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3   Cr$_2$O$_3$ in Corundum: Ultra-high contents under reducing conditions

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15

16   **Abstract**

17   Xenocrysts and xenoliths in Upper Cretaceous pyroclastics on Mount Carmel (N. Israel)

18   represent a series of similar magma-fluid systems at different stages of their evolution, recording a

19   continuous decrease in oxygen fugacity (fO$_2$) as crystallization proceeded.

20   Corundum coexisting with Fe-Mg-Cr-Al spinels , other Fe-Mg-Al-Na oxides and Fe-Ni alloys

21   in apparent cumulates crystallized at fO$_2$ near the iron-wüstite (IW) buffer (fO$_2$ = IW±1) and is

22   zoned from high-Cr cores to lower-Cr rims, consistent with fractional crystallization trends. The

23   reconstructed parental melts of the cumulates are Al-Cr-Fe-Mg oxides with ca 2 wt% SiO$_2$.

24   Corundum in other possible cumulates that contain Cr-Fe (Fe 45 wt%) alloys has low-Cr cores and

25   still lower-Cr rims. Corundum coexisting with Cr^0 (fO$_2$ = IW-5) in some possible cumulates has low-

26   Cr cores, but high-Cr rims (to >30% Cr$_2$O$_3$). These changes in zoning patterns reflect the strong

27   decrease in the melting point of Cr$_2$O$_3$, relative to Al$_2$O$_3$, with decreasing fO$_2$. EELS analyses show

28   that all Cr in corundum that coexists with Cr^0 is present as Cr^{3+}. This suggests that late in the

29   evolution of these reduced melts, Cr^{2+} has disproportionated via the reaction 3Cr^{2+}(melt) →

30   2Cr^{3+}(Crn) + Cr^0.

31   The most Cr-rich corundum crystallized together with β-alumina phases including

32   NaAl$_{11}$O$_{17}$ (diaoyudaoite) and KAl$_{11}$O$_{17}$ (kahlenbergite) and β"-alumina phases; residual melts

33   crystallized a range of (K,Mg)$_2$(Al,Cr)$_{10}$O$_{17}$ phases with the kahlenbergite structure. The parental

34   melts of these assemblages appear to have been Al-Cr-K-Na-Mg oxides, which may be related to

35   the Al-Cr-Fe-Mg oxide melts mentioned above, through fractional crystallization or liquid

36   immiscibility.

37   These samples are less reduced (fO_2 from IW to IW-5) than the assemblages of the trapped

38   silicate melts in the more abundant xenoliths of corundum aggregates (fO_2 =IW -6 to -10).   They

39   could be considered to represent an earlier stage in the fO_2 evolution of an "ideal" Mt Carmel

40   magmatic system, in which mafic or syenitic magmas were fluxed by mantle-derived CH_4+H_2 fluids.

41   This is a newly recognized step in the evolution of the Mt Carmel assemblages, and helps to

42   understand element partitioning under highly reducing conditions.

43

44   **Introduction**

45   Cr is a common multivalent element, and its oxidation state in minerals potentially carries

46   information on the oxygen fugacity (fO_2) of their crystallization environment (Schreiber and Haskin

47   1976). However, this feature is not generally useful in mantle petrology because the redox

48   reactions that define steps in the valence state of Cr occur at relatively low fO_2 compared to most

49   igneous and metamorphic environments, so that Cr^{3+} is the most common form. The Cr^{3+}-Cr^{2+}

50   transition (as defined by the CrO-Cr_2O_3 buffer reaction) lies at fO_2 just above the Iron- Wüstite

51   (IW) buffer (IW +0.5) (Fig. 1a), and is potentially observable in the most reduced parts of the deep

52   subcontinental lithospheric mantle (SCLM) (e.g. Yaxley et al. 2012). At high temperatures, the

53   reduction of Cr^{2+} to Cr^0 occurs at fO_2 of ca IW -5 (Fig. 1a), conditions that are not common on

54   Earth but must (as will be shown here) occur locally. To illustrate the behavior of Cr under highly

55   reducing conditions, we describe zoning patterns in a series of corundum cumulates, and report

56   the occurrence of corundum (ruby) with >30 wt% Cr_2O_3 and inclusions of Cr^0 and Cr_2N; this

57   assemblage requires fO_2 near IW -5. We also attempt to define the petrological setting of this

58   assemblage within the evolution of a series of magmatic systems, some of which eventually

59   reached even more reduced conditions (Griffin et al. 2018a and references therein).

60

61   **Background**

62   The Cretaceous pyroclastic rocks of Mount Carmel (Northern Israel; Fig. SD-1) erupted

63   from 6-8 volcanic centres over the period 98-85 Ma, and over an area of at least 150 km^2.

64   Xenoliths and xenocrysts enclosed in these tuffs and in secondary alluvial deposits appear to

65   represent different aspects of similar magma-fluid systems at different stages of their evolution.

66   They record a wide range of oxidation states, including some of the most reducing conditions yet

67   reported in terrestrial rocks (Griffin et al. 2018a). As in other xenolith studies, a hypothetical

68   magma/fluid history has been constructed by piecing together information expressed in a suite of

69   xenoliths and xenocrysts. Specifically, it is possible to arrange the samples from Mt. Carmel in a

70   sequence of oxidation states (decreasing fO_2) that appears to record the evolution of magmas

71   fluxed by CH_4+H_2 at high fluid/rock ratios (Fig. 1b; Xiong et al. 2017; Griffin et al. 2018a, 2019a).

72   Grains of vesicular wüstite record fO_2 near the QFM buffer (fO_2 = IW+3 to +4). Large euhedral to

73   subhedral crystals of magnesian calcite have high-Sr cores with $^{87}Sr/^{86}Sr$ = 0.7033, suggesting a

74   magmatic origin, and probably crystallized near the EMOD (enstatite-magnesite-olivine-diamond)

75   buffer (IW +1.5). Spheres of quenched Fe oxide-silicate and Ti oxide-silicate melts, many with

76   cores of native iron (Fe^0), suggest fO_2 near IW.

77   Among the most common xenoliths are aggregates of skeletal/hopper crystals of

78   corundum, which trapped pockets of Ca-Mg-Al-Si-O melts with high contents of Ti, Zr and REE.

79   Petrographic observations show that the earliest phenocrysts in these pockets are Mg-Al-Ti spinel,

80   followed by tistarite (Ti_2O_3) and then carmeltazite ($ZrAl_2Ti^{3+}_4O_{11}$; Griffin et al. 2018b). More

81   evolved melts precipitated REE-rich hibonite ($CaAl_{12}O_{19}$), moissanite (SiC) and Zr-REE phases. The

82   melt pockets also contain a variety of immiscible carbon-rich Fe-Ti-Zr silicide/phosphide melts,

83   which crystallised TiC, SiC, TiB_2 (Griffin et al. 2020a) and silicide phases. Crystals of moissanite (up

84   to 4 mm) contain inclusions of Si^0 melts that crystallized Fe-, Ca- and Al silicides (Huang et al.

85   2020). The crystallization of SiC and the reduction of Ti^{4+} to Ti^{3+} require fO_2 = IW-6 to IW-7 (Fig.

86   1a). The most evolved silicate melts produced coarse-grained hibonite+grossite+spinel aggregates

87   with inclusions of V^0, requiring $fO_2 \leq$ IW-9 (Griffin et al. 2019a). Even lower fO_2 may be implied by

88   the presence of Ti^{2+}-bearing phases such as TiB_2 (Griffin et al. 2020a). The most reduced conditions

89   imply a hydrogen-saturated environment, which has been confirmed by the discovery of VH_2

90   (Bindi et al. 2019) and the presence of abundant H_2 in the hibonite crystals that have inclusions of

91   V^0 (Griffin et al. 2020b).

92   Paragenetic studies (Xiong et al. 2017; Griffin et al. 2018a, 2019a) suggest that these

93   xenocrysts formed at ca 1 GPa, close to the crust-mantle boundary, and crystallized over a T range

94   of approximately 1450°C to 1200°C. Dating of large xenocrystic zircons from the pyroclastic rocks

95   (Griffin et al. 2018b) suggests that the crust was underplated by mafic magmas from ca 285-100

96   Ma and that these magmas differentiated to syenitic (*s.l.*) melts that crystallized large zircons and

97   typical basaltic sapphire, which also is found in the tuffs and alluvial deposits. We have previously

98   suggested that lenses of these syenitic (*s.l.*) residual melts in the underplate were reduced by

99   interaction with mantle-derived CH_4+H_2 fluids (Griffin et al. 2018a). The detailed evolution of

100   these melts will be discussed elsewhere; it appears to have involved multiple episodes of melt

101   immiscibility.

102   The range of fO$_2$ described above, as well as a common mineralogy and mineral chemistry,

103   suggests a common process linking the different occurrences. Most of the work so far has

104   concentrated on the highly reduced corundum aggregates (trademarked by Shefa Yamim as

105   Carmel Sapphire^{TM}) (Griffin et al. 2016; Xiong et al. 2017; Griffin et al. 2018a) and the still more

106   reduced hibonite-grossite-V^0 assemblage (Griffin et al. 2019a).   Here we describe less-reduced

107   samples that illustrate the behaviour of Cr in one or more magmatic systems that were

108   crystallizing abundant corundum as fO$_2$ declined, ending with the appearance of native chromium

109   (Cr^0) at fO$_2$ near IW-5.

