are presumably epigenetic referring to the primary
483 orthopyroxenite and result from the superimposed mantle process. They are, however,
484 illustrative of the metasomatic processing of rock other than mantle-dominant peridotites,
485 indicating such type of metasomatism to influence not only peridotitic rock types but also those
486 of websterite-pyroxenite family.

487 Intergranular CGM-bearing oxide intergrowths such as those reported here and elsewhere
488 (Giuliani et al. 2018) contribute insights into the timing of their formation and/or modification.
489 Jones et al. (1989) established the links between kimberlite magmatism and exotic titanates of
490 the crichtonite group, and noted titanate chemistries as resembling enriched kimberlite. In the
491 proposed scenario (see Jones et al. 1982; Haggerty 1988, 1989; Jones 1989), complex titanates
492 may originate from residual liquids derived from magma trapped at depth, while titanate

493 minerals in metasomatized mantle sections may in turn represent a viable source of incompatible
494 elements for the generation of mantle melts. It is worth noting that earlier works on the SCLM
495 beneath the Daldyn field linked the episode of deep-seated metasomatism with incipient
496 kimberlite magmatism (Boyd et al. 1997; Shimizu et al. 1997; Solov'eva et al. 2012; Agashev et
497 al. 2013; Doucet et al. 2013; Ziberna et al. 2013; Howarth et al. 2014). By contrast, Giuliani et
498 al. (2014) and Griffin et al. (2014) attributed the origin of CGM-bearing metasomatic
499 assemblages from the Bultfontein and Jagersfontein mines, respectively, to the Karoo flood
500 basalt magmatism (174-185 Ma), which occurred long before the eruption of the kimberlite
501 magmas of the Kimberley cluster (80-90 Ma). By studying isotopic and elemental heterogeneity
502 between coeval CGM, Giuliani et al. (2018) further argued that multiple metasomatic fluids
503 affected the peridotitic substrates at broadly the same time, and these fluids have been unrelated
504 with the kimberlite magmatism. Taking into account the recently discovered potential of exotic
505 titanates to yield isotopic age datings (Bulanova et al. 2004; Giuliani et al. 2014, 2018; Griffin et
506 al. 2014), one may expect the data concerning the age constraints of titanate-producing
507 metasomatism to be expanded in nearest future, which will better clarify some aspects of YIHA
508 and CGM genesis, especially in case of inhomogeneous occurrences.

509 *P-T* equilibration values calculated for the orthopyroxenite ($T = \sim 800$ °C, $P = 35$ kbar) are
510 generally akin to those estimated for pyrope crystals with CGM inclusions from the Udachnaya
511 kimberlite pipe (850 °C, 37 kbar; Alifirova et al. 2012), Zagadochnaya pipe, Daldyn field (~ 830
512 °C, 33 kbar; Ziberna et al. 2013) Obnazhennaya pipe, Kuoyka field (830 °C, 28 and 34 kbar;
513 Alifirova et al. 2012), Internatsionalnaya pipe, Mirny field (720-820 °C, ~ 34 -42 kbar; Rezvukhin
514 et al. 2018), and lamprophyres of the Aldan shield (~ 650 -750 °C; ~ 25 -35 kbar; Nikolenko et al.
515 2017; Rezvukhin et al. in preparation). This evidence shows that the reworking of mantle
516 lithologies within the Siberian craton attended by the formation of complex LILE-bearing oxides
517 was mostly pronounced on the depth range ~ 80 -120 km. The estimated depth span significantly
518 overlaps with that for other cratonic lithologies worldwide, where mantle-derived YIHA- and

519 CGM-bearing associations have been found, e.g. metasomatized peridotite xenoliths sampled by
520 South African kimberlites (Haggerty 1983, 1988; Waters and Erlank 1988; Konzett et al. 2000,
521 2013; Giuliani et al. 2014). *P-T* constraints for YIHA and CGM in mantle sections together with
522 the absence of data on YIHA and CGM occurrences in high-*T* sheared peridotites indicate that
523 such metasomatism tended to be pervasive among relatively low-*T* coarse-grained mantle
524 lithologies rather than within deeper-seated high-*T* high-*P* deformed ones.

525

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798 **FIGURE CAPTIONS**

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800 Figure 1. A polished thin section from the xenolith UV-13-233 consisting of the orthopyroxenite
801 part and adjacent pyrope-rich intermediate domain.