110

Geological Setting and Provenance of Samples

112   The material described here is derived from Cretaceous volcanic centers and related alluvial

113   (placer) deposits in the Mt Carmel-Yizre'el Valley area of northern Israel (Fig. 1). This area lies

114   within a complex system of minor rifts and other faults, related to the Africa-Arabia plate

115   boundary that later developed into the Dead Sea Transform, with >100km movement since the

116   initiation of offset in Miocene time. The NW-SE Carmel Fault that bounds Mount Carmel on the

117   east (Fig. 1) is part of the Carmel-Gilboa system, which forms a 10-20 km wide belt of faulting

118   running through the Yisre'el Valley, and may extend across the continental margin (Segev and

119   Rybakov, 2011). The SW side of Mount Carmel is dissected by multiple N-striking vertical faults

120   with offsets up to a few hundred meters. The basement rocks, which are not exposed in this area,

121   are considered to have formed in Pan-African (Cadomian) time (>620 Ma; Stein and Goldstein,

122   1996). The Galilee area represents a zone of thin continental crust, with a Moho depth of 23-32

123   km (Segev and Rybakov, 2011). The geophysical data, and estimates of the Cretaceous geotherm

124   from mantle-derived xenoliths and xenocrysts (Apter, 2014; our unpublished data) suggest a thin

125   (<100 km), hot lithospheric mantle. It is not clear whether this is a remnant of a previously thicker

126   lithosphere that was thinned during rifting and drifting, or has developed later through magmatic

127   processes (Stein and Hofmann, 1992).

128   The Late Cretaceous (98-94 Ma, Turonian-Cenomanian) volcanic activity of northern Israel

129   took place in the Mount Carmel-Umm El Fahm area (Fig. 1), and field relations have been

130   described in detail by Sass (1980). The dominant volcanic rocks are pyroclastics of mafic to

131   ultramafic composition; lava flows played a minor role in this volcanic activity. The volcanoes

132   erupted in a shallow marine environment, in intimate contact with carbonate sediments

133   containing rich assemblages of fossils. Several outcrops of black and variegated pyroclastics in

134   isolated areas west of Kerem Maharal (Fig. 2) overlie the Yagur Formation of Albian (Bein, 1974;

135 Rosenfeld and Raab, 1984) to earliest Cenomanian age (Lewy, 1991) and represent the first

136 volcanic eruptions in the area.

137   The eruptive vents are filled with quite fresh massive "black pyroclastics" (Fig. 2; Sass, 1980).

138 The more strongly layered "variegated pyroclastics" (Fig. 3) occur as packages of various thickness

139 locally interbedded with the carbonates, indicating pulsed explosive eruptions and the

140 construction and levelling of small seamounts (Sass, 1980). Some centers may be monogenetic,

141 but recent detailed examination of good outcrops in the Rakefet Magmatic Complex has identified

142 two, and possibly three, separate vents surrounded by the layered variegated pyroclastics. The

143 eruptions in the area took place mainly between 98 Ma and 95 Ma but continued up to *ca* 85 Ma.

144 Further details of the regional setting, stratigraphy, timing and sources of the volcanic rocks are

145 given by Griffin et al. (2018a). The uplift of Mt Carmel relative to the adjoining valleys and hills

146 began in Pliocene time and is continuing today.

147   The few basalt flows spatially associated with the Cretaceous volcanoes are porphyritic

148 alkali-olivine basalts with OIB-type trace-element signatures (Kaminchik et al., 2014) and their

149 relationship to the explosive magmatism is unclear (Sass, 1980). The ejecta from the explosive

150 volcanoes are dominated by "ash, which is made up of microvesicular glass in various degrees of

151 preservation [and] lapilli and volcanic bombs [of] vitrophyric basalt, rich in vescicles and consisting

152 of black glass (sideromelane), altered olivine phenocrysts and microlites of augite and plagioclase"

153 (Sass, 1980). The chemical composition of the parental magmas is difficult to define, because the

154 glassy lapilli typically show evidence of physical mixing between compositionally distinct melts

155 (SiO_2 53.5 *vs* 40.2 wt%), and complex textures of lapilli within lapilli. Furthermore, the glasses may

156 have been modified in the marine environment, as they typically contain very little Na or K. Lapilli

157 of microcrystalline basalts analysed by wide-area SEM-EDS (n=50) have a mean composition

158 corresponding to tholeiitic picrite or meimechite (SiO_2 43.5 %, MgO 14.8%; Griffin et al., 2016),

159 but low values of Na and K suggest that these compositions are also modified ().

160   The gem placers of the Kishon River are concentrated in the Mid-Reach zone (Fig. SD-1)

161 where the valley narrows to a gorge next to the escarpment along the northeast side of Mt

162 Carmel, and entrains coarser material coming down from Mt Carmel in alluvial fans. The

163 combination of increased flow rates and a larger coarse fraction has provided the conditions

164 necessary for development of transient placers in the confined channel. The placers sampled in

165 this work do not come from the current bed of the Kishon River; they are paleo-placers developed

166 at the base of Plio-Pleistocene terraces that now lie ca 10 meters above the current drainage. The

167 placers occur in unlithified and uncemented coarse gravels that directly overlie bedrock and are

168 overlain in turn by 4-10 meters of undisturbed finer-grained sediments. A typical section is shown

169 in Figure SD-2 together with an illustration of the types of material recovered from this 333-tonne

170 bulk sample.

171 During Shefa Yamim's exploration program, most of the known volcanic centers have been

172 sampled to determine their contents of potential gem minerals. The procedures for sampling and

173 processing, which are designed to exclude contamination with synthetic materials, are described

174 in the Appendix. This sampling has demonstrated that the volcanic centers, which lie at altitudes

175 50-350 meters above the Kishon river (Figure SD-1), collectively contain all of the minerals found

176 in the alluvial deposits, in particular moissanite and the type of ruby described in this paper (Table

177 SD-1; Fig. SD-3).

178 Most heavy-mineral concentrates from both the volcanic centers and the placer deposits are

179 dominated by the assemblage of low-chromium garnet, clinopyroxene (Cr-diopside), olivine, and

180 spinel, representing a mantle section of spinel peridotite with significant amounts of garnet±spinel

181 clinopyroxenite. These rock types are also found as small xenoliths in the pyroclastic rocks

182 (Mittlefeldt 1986; Kaminchik et al. 2014; references therein; authors' collections).

183 Some of the gem minerals, including ruby and moissanite, are present in the volcanic centers

184 at very low abundances even in samples of several tonnes, and only the Rakefet body has been

185 well bulk-sampled (>100 tonnes). Therefore the apparent absence of some minerals from some

186 bodies may simply reflect insufficient sampling. However, the results of the exploration campaign

187 confirm that the volcanic centers on Mt Carmel represent the primary sources of the gem material

188 in the alluvial placers.

189 Corundum and moissanite, along with the peridotite-pyroxenite suite of minerals, also are

190 common in surficial sediments and modern streams across the drainage basin of the Kishon River.

191 This distribution reflects a shallow Miocene marine incursion which resulted in locally-preserved

192 carbonate-cemented, quartz-rich beach placers rich in garnet, diopside, spinel and moissanite (Fig.

193 SD-4; Griffin et al., 2019b), which have been recycled back into the Pliocene and Pleistocene-

194 recent drainages. It therefore is difficult to evaluate the possible contribution of the Pliocene-

195 Pleistocene basalts in the Yizre'el Valeey to the gem placers (Fig. SD-1).

196

197

198 **Sample Descriptions and Analytical Methods**

199

200   Because the samples represent several types/stages, we discuss the mineral chemistry for

201   each group together with the petrographic descriptions. The mineral chemistry is presented in

202   Tables 1-4; analytical methods are given in the Appendix.

203

204   **1. Corundum cumulate/quench aggregate (1174-1A; Table 1)**

205

206   This is a single micro-xenolith 1.5 mm across (Fig. 5a,b), recovered from an alluvial bulk

207   sample in the Kishon Mid Reach Zone 1 (Fig. 2). One half consists mainly of elongate prisms of

208   corundum, and the subparallel alignment of the prisms suggests a cumulate texture. Large grains

209   are zoned in Cr_2O_3, with high-Cr cores (*ca* 15 wt% Cr_2O_3) separated by a diffuse boundary from

210   rims that are zoned from 8-10 wt% Cr_2O_3 near the cores to *ca* 6 wt% Cr_2O_3 in small irregular

211   overgrowths. The spaces between corundum prisms are mostly filled by Al-Mg-Fe-Cr spinel. Rare

212   grains of an Fe-Ni alloy with 1-2 wt% Cr occur in the rims of corundum prisms. The other half of

213   the grain has a pronounced barred structure (Fig. 6), with alternating lamellae of spinel and

214   corundum (8-9% Cr_2O_3) compositionally similar to the rims of the large grains in the coarser-

215   grained half. The barred structure is similar to that formed during eutectic crystallisation in some

216   synthetic systems.

217   The interstitial spinel in the coarse-grained portion, and that in the barred intergrowth, are

218   identical in composition. The structural formula (Table 1) suggests that ca 1/3 of the Fe (11-12

219   wt% as FeO) in the spinel is present as Fe^{3+}, substituting for Al and/or Cr. In the barred

220   intergrowth, the spinel and corundum are crosscut by, and intergrown with, abundant laths of an

221   unknown Na-rich phase ($(Na,Fe,Mg)_2(Al,Ti,Cr)_6O_{11}$) with a large deficit in the analytical sum, fewer

222   dark laths of composition $(Fe,Mg)(Al,Cr,Ti,Si)_8O_{13}$, also with a deficit, and small grains of an Fe-Cr-

223   Al spinel ($(Fe,Mg,Ni)(Al,Cr)_2O_4$). Irregular patches of a phase with the composition of K-free

224   nepheline ($NaAlSiO_4$) occur interstitially between spinel and corundum. The Raman spectrum of

225   this phase (Figure SD1) does not correspond to that of the synthetic phase known as "carnegieite"

226   (Bowen 1912) and reported by Richet and Mysen (1999). Tiny grains of an unknown Zr oxide

227   (Zr_2O_3) are common, as are rare grains of an Fe-Ni-Cr alloy and an Fe-Cr alloy.

228   SEM-EDS areal analyses (in which an integrated spectrum is acquired in scanning mode)

229   were done for the central portions of both the barred area and the coarse-grained area, as well as

230   the whole grain (Fig. 5a; Table 1). The coarse-grained area is higher in Al_2O_3 and Cr_2O_3 than the

231   barred area, but the latter is higher is SiO_2, TiO_2, FeO, MgO and Na_2O. This would be consistent

232   with a cumulate-residual melt relationship between the two parts of the grain, as suggested by

233   the petrography. Ni is below detection in the EDS areal analyses; it is concentrated in the rare Fe-

7

234 Ni alloy grains and the Fe-Cr-Al spinel. Na is distributed between nepheline and the

235 $(Na,Fe,Mg)_2(Al,Ti,Cr)_6O_{11}$ phase, while Zr is concentrated in the Zr_2O_3 grains.

236

237 **2. Corundum "cumulates" with metal alloys (1210B-4, 5; 1125-2D; Table 2)**

238

239 Samples 1210B-4 and -5 were recovered from one alluvial bulk sample in the Kishon Mid

240 Reach Zone 1, and 1125-2D from another (Fig. 2). In the first two, the corundum crystals are

241 blocky and euhedral against a matrix of a K-Al oxide (Fig. 7a,b). The corundum crystals appear to

242 be touching, suggesting a cumulate texture. 1210B-4 (Fig. 7a) contains scattered balls of a Cr-Fe-

243 Ga alloy, mainly in outer parts of corundum grains or in the matrix. 1210B-5 (Fig. 7b) contains

244 abundant spheres of Cr metal (Cr^0) with ca 0.1 wt% Si, but no Fe or Ga; smaller spheres occur in

245 corundum cores, and larger ones in the rims. The spherical form of the metallic grains strongly

246 suggests an origin as immiscible melts.

247 Sample 1125-2D (Fig. 7c) has a different structure; similarly-sized laths of corundum and a

248 K-Al oxide are jumbled together, with no obvious foliation; this is especially apparent when

249 comparing the element-distribution maps for Al and K (Fig. 7c). The corundum cores contain 4-5

250 wt% Cr_2O_3, and each has a well-defined rim with a mean 27 wt% Cr_2O_3, grading rapidly to

251 outermost rims with ca 34 wt% Cr_2O_3. Numerous spheres of Cr^0 occur in the corundum rims, and

252 many smaller ones at their contacts with the K-Al oxides; larger spheres in the corundum rims are

253 surrounded by narrow zones depleted in Cr. There are also numerous angular voids between

254 crystals of the K-Al oxide.

255 The corundum grains in 1210B-4 are zoned from 2.5 wt% Cr_2O_3 in the cores, to a mean of

256 1.3 wt% in the rims, but there are local overgrowths containing up to 5 wt% Cr_2O_3. The corundum

257 in 1210B-5 is mostly low in Cr; cores of grains contain 0.2 % Cr_2O_3, and most rims 0.4%, but locally

258 rims contain up to 2.4 wt% Cr_2O_3. In both cases Cr is concentrated in the metallic melts, but these

259 melts appear to have separated from the oxide melt before corundum crystallized in 1210B-5 and

260 later in 1210B-4 and 1125-2D. It is notable that these samples contain no Fe other than that in the

261 alloy grains in 1210-B4. The matrix ranges in composition from $Na(Al,Cr)_{11}O_{17}$ (diaoyudaoite; Shen

262 et al. 1986) in 1210B-4 to $KAl_{11}O_{17}$ (kahlenbergite; Krüger et al. 2019) in 1210B-5 and 1125-2D.

263 Raman spectroscopy (Fig. SD2) confirms the identification of the K-Al oxide in 1210B-5 as

264 kahlenbergite.

265

266 **3. Large hopper crystals of Cr-rich ruby (1174-C; 1175-A; Table 3)**

267

268   These two samples were recovered from separate alluvial bulk samples in the Kishon Mid

269   Reach Zone 1 (Fig. 2). Sample 1174-C is a 1.7-mm grain with a hollow center and raised rims,

270   indicating hopper growth, and it has an intense purple-red colour (Fig. 8a). The surface of the

271   crystal (Fig. 8b, c) is decorated with balls of Cr^0 up to 60 microns across, and very small grains of an

272   Fe-Ni alloy. It is strongly zoned in Cr from central parts with 1-4% Cr_2O_3, rising to mean values of

273   ca 23 wt% Cr_2O_3 toward both the outer rim and the edge of the central cavity. Single EMP spots in

274   these zones contain up to 33% Cr_2O_3, and corundum adjacent to the Cr^0 balls has mean values >31

275   wt% Cr_2O_3. The most Cr-rich portions of the crystal are finely granular in BSE imagery, suggesting

276   an intergrowth of higher- and lower-Cr corundum on the scale of a few microns (Figs 8a,c). TEM

277   images (Fig. 8d) of these zones show an intergrowth of micrograins with *ca* 30% (Cr# = 0.22) and

278   *ca* 58% Cr_2O_3 (Cr# = 0.48) respectively. The Cr^0 sphere shown in the FIB foil is separated from the

279   Cr-rich corundum by a 5-μm zone of a chromium nitride. In other areas the Cr^0 spheres are

280   separated from the corundum by a Mg-Cr-Al spinel.

281   LA-ICPMS analysis (Table 3) shows that the high-Cr areas of grain 1174-C also have more

282   Mg, P, Ti, V, Ga and Zr than the low-Cr portions. However, Ga levels are extremely low in both

283   types, compared to most natural corundum (cf Sutherland et al., 2014). A K-Al-oxide phase with

284   low contents of Cr and a composition corresponding to kahlenbergite occurs as a patchy outer rim

285   and within the central cavity (Fig. 5b,c). EMP analysis and TEM-EDS show that the largest Cr^0 ball

286   is essentially pure Cr (Fig. 5c) with traces of Si, Al and Mn. EELS analysis (Fig. 9) shows that Cr in

287   both the low-Cr and high-Cr parts of the corundum occurs as Cr^{3+}.

288   The Cr-nitride phase has the composition $Cr_{1.8}N$, based on TEM-EDS analysis. EELS analysis

289   (Fig. 9; cf. Daulton and Little 2006) suggests that Cr in the nitride phase has a valence ≤2. Electron

290   diffraction images indicate that the crystal structure of the nitride is similar to that of synthetic

291   Cr_2N (*P*-31m, ordered structure). A natural phase with the composition Cr_2N has been reported

292   previously by Harries and Langenhors (2011) in the chondritic meteorite CM2 Y-793321.

293   Sample 1175A was a 2-mm hopper crystal prior to polishing, and shows irregular zoning in

294   Cr, some related to internal crystal faces (Fig. 10). The original parts of the grain (dark in BSE

295   images) contain <1% Cr_2O_3, while tendrils of higher-Cr corundum extend outward from a euhedral

296   crystal of a K-Al oxide ($KAl_{11}O_{17}$; probably also kahlenbergite) near the middle of the crystal. These

297   tendrils (lighter in BSE images) range from 7.7 - 10.6 wt% Cr_2O_3, with the highest-Cr corundum

298   concentrated around the central K-Al-oxide. The higher-Cr zones include several small grains of an

299   Mg-Al-Cr spinel and one of a Mg-Cr spinel. A single large metallic inclusion (Fig. 10) is divided

300   60:40 between Cr^0 and a nitride phase. SEM-EDS analysis gives the approximate composition

301    $Cr_{1.3}N$, but N is likely to be underestimated relative to the windowless EDS technique used in the

302   TEM-EDS analyses (cf. Table 3).

303
304   **4. Irregularly zoned ruby grains with alloy inclusions (1210A-1,2; 1210B1-3; Table 4)**
305
306   These five xenocrysts are similar in colour to those described in section (3) above, and

307   show irregular zoning visible in BSE images and maps of Cr distribution. In samples 1210A-1,2 and

308   1210B-1 (Fig. 11a, b), mm-scale prisms of low-Cr corundum are roughly aligned, suggesting a

309   cumulate texture. The laths are irregularly overgrown and partially replaced by zoned rims of

310   higher-Cr corundum, associated with abundant spheres and elongated amoeboid grains of Cr

311   metal (Cr^0). In some cases the metal grains are aligned along the contact between the core and

312   rim. Others are interstitial to low-Cr laths that show no overgrowth by Cr-rich corundum. Some

313   grains contain interstitial void spaces. Small interstitial patches of the K-Al-oxide phases seen in

314   other samples are present in the grains shown in Figure 11, and some contain rare grains of spinel

315   with inclusions of Cr^0. Sample 1210-B1 (Table 4; Fig. 11b) contains spheres of a Cr-Fe-Ga alloy

316   similar to that in 1210B-4 (Table 2), many aligned along a single crystal face.

317   Sample 1210B-3 (Fig. 11c) is a skeletal crystal, consisting mainly of low-Cr corundum (<1

318   wt% Cr_2O_3), with the internal channels filled with a K-Mg-Al-oxide phase (($K,Mg)_{2.12}Al_{10.62}O_{17}$;

319   probably β"- alumina). The Cr_2O_3 content of the corundum rises to >7 wt% in the rims adjacent to

320   these channels.