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803 Figure 2. BSE images showing overall textures of the orthopyroxenite. Type 1 Cr-spinel and
804 clinopyroxene inclusions – preferentially oriented thin (0.1-5 μm) exsolution lamellae; Type 2
805 inclusions – irregularly shaped anhedral grains (see text). Note that inclusions of YIHA and
806 CGM in all instances follow the general orientation of Type 1 lamellae in orthopyroxene. YIHA
807 – yimengite-hawthorneite; CGM – crichtonite-group mineral; Spl – spinel; Rt – rutile, Ilm –
808 ilmenite; Opx – orthopyroxene; Cpx – clinopyroxene, Phl – phlogopite.

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810 Figure 3. BSE images showing inclusions of YIHA (a-e) and CGM (f-i) in orthopyroxene. YIHA
811 – yimengite-hawthorneite; CGM – crichtonite-group mineral; Spl – spinel; Rt – rutile; Ilm –
812 ilmenite; Opx – orthopyroxene; Cpx – clinopyroxene (Type 2); Pn – pentlandite.

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814 Figure 4. Transmitted-light images showing mineral relationships and occurrences of crichtonite-
815 group minerals in silicates. CGM – crichtonite-group mineral; Spl – spinel; Rt – rutile; Opx –
816 orthopyroxene; Grt – garnet.

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818 Figure 5. X-ray maps of elemental abundances in the representative composite oxide intergrowth
819 located in intergranular space of the orthopyroxenite. Scale bar 50 μm . CGM – crichtonite-group
820 mineral.

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822 Figure 6. A-site occupancy of the studied yimengite-hawthorneite (a) and crichtonite-group
823 minerals (b) showed within Ba – K – Ca+Sr+Na+LREE ternary space in comparison with

824 literature data. 1 – inclusions of yimengite-hawthorneite in orthopyroxene (this study); 2 –
825 mantle-derived magnetoplumbite-group minerals reported in metasomatized xenoliths and as
826 inclusions in diamonds worldwide (Dong et al. 1984; Haggerty et al. 1989; Nixon and Condliffe
827 1989; Zhao 1991; Lu and Chou 1994; Zhou et al. 1996; Sobolev et al. 1997; Bulanova et al.
828 2004; Lu et al. 2007); 3 – haggertyite from the Prairie Creek lamproite, USA (Grey et al. 1998;
829 Velde 2000); 4 – inclusions of crichtonite-group minerals in orthopyroxene (this study); 5 –
830 crichtonite-group minerals in interstitial oxide intergrowths (this study); 6 – inclusions of
831 crichtonite-group minerals in pyrope (this study). Compositional fields for “Inclusions in
832 pyropes” (red) and “LIMA (South Africa)” (green) are after (Rezvukhin et al. 2018) and
833 references therein.

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835 Figure 7. Major-element compositional variations in Ti-bearing oxide minerals. Type 1 Spl –
836 average composition of Type 1 spinel lamellae in the orthopyroxenite (Spl in Table 4). YIHA –
837 yimengite-hawthorneite; CGM – crichtonite-group mineral; Spl – spinel; Rt – rutile; Ilm –
838 ilmenite.

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850 **Table 1.** Compositions (wt%) of silicate minerals in the xenolith

Mineral	Opx1	Opx2	Opx3	Cpx1	Cpx2	Cpx3	Grt1	Grt2
Analysis	WDS	–	–	EDS	WDS	WDS	WDS	WDS
N of analyses	9	–	–	28	22	10	10	1
SiO ₂	57.13(21)	56.80	56.50	54.50(33)	54.73(22)	54.61(18)	41.35(16)	41.75
TiO ₂	0.08(2)	0.09	0.09	0.26(5)	0.22(3)	0.24(3)	0.23(6)	0.22
Al ₂ O ₃	0.80(2)	0.90	1.14	3.06(22)	2.81(28)	2.83(10)	18.35(41)	20.51
Cr ₂ O ₃	0.33(2)	0.59	0.80	2.43(14)	2.27(9)	2.15(5)	6.12(38)	3.26
FeO*	5.14(15)	5.17	5.21	2.23(21)	2.15(22)	1.96(6)	8.91(30)	10.62
MnO	0.10(1)	0.10	0.10	0.03(5)	0.06(1)	0.06(1)	0.45(2)	0.34
MgO	35.83(22)	35.50	35.00	15.17(49)	14.80(26)	14.96(12)	18.00(31)	18.19
CaO	0.26(1)	0.48	0.77	19.39(48)	19.69(21)	19.93(11)	6.25(23)	5.17
Na ₂ O	0.06(3)	0.10	0.13	2.68(15)	3.00(12)	2.65(24)	0.05(1)	0.05
K ₂ O	bdl	0.00	0.00	bdl	0.02(2)	0.01(1)	bdl	bdl
Total	99.73	99.73	99.74	99.75	99.75	99.40	99.71	100.11
Mg#	92.6	92.4	92.3	92.4	92.5	93.2	78.3	75.3