321   The dark-BSE cores of these grains typically contain <3 wt% Cr_2O_3. The inner parts of light-

322   BSE zones, and rims without further overgrowths, have 8-20 wt% Cr_2O_3 while the outer parts near

323   the metallic inclusions may contain 35-40% Cr_2O_3. The metallic spheres are Cr^0 with 0.2-0.9 wt%

324   Si. The highest Si values tend to be found in spheres sited between the cores and rims of the

325   corundum laths, while lower values occur in Cr^0 balls in the highest-Cr outer rims of the corundum.

326   One analysis of a spinel shows 35 wt% Cr_2O_3; the structural formula indicates that ca 16% of the Cr

327   substitutes in the Mg site, suggesting the presence of both Cr^{2+} and Cr^{3+}. The composition of the

328   β−alumina phase varies from grain to grain. The Mg,Cr-rich variety ranges from

329   ($K,Mg)_{1.21}(Al,Cr)_{10.93}O_{17}$ to ($K,Mg)_{2.13}(Al,Cr)_{10.63}O_{17}$, and the K-rich one from $K_{1.36}(Al,Cr)_{10.88}O_{17}$ to

330    $K_{1.09}Al_{10.97}O_{31}$.

331
332   **Discussion**

333   This discussion is based on the working hypothesis outlined above, that the Mt Carmel

334   xenoliths represent snapshots of similar melt-fluid systems, captured at different stages of their

335   evolution by ascending magmas over a period of *ca* 15 million years.

336   1. *Cr-nitrides*

337   The Cr-nitride phases present in samples 1174C and 1175A (Table 3; Figs 8 and 11) are

338   significant in understanding the evolution of the system. In the phase diagram for the Cr-N binary

339   (Fig. 12) $Cr_{2+x}N_{1-x}$ crystallizes together with Cr^0 at a eutectic point (ca 1640 °C), and approaches the

340   Cr_2N stoichiometry on cooling to below 500°C. At higher N/Cr, Cr_2N crystallizes together with

341   nearly stoichiometric CrN at another eutectic near 1640 °C, and thus CrN should not be in

342   equilibrium with Cr^0. It is likely that the presence of abundant C and H in the system would

343   significantly lower the liquidus temperatures of the metallic melts (Griffin et al. 2020b).

344   The EELS spectra of the $Cr_{1.8}N$ phase in sample 1174C (Fig. 9) are most consistent with a

345   valence ≤2 (Dalton and Little 2006). In Cr_2N the nominal valence of Cr would be $Cr^{1.5+}$, but Cr_2N is

346   an interstitial compound, in which the N atoms occupy octahedral holes among the Cr atoms, and

347   neither element actually exists as ions. Several experimental studies suggest that the Cr_2N

348   observed in sample 1174C could be the product of a subsolidus reaction, rather than

349   crystallisation from a melt. For example, Lyutaya and Kulik (1974) demonstrated that the reaction

350   of N with Cr can result in the simultaneous formation of Cr_2N and CrN, but that Cr_2N is more

351   stable. In experiments with the oxidation of Cr-N alloys (Krzanowski and Foley 2014), a layer of

352   Cr_2N typically formed between the Cr and the surficial oxide (Cr_2O_3, analogous to the high-Cr

353   corundum in sample 1174C (Fig. 8d)). We therefore suggest that the Cr_2N in this example formed

354   through the exsolution of N from the crystallizing droplets of Cr melt on the surface of the

355   corundum crystal, and the back-reaction of N with the solidified Cr^0.

356

357   2. *β–alumina*, *β"-alumina and K-Na-Mg-alumina phases*

358   The alumina phases coexisting with Cr-rich corundum ± Cr^0 fall into four groups. One

359   (sample 1210B-4, Table 2) is Na-rich, with the formula $(Na_{0.99}K_{0.03}Ca_{0.02})_{\Sigma\,1.03}(Al_{10.58}Cr_{0.35}Mg_{0.05})_{\Sigma}$

360    $_{11.01}O_{17}$; this corresponds to the synthetic phase Na-β-alumina ($NaAl_{11}O_{17}$) (Beevers and Ross 1937)

361   and the mineral diaoyudaoite (Shen et al. 1986). The analogous K-β-alumina phase is observed in

362   *inter alia* sample 1210B-1 (Table 4), with the composition

363    $(K_{0.95}Na_{0.01}Ca_{0.01})_{\Sigma0.97}(Al_{10.70}Mg_{0.22}Cr_{0.16})_{\Sigma11.08}O_{17}$. These two phases are typically found as the cores

364   of lath-shaped grains. In a third population, which includes some overgrowths on K-rich laths, the

365   ratio (Al+Cr)/(K+Na+Mg) (atomic %) has a narrow range of lower values (5.9-6.4) and slightly

366 higher Mg, corresponding to a formula of $K_{1.4}(Al,Cr)_{9.5}O_{17}$. This is similar to the formula for the

367 synthetic phase β''-alumina, $K_{1.6}Al_{10.7}O_{17}$, and in the binary liquidus plot of the K_2O-Al_2O_3 system

368 (Fig. 13; Kim et al. 2018) the analytical points cluster around the molar composition of β''-alumina.

369 Synthetic β''-alumina is commonly stabilized by the addition of Mg, and like the β form, can have

370 widely variable stoichiometry. A wide range of divalent and even trivalent β''-alumina phases has

371 been synthesised; most are stable over only a narrow T range (Farrington and Dunn 1982;

372 Schaeffer et al. 1990).

373   A fragment of the K-β-alumina phase from sample 1210B-1 (Table 4) was separated and

374 analysed by single-crystal XRD. It proved to be almost pure kahlenbergite, hexagonal $P6_3/mmc$,

375 with a = 5.59765(10) Å, c = 22.7141(4) Å, V = 616.366(18) Å^3, Z =2. A complete data collection of

376 diffraction intensities was performed, and the structure was solved and refined (CIF file deposited

377 as supplementary material). A fragment of the diaoyudaoite from sample 1210B-4 (Table 4) has

378 the hexagonal space group $P6_3/mmc$, cell parameters a = 5.60170(10) Å and c = 22.6604(4) Å, V =

379 615.797(19) Å^3, Z =2. A complete data collection of diffraction intensities was performed, and the

380 structure was solved and refined (CIF file deposited as supplementary material). These are

381 comparable to a = 5.64860(6) and c = 22.8970(3) for the type material from the Hatrurim basin

382 (Israel; Krüger 2019; Krüger et al. 2019), corresponding to synthetic K-β-alumina (Dernier and

383 Remeika 1976), and a = 5.602(1) Å and c = 22.626(5) Å for diaoyudaoite (Shen et al. 1986), also

384 corresponding to synthetic Na-β-alumina (Edström et al. 1991).

385   The type material of kahlenbergite occurs in pyrometamorphic hornfelses,

386 metamorphosed at ca 1200 °C. It contains 17% Fe_2O_3, while the phase analyzed in our samples

387 contains no Fe, but minor amounts of Na, Mg and Cr; these chemical differences probably account

388 for the small differences in unit-cell values between our material and the type specimen.

389 Diaoyudaoite has been found in the heavy-mineral (S.G. > 2.8) fraction that makes up about 1.4

390 wt% of the surface layer of sea-floor muds at a depth of about 1500 m near the island of

391 Diaoyudao, a few kilometers northeast of Taiwan. Diaoyudaoite from the type locality contains

392 inclusions of Cr^0, indicating a strongly reduced environment like the one described in this work.

393   The fourth type of alumina has much higher Mg contents, generally higher Cr and lower Na

394 contents, and (Al+Cr)/(K+Na+Mg) of 2.6-4.7 (mean 3.2), corresponding to a formula of

395 $(K_{0.51}Mg_{0.46}Na_{0.03})_{2.12}(Al_{0.94}Cr_{0.06})_{9.78}O_{17}$. The examples analysed here contain 15-20 mol% MgO

396 (mean molar MgO/K_2O = 1.9) and 4.2 mol% Cr_2O_3.

397   The most reliable available experimental and theoretical data on the K_2O-MgO-Al_2O_3

398 system are summarized by Kim et al. (2018). In the K_2O-Al_2O_3 binary (Fig. 13), the β phase

399   crystallizes via the peritectic reaction Crn+Liq → β-alumina, while the β" phase appears at

400   subsolidus temperatures as a result of reaction between β-alumina and $KAlO_2$. The petrographic

401   relationships between corundum, the β-alumina phases and the K,Mg-alumina phase suggest that

402   the β-alumina (both Na- and K- variants) represents primary igneous phases, crystallizing together

403   with the corundum to produce cumulate-like textures, while the K,Mg-alumina phase represents

404   interstitial melts and/or products of reaction between residual melts and the cumulate phases.

405   This is consistent with the K_2O-MgO-Al_2O_3 liquidus diagram (Fig. 14), in which the K,Mg-alumina

406   phases plot along the β–alumina + spinel + liq cotectic, consistent with them representing MgO-

407   rich liquids in equilibrium with solid β-alumina phases. The reaction point β+Al_2O_3+spinel+melt at

408   1932 °C corresponds to the assemblages observed in samples 1174 and 1175A (Table 3). The

409   range of intermediate compositions may reflect analysis of fine-grained mixtures of these

410   components.

411   We are not aware of any data pertaining to the effect of pressure on the phase diagram in

412   this system. However, crystallization temperatures may have been significantly lowered (to 1400-

413   1500 °C; Griffin et al. 2018a, 2019a) by the reduced volatile components required to produce the

414   very low fO_2.

415

416   3. *Oxygen fugacity of different assemblages; behaviour of Fe, Ni, Ga and Cr*

417   These samples cover a significant range of fO_2; their common feature is the presence of Cr-

418   rich corundum. Sample 1174-1A (section (1) above) differs from the others in that several of the

419   analysed phases contain small amounts of Fe, especially concentrated in the spinel, in which *ca*

420   1/3 of the Fe is present as Fe^{3+}. The distribution of Al/(Al+Cr) between spinel and corundum in

421   sample 1174-1A (Table 1) is consistent with equilibrium at ca 1200°C and fO_2 = IW to IW+4 (Jung et

422   al. 2005; Fig. 1). This distinguishes the sample from the more strongly reduced assemblages

423   observed in the melt pockets of the Carmel Sapphire aggregates from Mt Carmel, in which Fe is

424   found only in alloy phases and Fe-Ti silicides, with estimated fO_2 = IW-6 to -7 (Griffin et al. 2016,

425   2018a). We suggest that the assemblage in sample 1174A-1 probably crystallized at fO_2 somewhat

426   higher than IW, where Fe alloys could coexist with FeO-Fe_2O_3 bearing phases like spinel. The

427   spinel in sample 1175A, in contrast, contains no Fe, and the structural formula

428   (($Mg_{0.85}Cr_{0.15}$)($Cr_{0.43}Al_{1.57}$)O_4) suggests that some of the Cr is divalent, consistent with the

429   coexistence of this spinel with Cr^0.

430   The behaviour of Fe and Ni in these samples is consistent with a progressive lowering of fO_2.

431   These elements are concentrated in both oxide phases and minor Fe-Ni alloys in Sample 1174-1A,

432 and the minor amounts of Fe in the corundum (Table 1) may be present as Fe^{3+}. Small grains of

433 Fe-Ni alloys occur on the surface of grain 1174C (Fig. 8b), but no Fe is present in either the

434 corundum or the Cr^0 on its surface. In samples 1210B-4 (Table 2) and 1210B-1 (Table 4) Fe occurs

435 only as a minor component in Cr-Fe-Ga alloys; in the remainder of the samples the Cr alloys

436 contain trace amounts of Si, but no Fe, Ni or Ga. This suggests that by the point that fO_2 had

437 dropped to near that of the CrO-Cr^0 buffer, most Fe, Ni and Ga had been removed from the

438 system. It is notable that the Ga contents of the corundum varieties described here (< 0.3 ppm;

439 Table 3) are dramatically lower than those of other mantle-derived corundum (typically 50-150

440 ppm Ga_2O_3; Giuliani et al. 2015; Sutherland et al. 2009). This depletion may reflect the

441 sequestration of Ga in the metallic alloys at fO_2 ≤IW.

442   The Electron Energy Loss Spectroscopy (EELS) analyses (Fig. 9) of sample 1174C (section 3,

443 above) indicate that the oxidation state of the Cr varies from Cr^{3+} in the corundum (both low-Cr

444 and high-Cr types) to Cr^{2+} (or possibly Cr^{1+}) in the Cr-nitride and to Cr^0 in the chromium metal. As

445 discussed above, Cr_2N crystallizes together with Cr^0 (containing 3-4 wt% N) at a eutectic at 1640

446 °C, at 1 atm. These temperatures are almost certainly maximum values, with the real

447 temperatures being lowered by the presence of abundant volatiles (CH_4, H_2; Griffin et al. 2019a,

448 2020b; Bindi et al. 2019) in the Mt Carmel system. Pressure effects (from 1 atm to ca 1 GPa) are

449 difficult to quantify, but the melting points of alloys and metals typically increase only by ≤100

450 °C/GPa (e.g. Sinmyo et al., 2019).

451   The fO_2 of the CrO-Cr^0 buffer (Fig. 1a) lies at ca IW-5, less reducing than the conditions

452 inferred from the Ti^{3+}-bearing, but Cr-free, assemblages in the Carmel Sapphire, but more

453 reducing than in the Fe^{3+}-bearing sample 1174A-1. Following the working hypothesis outlined

454 above, the high-Cr rubies described here thus appear to represent an intermediate stage in the

455 crystallization of the Mt Carmel magmas, preceding the onset of immiscibility between silicate

456 melts and Fe-Ti-silicide melts, and the crystallization of the Carmel Sapphire aggregates..

457

458 *4. Evolution of the Crn-Esk system*

459

460   The corundum-eskolaite (Al_2O_3-Cr_2O_3) system at 1 atm in air (Fig. 15) is described by a

461 continuous solid-solution loop, such that a melt with a given Cr# will precipitate a Cr-Al oxide with

462 higher Cr#, and fractional crystallization with decreasing *T* will precipitate corundum with

463 progressively lower Cr#.   The subsolidus system contains a solvus and a spinodal, with critical

464 temperature at 945 °C (Fig. 15), and limited data suggest that these are not pressure-sensitive

465 (Degterov and Pelton 1996). The two populations of Cr-rich corundum identified in the TEM study

466   of sample 1174c (Table 2) do not define an isothermal pair on the solvus curve or the spinodal;

467   their separation could suggest that the crystal may have cooled to these temperatures prior to

468   eruption and quenching, but the solvus may also be shifted, relative to the experimental system,

469   by the presence of minor elements.

470   While the melting point of Al_2O_3 does not vary with fO_2, the melting point of Cr_2O_3 is

471   strongly fO_2-dependent (Fig. 16; Degterov and Pelton 1996; Jung et al., 2005). At $fO_2 \geq$ IW, the

472   melting point of the Cr_2O_3 end member is ca 300 °C higher than that of Al_2O_3, and fractional

473   crystallization of corundum will produce "normal" zoning in which rims of grains will be less Cr-rich

474   than the cores. At $fO_2 = ca$ IW -1, the Al_2O_3 and Cr_2O_3 end members have similar melting points,

475   and the solidus and liquidus converge to a minimum close to the Al_2O_3 side. At the CrO-Cr^0 buffer

476   (fO_2 = IW-5) the melting point of the Cr oxide is ca 200°C below that of Al_2O_3 (Fig. 16d), and

477   fractional crystallization of low-Cr# corundum will drive the melt, and the later-crystallizing

478   corundum, toward higher Cr# ("reverse" zoning).

479   This behaviour offers an experimental explanation for the types of zoning displayed by the

480   samples described here. The large high-Cr corundum cores in sample 1174A-1 (Table 1) have Cr#

481   = 0.11, consistent with crystallisation from the reconstructed melt with Cr# = 0.07 at fO_2 >IW+1,

482   when the solid-solution liquidus-solidus loop is still tilted downward from Cr to Al (Fig. 13a).

483   However, the Cr# of the reconstructed melt is effectively identical with the Cr# of the rims on the

484   large corundum prisms, and the corundum in the barred intergrowths. This situation is consistent

485   with a drop in fO_2 from ≥IW+1 to ca IW -1 during the crystallisation of the residual melt, such that

486   the solid-solution loop becomes nearly horizontal (Fig. 13b).

487   Most of the other grains described here (Tables 2, 4) have cores with low Cr#, zoned to

488   rims with higher Cr#. The core-rim differences in Cr# among these grains range from 0.04 to 0.20.

489   This is the predicted trend of fractional crystallisation at fO_2 << IW, as the slopes of both the

490   solidus curve and the liquidus curve become more steeply negative with falling fO_2, and the gap

491   between them widens (Fig. 16d). At such low fO_2, continued fractional crystallization of low-Cr

492   corundum will drive the melt, and the crystallizing corundum, toward higher Cr#, and eventually

493   to the separation of immiscible Cr-rich metallic melts.

494   Core-rim tie lines plotted on Figures 16c,d show that in most cases the rims are more Cr-

495   rich than the melt that would coexist with the cores, and overgrowths on the rims, where present,

496   are even more Cr-rich. If crystallization occurred in closed systems, these compositions suggest

497   that the melts continued to evolve to higher Cr# as temperature declined by ca 100-150 °C. As

498   noted above, the real temperatures would be significantly below those in the experimental

499 system, in the presence of fluids dominated by CH_4+H_2. For example, a hydrogen pressure of 1

500 GPa would lower the melting point of Cr^0 by *ca* 700 °C (to *ca* 1350 °C) relative to the H-free

501 system (Fukai, 1992). A corundum-dominated fractional-crystallization process linking cores and

502 rims is also consistent with the increase in Mg, P, Ti, V and Zr from low-Cr cores to high-Cr rims in

503 sample 1174C (Table 3).

504   However, some of the highest Cr contents in the corundum may reflect another process.

505 In sample 1174C (Table 3, Fig. 8) the coexistence of Cr in at least three oxidation states (Cr^0, Cr^{1+}?,

506 Cr^{2+}, Cr^{3+}) suggests that the highest mean Cr contents of the corundum (33-40% Cr_2O_3) may reflect

507 the reaction $3Cr^{2+}$ (in melt) → $2Cr^{3+}$(in corundum)+ Cr^0. As noted above, some Cr^0 spheres in

508 corundum appear to have narrow "haloes" depleted in Cr relative to the corundum a few microns

509 away (see Fig. 11a). This feature suggests that once they were trapped, the metallic balls

510 continued to grow by extracting Cr^{3+} from the corundum; this could imply even further reduction

511 during cooling.

512
513 *5. Origin of the parental melts*

514   Two different types of Al-rich oxide melts are represented by the samples described here,

515 one enriched in Fe, Ti, Zr and Cr (Table 1), and the other enriched in Cr, Na and K; their common

516 link is their Cr content. This dichotomy suggests the development of liquid immiscibility during the

517 evolution of an original parental oxide melt. Small-scale separation into silica-poor mafic melts

518 enriched in HFSE and transition elements, *versus* silica-alumina-rich melts that concentrate alkali

519 elements, has been noted in basaltic systems worldwide, but oxide melts generated through liquid

520 immiscibility are rarely erupted due to their high density (e.g. Philpotts and Doyle 1983; Charlier et

521 al. 2011; Kamenetsky et al. 2013).