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852 Notes: Opx1 – enstatite in the orthopyroxenite; Opx2 – reconstructed composition of pre-exsolved orthopyroxene
 853 assuming the exsolution origin of Cr-spinel and clinopyroxene lamellae; Opx3 – reconstructed composition of pre-
 854 exsolved orthopyroxene assuming the exsolution of Cr-spinel and clinopyroxene lamellae, *as well as* intergranular
 855 pyrope, diopside, and Cr-spinel; Cpx1 – thin exsolution lamellae in enstatite (Type 1 inclusions); Cpx2 – irregular in
 856 shape grains in enstatite (Type 2 inclusion); Cpx3 – interstitial to enstatite grains in the orthopyroxenite; Grt1 –
 857 vein-like (necklace) pyrope in the orthopyroxenite; Grt2 – pyrope with inclusions of crichtonite-group mineral
 858 adjacent to the orthopyroxenite.

859 Opx – orthopyroxene; Cpx – clinopyroxene; Grt – garnet.

860 Numbers in parentheses are one standard deviation in terms of the last significant digits.

861 bdl – below detection limit.

862 *Total iron is FeO.

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Table 2. Representative EMP analyses of yimengite-hawthorneite inclusions in enstatite

Grain №	2	18	19	20	21	31	39	53	55	63
SiO ₂	0.22	0.23	0.21	0.20	0.18	0.20	0.19	0.19	0.19	0.33
TiO ₂	23.61	27.08	27.09	25.24	25.30	23.17	25.03	25.65	28.08	24.69
Cr ₂ O ₃	34.11	32.16	32.53	33.38	34.39	34.59	32.70	32.90	31.08	32.97
Al ₂ O ₃	7.69	6.23	6.21	5.81	6.04	6.70	6.77	6.36	7.50	5.74
V ₂ O ₃	0.31	0.42	0.42	0.45	0.44	0.40	0.47	0.45	0.36	0.47
FeO*	17.45	18.62	18.77	18.54	17.37	18.46	17.93	18.17	17.10	18.15
MgO	6.45	5.57	5.52	5.36	5.85	6.01	5.70	5.57	6.14	5.71
MnO	0.17	0.14	0.13	0.14	0.15	0.18	0.14	0.15	0.16	0.12
NiO	0.14	0.17	0.19	0.13	0.14	0.17	0.17	0.14	0.15	0.14
BaO	6.58	4.91	4.67	7.01	6.99	6.97	7.20	5.85	4.30	7.80
K ₂ O	2.30	3.17	3.18	2.45	2.12	2.13	2.48	2.83	3.37	2.25
CaO	0.09	0.21	0.27	0.18	0.06	0.13	0.11	0.10	0.45	0.07
Na ₂ O	0.08	0.13	0.10	0.09	0.07	0.08	0.06	0.05	0.20	0.07
Total	99.20	99.04	99.29	98.98	99.10	99.19	98.95	98.41	99.08	98.51
Si	0.035	0.037	0.033	0.032	0.029	0.032	0.031	0.031	0.030	0.054
Ti	2.834	3.245	3.235	3.081	3.061	2.816	3.040	3.113	3.306	3.038
Cr	4.303	4.050	4.083	4.283	4.373	4.418	4.174	4.197	3.846	4.264
Al	1.446	1.170	1.162	1.111	1.145	1.276	1.288	1.209	1.384	1.107
V	0.040	0.054	0.053	0.059	0.057	0.052	0.061	0.058	0.045	0.062
Fe ²⁺	2.329	2.480	2.492	2.516	2.337	2.494	2.421	2.452	2.238	2.483
Mg	1.534	1.322	1.306	1.297	1.403	1.447	1.372	1.340	1.432	1.392
Mn	0.023	0.019	0.017	0.019	0.020	0.025	0.019	0.020	0.021	0.017
Ni	0.018	0.022	0.024	0.017	0.018	0.022	0.022	0.018	0.019	0.018
Ba	0.412	0.307	0.291	0.446	0.441	0.441	0.456	0.370	0.264	0.500
K	0.468	0.644	0.644	0.507	0.435	0.439	0.511	0.582	0.673	0.470
Ca	0.015	0.036	0.046	0.031	0.010	0.023	0.019	0.017	0.075	0.012
Na	0.025	0.040	0.031	0.028	0.022	0.025	0.019	0.016	0.061	0.022
Total	13.482	13.426	13.417	13.427	13.351	13.510	13.433	13.423	13.394	13.439
Total A	0.920	1.027	1.012	1.012	0.908	0.928	1.005	0.985	1.073	1.004