522   In the aggregates of Carmel Sapphire that crystallized at lower fO_2 than the Cr-rich

523 assemblages, melt immiscibility is texturally evident in the apparent coexistence of Fe-Ti-Si-C

524 melts, the Si-rich but oxygen-poor melts that crystallized most Mt Carmel SiC (Huang et al., 2020),

525 and the residual Ca-Al-Mg silicate melts from which the Carmel Sapphire crystallized (Griffin et al.,

526 2016, 2018, in prep.).

527   The skeletal/hopper morphology of the Carmel Sapphire aggregates (Griffin et al., 2016)

528 reflects rapid growth from a magma supersaturated in Al_2O_3, and this apparently coincided with

529 desilication of the silicate melt via the separation of Fe-Ti-silicide melts. Modelling of the growth

530 patterns preserved in the zoning of Ti^{3+} in the individual crystals (Bravo et al., 2020) suggests that

531 the Carmel Sapphire aggregates formed in very short-lived (days to years) channels filled with

532   flowing melts, immediately prior to eruption of the host magma. In contrast, the cumulate nature

533   of the Cr-rich samples described here suggests a process occurring in a more stable environment,

534   such as small magma chambers or mush pools.

535   The megacrystic sapphire and zircon found in the Mt Carmel tuffs are also well-known as

536   xenocrysts in alkali basalts worldwide. They are generally ascribed to crystallization from syenitic

537   (s.l.) differentiates of deep-seated basalts (Sutherland et al., 2009, references therein), which

538   would be consistent with other evidence for a thick basaltic underplate near the crust-mantle

539   boundary beneath Mt Carmel (Griffin et al., 2018c). Melt immiscibility in such systems, already

540   saturated in Al_2O_3 to the extent of crystallizing large corundum crystals, could be a starting point

541   for the development of oxide melts of the type represented by sample 1174A of this paper (Table

542   1). The conjugate silicate melts may be represented among the silicate-glass rims found on many

543   xenocrysts. Many details of such an evolution remain to be clarified, and will be reported

544   elsewhere.

545

546   *6. Comparison with other Cr-rich corundum*

547

548   The rubies described here include many that are more Cr-rich than any previously known

549   examples. Cr-rich rubies in serpentinites and eclogites can contain up to 13 wt% Cr_2O_3 (Grapes

550   and Palmer 1996; Janak et al. 2015). For mantle-derived samples, high-Cr rubies found as

551   inclusions in diamonds from the Juína kimberlite and the related Sao Luis alluvial deposits in Brazil

552   have held the previous records; Hall et al. (1994) reported an inclusion with 8.6 wt% Cr_2O_3, and

553   Hutchinson et al. (2004) reported one with 13.4 wt% Cr_2O_3. These are similar to the compositions

554   observed in sample 1174-1A (Table 1, Fig.2), but much lower in Cr than the rubies that coexist with

555   Cr^0. The latter also are much more Cr-rich than synthetic rubies made by reaction of chromite

556   with Al^0 to give Cr-corundum + Cr^0, and differ from such synthetic rubies in having much lower

557   contents of Mg, Fe, Mn, Ni, Ti, Ga, Sr and Ca (Hutchinson et al. 2004).

558   The corundum-bearing diamonds from Juína are Type II stones, which recently have been

559   shown to be derived from sublithospheric depths (Smith et al. 2016). Hall et al. (1994) suggested

560   that the high Cr_2O_3 content of their Juína inclusion could reflect a pressure effect. However,

561   studies of inclusions in a range of Type II diamonds have shown that these diamonds probably

562   grew in pools of molten Fe (Smith et al. 2018), which is consistent with the presence of ca 1% FeO

563   in the corundum inclusions. Under these conditions any COH fluid will be dominated by CH_4+H_2,

564   as shown by the gas inclusions observed in Type II diamonds (Smith et al. 2016). In an ultramafic

565   mantle, the presence of molten Fe would constrain fO_2 to near the IW buffer, where Cr would

17

566 exist mainly as Cr^{3+} or Cr^{2+}, and thus would concentrate in other melts/fluids rather than in the

567 molten Fe. The Cr-rich corundum inclusions in the Juína diamonds, and those in sample 1174-1A,

568 thus may approximate the maximum possible Cr_2O_3 content in corundum at fO_2 = IW.

569

570 **Summary**

571 The Cr content of corundum crystallizing from Al-rich melts beneath Mt Carmel in

572 Cretaceous times reflects the evolving oxygen fugacity of one or more magmatic systems,

573 probably located near the crust-mantle boundary. Corundum in cumulates that include Fe-

574 bearing silicates, Fe-Mg-Cr-Al spinels and Fe-Ni alloys crystallized at fO_2 = IW±1, are zoned from

575 high-Cr cores to lower-Cr rims, consistent with fractional crystallization from a melt. The

576 reconstructed parental melts of such cumulates are Al-Cr-Fe-Mg-oxides. Cumulates that contain

577 Cr-Fe alloys, and which probably crystallized at somewhat lower fO_2, have low-Cr cores, and even

578 lower-Cr rims. However, corundum crystals that coexist with Cr^0 have crystallized near the

579 CrO/Cr^0 buffer (fO_2 = IW-5; Fig. 1a), and have low-Cr cores, but high-Cr rims (up to >30% Cr_2O_3).

580 These changes in zoning patterns reflect the strong relative decrease in the melting point of the

581 Cr_2O_3 end member with decreasing fO_2 (Fig. 16). EELS analyses show that all Cr in these corundum

582 crystals is present as Cr^{3+}, although most samples crystallized at or below the fO_2 of the Cr_2O_3-CrO

583 buffer (Fig. 1a). This suggests that at least near the end of the evolution of these melts, Cr^{2+} in the

584 parental melt has disproportionated via the chemical reaction $3Cr^{2+}$(melt) $\rightarrow$ $2Cr^{3+}$(Crn)+ Cr^0.

585 The most Cr-rich corundums have crystallized together with a range of β-alumina phases

586 including $NaAl_{11}O_{17}$ (diaoyudaoite), $KAl_{11}O_{17}$ (kahlenbergite) and β"-alumina phases. From textural

587 evidence, these appear to have crystallized from melts, leaving residual melts that crystallized a

588 range of $(K,Mg)_{1+x}Al_{11-x}O_{17}$ phases. The parental melts of these assemblages appear to have been

589 Al-Cr-K-Na-Mg oxides, which may be related to the Al-Cr-Fe-Mg oxide melts mentioned above

590 (Table 1), through either fractional crystallization or liquid immiscibility.

591 The samples described here cover a range in fO_2 from IW±1 to IW-5, and thus are less

592 reduced than the assemblages in the melts trapped in the more abundant xenoliths of corundum

593 aggregates (fO_2 = IW-6 to -9; Griffin et al. 2019a).   They are interpreted as representing an

594 intermediate stage in the fO_2 evolution of the hypothetical "ideal" magmatic system, in which

595 deep-seated evolving mafic magmas were fluxed by mantle-derived CH_4+H_2 fluids (Griffin et al.

596 2018a). This is a newly recognized facet of the Mt Carmel assemblages, and helps to further

597 understand element partitioning under highly reducing conditions.

598

599 **Implications**

600   The zoning patterns of Cr in Cr-rich corundum crystals from Mt Carmel record changes in

601   the direction of fractional crystallization and the enrichment of Cr in oxide melts, controlled by a

602   decrease in fO_2 by five orders of magnitude during crystallization. This implies the supply of a

603   strongly reducing fluid to the magmas during crystallization, at high fluid/melt ratios. This in turn

604   provides a clear link to the still more reduced mineral assemblages trapped in the Cr-poor

605   corundum aggregates (Carmel Sapphire) found as xenoliths in the same volcanoes. Taken

606   together, these two groups of xenoliths define a magmatic system in which fO_2 decreased from *ca*

607   IW to IW-7 during the crystallization of the melts. The extremely low fO_2 reached toward the end

608   of this process (IW-9 to -10; Griffin et al. 2019a) requires a hydrogen-dominated environment, and

609   is strong evidence for the flux of mantle-derived CH_4+H_2 fluids at high melt-rock ratios during

610   basaltic eruptions over a period of 10-15 m.y. and an area of 150 km^2. This "mantle outgassing" is

611   a previously unrecognized process related to intraplate magmatism, with implications for the

612   oxidation state of the sublithospheric mantle and fluid transfer from mantle to crust.

613   Two different types of Al-rich oxide melts are represented by the samples described here,

614   one enriched in Fe, Ti, Zr and Cr, and the other enriched in Cr, Na and K; their common link is their

615   Cr content. This dichotomy suggests the development of liquid immiscibility during the evolution

616   of an original parental melt. Small-scale separation into silica-poor mafic melts enriched in HFSE

617   and transition elements, *versus* silica-alumina-rich melts that concentrate alkali elements, has

618   been noted in basaltic systems worldwide (e.g. Philpotts and Doyle 1983; Charlier et al. 2011;

619   Kamenetsky et al. 2013) and these processes may have operated at larger scales beneath Mt

620   Carmel. Oxide melts generated through liquid immiscibility are rarely erupted due to their high

621   density, and the unusual trapping of such melts in corundum aggregates at Mt Carmel may be

622   providing new insights into these processes.