877 Notes: The oxide values are wt% and the element values are atoms per formula unit (a.p.f.u.) calculated on the basis
 878 of 19 oxygens.
 879 *Total iron is FeO.

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888 **Table 3.** Representative EMP analyses of crichtonite-group minerals

Mineral	CGM1	CGM1	CGM1	CGM1	CGM1	CGM2	CGM3	CGM3	CGM3	CGM3
Grain №	4	16	25	41	56	3	8	11	12	13
SiO ₂	0.06	0.03	0.03	0.04	0.05	0.15	0.01	0.04	bdl	0.03
TiO ₂	64.46	64.48	65.19	66.71	67.05	63.25	58.80	64.66	67.87	55.14
Cr ₂ O ₃	12.95	13.86	13.34	12.81	13.59	9.62	16.69	13.15	11.95	20.40
Al ₂ O ₃	1.40	1.30	1.48	1.40	1.44	1.44	1.97	1.29	0.21	1.60
V ₂ O ₃	0.44	0.42	0.40	0.37	0.35	0.45	0.59	0.50	0.23	0.46
FeO*	10.40	9.24	9.12	9.05	8.46	11.33	9.85	9.98	9.62	8.82
MgO	3.11	3.48	3.55	3.66	3.78	3.33	2.90	3.25	4.34	3.18
MnO	0.09	0.12	0.10	0.13	0.13	0.09	0.09	0.06	0.18	0.12
NiO	bdl	0.04	0.03	0.05	0.05	0.05	0.02	0.05	0.02	0.01
ZrO ₂	1.72	0.11	0.17	0.24	0.08	4.64	4.21	1.13	0.57	2.80
Nb ₂ O ₅	bdl	bdl	0.02	0.01	bdl	bdl	bdl	0.02	0.43	bdl
HfO ₂	0.08	bdl	0.04	0.05	bdl	0.04	0.04	bdl	0.01	0.07
Y ₂ O ₃	0.03	0.03	0.01	bdl	bdl	0.02	bdl	0.03	0.02	bdl
BaO	2.56	4.28	4.12	3.03	2.33	1.90	0.72	2.93	0.75	1.60
SrO	0.07	0.09	bdl	0.06	0.01	0.04	0.20	0.06	1.16	1.35
CaO	0.86	0.81	0.85	1.08	1.02	1.01	1.61	0.96	1.67	0.40
Na ₂ O	0.09	0.08	0.10	0.08	0.10	bdl	0.19	0.11	0.42	bdl
K ₂ O	1.04	0.76	0.77	0.82	1.05	1.38	0.39	0.79	0.23	0.10
La ₂ O ₃	0.07	0.01	bdl	0.04	bdl	0.03	0.40	0.13	0.20	1.29
Ce ₂ O ₃	0.07	bdl	bdl	0.03	0.05	0.09	0.48	bdl	0.27	0.95
Total	99.50	99.14	99.32	99.66	99.54	98.86	99.16	99.14	100.15	98.32
Si	0.017	0.009	0.009	0.011	0.014	0.043	0.003	0.011	0.000	0.009
Ti	13.811	13.894	13.967	14.123	14.113	13.710	12.705	13.880	14.240	12.244
Cr	2.916	3.139	3.004	2.850	3.007	2.192	3.790	2.967	2.635	4.761
Al	0.470	0.439	0.497	0.464	0.475	0.489	0.667	0.434	0.069	0.557
V	0.100	0.096	0.091	0.083	0.079	0.104	0.136	0.114	0.051	0.109
Fe ²⁺	2.477	2.214	2.172	2.130	1.980	2.730	2.366	2.382	2.244	2.177
Mg	1.320	1.486	1.507	1.535	1.577	1.430	1.242	1.383	1.804	1.399
Mn	0.022	0.029	0.024	0.031	0.031	0.022	0.022	0.015	0.043	0.030
Ni	0.000	0.009	0.007	0.011	0.011	0.012	0.005	0.011	0.004	0.002
Zr	0.239	0.015	0.024	0.033	0.011	0.652	0.590	0.157	0.078	0.403
Nb	0.000	0.000	0.003	0.001	0.000	0.000	0.000	0.003	0.054	0.000
Hf	0.007	0.000	0.003	0.004	0.000	0.003	0.003	0.000	0.001	0.006
Y	0.005	0.005	0.002	0.000	0.000	0.003	0.000	0.005	0.003	0.000
Ba	0.286	0.481	0.460	0.334	0.256	0.215	0.081	0.328	0.082	0.185
Sr	0.012	0.015	0.000	0.010	0.002	0.007	0.033	0.010	0.188	0.231
Ca	0.262	0.249	0.259	0.326	0.306	0.312	0.496	0.294	0.499	0.127
Na	0.050	0.044	0.055	0.044	0.054	0.000	0.106	0.061	0.227	0.000
K	0.378	0.278	0.280	0.294	0.375	0.507	0.143	0.288	0.082	0.038
La	0.007	0.001	0.000	0.004	0.000	0.003	0.042	0.014	0.021	0.140
Ce	0.007	0.000	0.000	0.003	0.005	0.009	0.050	0.000	0.028	0.103
Total	22.386	22.403	22.364	22.291	22.296	22.443	22.480	22.356	22.353	22.521
Total A	1.002	1.068	1.054	1.015	0.998	1.053	0.951	0.995	1.127	0.824