623
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625

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641

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844
845
846 **Figure Captions**

847
848 Figure 1. (a) oxidation state (log fO_2 relative to IW buffer) represented by various redox reactions

849 recorded in the xenolith suite. After Papike et al. (2016). (b) Evolution of an idealized magmatic

850 system beneath Mt Carmel, in which an evolved mafic/syenitic melt is fluxed by mantle-derived

851 CH_4+H_2 fluids. The reconstructed succession of key mineral associations is based on xenoliths in

852 the tuffs of the Cretaceous volcanoes, while their respective oxidation states are derived from

853 observed redox reactions and/or dominance of specific valence states of Fe, Cr, Ti and V.

854
855 Figure 2. Maps summarizing regional setting and geological information, including the locations of

856 Cretaceous volcanic centers and main alluvial deposits.

857
858 Figure 3. (a) The black massive pyroclastic rocks in Vent #1 of the Rakefet Magmatic Complex;

859 geological hammer for scale. White clasts are from the country-rock limestones; (b), closer view

860 of massive pyroclastics in the Rakefet Magmatic Complex.

861
862 Figure 4. (a) Variegated pyroclastics from the Rakefet Magmatic Complex, showing layering of

863 coarse and fine lapilli, xenoliths and xenocrysts, with carbonate cement; (b) Polished slab of the

864 variegated pyroclastics from the Rakefet Magmatic complex.

865
866 Figure 5. (a) Back-scattered electron (BSE) image of sample 1174-1A. Most of the sample appears

867 to be a cumulate of touching corundum prisms, with high-Cr cores (to 15 wt% Cr_2O_3) and lower-Cr

868 (ca 10 wt% Cr_2O_3) rims. The barred area in the lower part of the grain is interpreted as the

869 crystallization products of a eutectic melt (see Table 1). (b) Element maps and multi-element

870 phase map of the grain. Mg map is dominated by an interstitial Fe-Mg-Cr-Al spinel.

871
872 Figure 6. (a) Close-up BSE image of the barred area in sample 1174-1A, showing texture

873 interpreted in terms of eutectic crystallization. (b) Element maps and layered-EDS phase map

874 showing the distribution of individual phases.

875

876   Figure 7. BSE images and ELEMENT maps of possible corundum cumulates or skeletal crystals

877   (Table 2).   (a) BSE image of sample 1210B-4, with corundum prisms zoned from higher-Cr cores

878   (2.5 wt% Cr_2O_3 to lower-Cr (ca 1 wt%) rims; matrix is dominated by Na-β-alumina (diaoyudaoite);

879   metallic droplets are a Cr-Fe-Ga alloy. (b) BSE image of sample 1210B-5 showing blocky corundum

880   crystals with high-Cr cores (6.7% wt% Cr_2O_3) and Cr-poor rims (0.4 wt% Cr_2O_3); matrix is K-β-

881   alumina (kahlenbergite), metallic droplets are Cr^0. (c) BSE image, layered-EDS map and element

882   maps of sample 1125-2D. The texture suggests a cumulate of corundum prisms with low-Cr cores

883   (ca 4 wt% Cr_2O_3) and Cr-rich rims (27 wt% Cr_2O_3). Interstitial material is a K-β-alumina, some as

884   apparently lath-shaped crystals; metallic droplets are Cr^0.

885

886   Figure 8. Images of sample 1174C. (a) BSE image and transmitted-light photomicrograph showing

887   colour, and distribution of highest-Cr parts (light areas in BSE). Note ball of Cr^0 on edge of crystal.

888   (b) 3D oblique SEM-view with overlain layered-EDS map of the surface of 1174C before sectioning.

889   Rough dark green in lower part of the image is the ruby; smooth dark green in the upper part is

890   the K-β-alumina. Small bright grains along rim of crystal in middle of image are Ni-bearing Fe^0.

891   Bright pink-purple "mushrooms" are Cr^0. (c) Layered-EDS map and Al distribution map of the

892   contact between the largest Cr sphere, showing higher Cr (lower Al) toward the Cr ball, and the

893   compositional granularity of the high-Cr zone. Red line shows location of FIB foil. Note granularity

894   in the Cr and Al maps of the corundum, interpreted as the result of spinodal breakdown. (d) TEM-

895   BSE image and element maps of FIB foil across contact between Cr^0 and Cr-rich corundum,

896   separated by a zone of Cr_2N.

897

898   Figure 9. EELS spectra of corundum, Cr-nitride and Cr^0 from the FIB foil shown in Fig. 5d. The

899   shifts in Cr peak positions indicate that Cr is present in both high-Cr and low-Cr corundum as Cr^{3+},

900   and in the nitride as Cr^{2+}, or a mixture of Cr^{2+} and Cr^{1+}.

901

902   Figure 10. Incident-light photograph (rough stone) and BSE image (after polishing) of sample

903   1175A. The light grey material veining the corundum and surrounded by high-Cr (8% Cr_2O_3)

904   corundum is a K,Mg-β-alumina (Table 3). The large metallic grain (inset) is divided 60:40 between

905   darker Cr^0 and lighter $Cr_{1.3}N$.

906

907   Figure 11. Images of individual corundum grains with abundant Cr^0. (a) Optical (rough stones) and

908   BSE images (polished samples) of samples 1210A-1 (right) and 1210A-2 (left). Dark cores of

909   corundum contain <0.5 wt% Cr_2O_3, while lighter zones contain 10-12 wt%. Cr^0 droplets are mostly

910   associated with a K-β"-alumina (Table 4). (b) BSE image of sample 1210B-1, showing possible

911   skeletal structure. Dark corundum contains 6 wt% Cr_2O_3, while light rims have >35 wt%. Metallic

912   grains are a Cr-Fe-Ga alloy. Laths of K-β-alumina are overgrown by K-β"-alumina with 17-18%

913   Cr_2O_3. (c) BSE image of sample 1210B-3 with possible skeletal structure. Dark corundum cores

914   contain <1 wt% Cr_2O_3, and lighter rims ca 7 wt %. Metallic grains are Cr^0, and mostly occur within a

915   matrix of K,Mg-β"-alumina (Table 4).

916

917   Figure 12. Phase diagram of the Cr-N system, showing relationships of the CrN (FCC) and Cr_2N

918   (HCP) phases. Data from SGTE 2007 alloy database; see also

919   http://www.crct.polymtl.ca/fact/documentation/SGTE2017/SGTE2017_Figs.htm

920

921

922   Figure 13. Phase diagram for the K_2O-Al_2O_3 binary, showing compositions of the alumina phases

923   analyzed in this work. After Kim et al. (2018).

924

925   Figure 14. Liquidus diagram for the MgO-K_2O-Al_2O_3 ternary, showing compositions of the alumina

926   phases analyzed in this study. Symbols correspond to populations shown on Figure 13. After Kim

927   et al. (2018).

928

929   Figure 15. Liquidus-solidus-subsolidus relationships in the Al_2O_3 (corundum)-Cr_2O_3 (eskolaite)

930   binary at 1 atm. Cr# = molar Cr/(Cr+Al). Vertical black bars mark compositions of coexisting

931   phases in the granular texture shown in Figure 8. After Degterov and Pelton (1996).

932

933   Figure 16. Evolution of the liquidus-solidus loop in the corundum-eskolaite (Cr_2O_3) binary with

934   decreasing fO_2. At high fO_2 a crystallizing oxide has higher Cr/Al than the coexisting melt; at lower

935   fO_2 this relationship is reversed, because the melting point of the Cr-oxide drops with decreasing

936   fO_2, while the melting point of Al_2O_3 remains constant. After Degterov and Pelton (1996). Tie

937   lines connect mean cores, rims and overgrowths of corundum crystals in individual samples. Some

938   rims approach the predicted Cr/Al of the melt coexisting with the core of the grain, but most rims,

939   and all overgrowths, have higher Cr/Al than the predicted melts, implying further fractional

940   crystallization and probably lower temperatures. For the fixed P_{O2} values of each panel, the fO_2

941 relative to IW varies over the temperature range of crystallization: (a) IW +1 to +2; (b) *ca* IW; (c) *ca*

942 IW-2; (d) IW-3 to IW-4.

943

944 **Supplementary Data**

945

946 Figure SD-1. A source-to-sink geological model showing the 3-fold division of the Kishon River

947 catchment (3D view, not to scale). Two of the Cretaceous volcanoes, Rakefet (RMC) and

948 Muharaka are shown to illustrate their situation high above the valley. Cretaceous volcanic

949 centers in red, Cover Basalts in pink and Miocene basalts in purple. Recovered indicator minerals:

950 C, corundum; M, moissanite; H, hibonite; D, diamond. The recovery of corundum and other

951 minerals from the cover basalts is inferred from drainage sampling. However, these occurrences

952 also coincide with the maximum extent of Miocene beach deposits, which may be the source of

953 the alluvial minerals.

954

955 Figure SD-2. (a) Typical stratigraphic section (sample BS1253) of a terrace above the Kishon River,

956 with paleo-placers confined to the coarser basal stratum (site BS1253; green box); (b) Selected

957 minerals recovered from BS1253 (333 tons of gravel processed).

958

959 Figure SD-3. Rubies (0.3-1 mm fraction) separated from vent tuffs of the Rakefet Magmatic

960 Complex (bulk sample SY-479); Cr_2O_3 contents are 1.5-2 wt%.   Cf Figure 11.

961

962 Figure SD-4. Binocular-microscope photo of typical Miocene carbonate-cemented beach placer

963 (Shefa Yamim Sample SY-186, collected in 2003) from near Migdal-Ha-Emec (Figure SD-1). Note

964 abundant moissanite and garnet (orange). Scale is in mm.