889 Notes: The oxide values are wt% and the element values are atoms per formula unit (a.p.f.u.) calculated on the basis
 890 of 38 oxygens.

891 CGM1 – inclusion in enstatite; CGM2 – inclusion in pyrope; CGM3 – part of an interstitial oxide intergrowth.

892 bdl – below detection limit.

893 *Total iron is FeO.

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897 **Table 4.** Representative analyses (wt%) of spinel, rutile and ilmenite

Mineral	Spl1	Spl2	Spl2	Spl3	Spl4	Spl4	Rt1	Rt2	Rt2	Ilm1	Ilm2
Grain №	—	81	15	48	83	84	22	85	86	66	87
Analysis	EDS	WDS	WDS	WDS	WDS	WDS	WDS	WDS	WDS	WDS	WDS
SiO ₂	0.31(24)	0.04	0.12	0.05	na	na	0.04	0.05	0.04	0.12	0.11
TiO ₂	1.11(14)	1.83	4.27	1.09	1.93	6.31	97.50	90.46	94.15	55.42	55.51
Cr ₂ O ₃	50.26(55)	50.15	49.21	52.16	53.42	47.93	1.71	3.36	2.62	3.93	5.08
Al ₂ O ₃	15.26(53)	11.86	10.36	13.68	8.35	9.05	0.01	bdl	bdl	bdl	bdl
V ₂ O ₃	0.19(5)	0.30	0.50	0.17	0.32	0.53	0.33	0.40	0.20	0.28	0.44
FeO*	20.03(16)	23.60	22.04	19.74	24.52	25.46	0.24	0.23	0.50	24.80	24.71
MgO	12.65(9)	11.16	12.45	11.85	9.85	10.56	0.03	na	0.30	14.83	12.89
NiO	na	0.16	0.32	0.17	0.38	0.28	na	na	na	0.21	na
MnO	0.44(7)	0.20	0.22	0.26	0.30	0.30	na	na	na	0.20	0.79
ZrO ₂	na	na	na	na	na	na	bdl	0.36	0.77	bdl	0.07
Nb ₂ O ₅	na	na	na	na	na	na	bdl	4.26	1.09	0.01	0.40
Total	100.25	99.30	99.49	99.17	99.07	100.42	99.86	99.12	99.67	99.80	100.00

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899 Notes: Spl1 – thin exsolution lamellae in enstatite (Type 1 inclusions, average of 10 analyses); Spl2 – irregular in
 900 shape grain in enstatite (Type 2 inclusions); Spl3 – individual large grain (~ 500 μm) interstitial to enstatite; Spl4 –
 901 part of an interstitial oxide intergrowth, in association with Ti-rich oxides; Rt1, Ilm1 – inclusions in enstatite; Rt2,
 902 Ilm2 – parts of an interstitial oxide intergrowth.

903 Spl – spinel, Rt – rutile, Ilm – ilmenite.

904 Numbers in parentheses are one standard deviation in terms of the last significant digits.

905 na – not analyzed; bdl – below detection limit.

906 *Total iron is FeO.

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