965

966 Figure SD5. Raman spectrum of the $NaAlSiO_4$ phase in sample 1174A-1 (Figs 5,6) compared with

967 the spectrum of the synthetic phase ("carnegieite"). The Raman spectrum was collected on

968 $NaAlSiO_4$ grains (532 nm laser, 20 sec acquisition, 32.25 nW). Light blue peaks are Gaussian fit

969 (fitted peak positions reported on top). The spectrum of carnegieite at 298 K (488 nm argon ion

970 laser, 100 sec acquisition, 500 mW) modified from figure 1 of Richet and Mysen (1999) is shown as

971 a dashed line for comparison. While a few peaks have close Raman shifts, it is evident that the

972 spectra correspond to two different phases.

973

974   Figure SD6. Raman spectrum of kahlenbergite from sample 1210B-1 (Fig. 7b) compared with the

975   spectrum of the synthetic material. The Raman spectrum was collected on a kahlenbergite from

976   grain 1210B-1 (532 nm laser, 20 sec acquisition, 32.25 nW). Light blue peaks are Gaussian fit (fitted

977   peak positions reported on top). The spectrum of Na-β-alumina at 20 K (488 nm argon ion laser)

978   modified from figure 3b of Colomban and Lucazeau (1980) is shown as a dashed line for

979   comparison. The match is good considering the difference in composition (K instead of Na) and

980   temperature.

981
982   Table SD-1. Xenocryst minerals recovered from pyroclastic rock samples from individual

983   Cretaceous volcanic centers, Mt Carmel.

984
985   Appendix: Sampling, Analytical methods
986   CIF files of diaoyudaoite 1210B4-1b and kahlenbergite 1210B1-1b
987

Table 1. Analytical data for sample 1174-1A

Fe-Ni alloy			corundum		spinel		
			cores	rims	SEM		EMP
	$n=3$	wt %	$n=2$	$n=5$	$n=12$	stdev	$n=8$
Si	0.07	SiO_2	0.02	0.06			0.11
Al	0.04	ZrO_2	0.00	0.00			0.01
Cr	0.92	TiO_2	0.19	0.62	0.31	0.19	0.36
Mn	0.00	Al_2O_3	84.52	87.6	52.26	2.29	52.64
Fe	87.64	Cr_2O_3	14.76	10.32	12.8	0.95	11.38
Ni	10.28	V_2O_5	0.03	0.05			0.02
P	0.28	FeO	0.08	0.14	11.8	0.82	11.45
total	98.95	NiO	n/a	n/a			n/a
		MnO	0.08	0.02			0.16
at. %		MgO	0.00	0.22	20.2	1.42	20.96
Si	0.13	CaO	0.01	0.00			0.01
Al	0.08	Na_2O	0.00	0.00			0.04
Cr	1.01	K_2O	0.00	0.00			0.00
Mn	0.00	total	99.69	99.03	97.37		97.28
Fe	88.6						
Ni	9.71						
P	0.48	at.%					
		Si		0.03			0.04
		Zr					
		Ti	0.05	0.17	0.09	0.05	0.10
		Al	35.7	36.73	23.70	0.19	22.09
		Cr	4.37	2.90	3.78	0.32	3.20
		V	0.01	0.02			0.01
		Fe	0.02	0.04	3.70	0.23	3.41
		Ni					
		Mn	0.02				0.05
		Mg		0.12	11.80	0.41	11.12
		Ca					0.01
		Na					
		O	60.00	60.00	56.90	0.11	60.00
		Cr#	0.109	0.073	0.14		0.13

	K-free nepheline		$(Fe,Mg,Ni)(Al,Cr)_2O_4$		Zr_2O_3	$(Na,Fe,Mg)_2(Al,Ti,Cr)_6O_{11}$			
	SEM	EMP	SEM	EMP	SEM	SEM		EMP	
	$n=7$	$n=5$	$n=5$	$n=1$	$n=3$	$n=11$	stdev	$n=11$	stdev
SiO_2	41.7	43.66		0.03				0.51	0.24
ZrO_2		0.00		0.00	82.40	1.21	0.41	1.22	0.35
TiO_2	0.15	0.42	0.55	0.39	3.16	14.10	2.43	13.05	1.52
Al_2O_3	34.50	37.64	42.30	43.41	3.24	48.80	3.32	51.30	2.11
Cr_2O_3	0.18	0.62	14.9	16.46	0.69	7.37	0.68	7.61	0.05
V_2O_5		0.05		0.05				0.19	0.02
FeO	0.85	1.14	36.10	36.89	0.75	13.3	0.83	13.10	0.67
NiO		n/a	1.56	0.03				n/a	
MnO		0.024						0.01	0.08
MgO		0.47	0.97	1.31		3.94	0.28	4.10	0.13
CaO	0.22	0.30		0.01		2.33	1.15	2.81	0.97
Na_2O	17.10	14.18		0.01	0.17	2.21	0.74	2.17	
K_2O		0.17		0.00				0.01	
total	94.75	98.66	96.37	98.56	90.38	93.21		94.90	
at.%									
Si	14.29	14.76						0.20	0.23
Zr					28.5	0.26	0.08	0.23	0.10
Ti	0.04	0.12	0.15	0.13	1.68	4.46	0.75	3.87	0.89
Al	13.93	15.00	21.70	21.03	2.68	24.20	1.21	23.82	1.60
Cr	0.05	0.17	5.30	5.35	0.39	2.45	0.17	2.37	0.29

V								0.06	0.01
Fe	0.24	0.32	13.00	12.68	0.44	4.68	0.27	4.32	0.37
Ni			2.40	0.01					
Mn								0.00	0.01
Mg		0.24	0.57	0.80		2.47	0.10	2.31	0.17
Ca	0.08	0.11				1.05	0.52	1.69	0.60
Na	11.36	9.29				1.80	0.59		
O	60.0	60.0	56.80	60.00	66.30	58.60	0.04	61.10	
Cr#			0.20	0.20	0.13	0.09		0.09	

	(Fe,Mg)(Al,Cr,Ti,Si)$_8$O$_{13}$	Reconstruction (Fig. 2)		
	EMP	barred	coarse	whole
	n=4	area	area	grain
SiO$_2$	3.02	2.1	1.1	1.7
ZrO$_2$	0.00	0.0	0.0	0.2
TiO$_2$	0.58	1.7	1.1	1.7
Al$_2$O$_3$	75.46	77.6	81.8	77.5
Cr$_2$O$_3$	5.19	8.4	9.4	8.2
V$_2$O$_5$	0.01	0.0	0.0	0.1
FeO	6.98	4.6	2.9	4.5
NiO	n/a	0.0	0.0	0.0
MnO	0.08	0.0	0.0	0.0
MgO	4.18	4.3	3.0	4.5
CaO	0.01	0.2	0.1	0.2
Na$_2$O	0.25	1.1	0.6	1.3
K$_2$O	0.05			
total	95.81	100.0	100.0	100.0
at.%				
Si	1.48			
Zr	0.01			
Ti	0.35			
Al	39.87			
Cr	3.58			
V	0.01			
Fe	5.37			
Ni				
Mn	0.07			
Mg	2.55			
Ca	0.01			
Na	0.20			
O	42.4			

Table 2. Analytical data for corundum "cumulates"

	1210B-4								1210B-5				1125-2D				
	corundum			β-alumina		Cr-alloys			β-alumina	corundum		Cr-alloy	β-alumina	corundum			Cr alloy
wt %	cores	rims	outer	Na-Cr	wt%	SEM				cores	rims			cores	rims	outer	
	n=3	*n*=3	*n*=3	*n*=3		*n*=2	*n*=1	*n*=1	*n*=3	*n*=6	*n*=4	*n*=3	*n*=5	*n*=4	*n*=3	*n*=2	*n*=2
SiO2	0.02	0.01	0.02	0.07	Si	0.10	0.06	0.05	0.00	0.02	0.01	0.04 (Si)	0.01	0.02	0.02	0.00	0.11
ZrO2	0.01	0.00	0.00	0.02	Cr	51.68	49.69	78.89	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.02	
TiO2	0.01	0.01	0.01	0.01	Fe	44.78	46.12	16.68	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.13	
Al2O3	97.63	98.39	94.29	88.06	Ga	2.76	n/a	n/a	87.25	99.65	94.02	0.15 (Al)	85.96	96.27	72.38	64.62	0.07
Cr2O3	2.17	1.26	5.33	4.40	total	99.31	95.87	95.62	1.96	0.40	6.07	99.47(Cr)	2.97	3.78	27.05	34.19	99.5
V2O3	0.00	0.01	0.00	0.00					0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.04	
FeO	0.02	0.01	0.00	0.02	at.%				0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	
MnO	0.00	0.01	0.03	0.01	Si	0.20	0.12	0.1	0.00	0.02	0.01	0.27(Mn)	0.02	0.02	0.07	0.06	0.23
MgO	0.00	0.01	0.00	0.34	Cr	53.89	53.58	83.47	1.39	0.03	0.01	0.00	0.06	0.00	0.00	0.02	
CaO	0.00	0.00	0.01	0.14	Fe	43.47	46.30	16.43	0.08	0.00	0.00	0.00	0.02	0.01	0.01	0.01	
Na2O	0.00	0.00	0.00	5.01	Ga	2.14			0.06	0.00	0.01	0.02	0.07	0.01	0.01	0.02	
K2O	0.00	0.00	0.01	0.21					7.17	0.00	0.01	0.00	11.50	0.00	0.01	0.02	
total	99.81	99.69	99.68	93.30					97.88	100.13	100.10	99.99	100.6	100.1	99.6	99.11	100.00
at %																	
Si	0.01		0.01	0.02								0.09		0.01	0.01		0.20
Zr																	
Ti																0.04	
Al	39.4	39.65	38.53	36.51					35.31	39.88	38.33	0.29	34.17	38.94	31.92	29.46	0.13
Cr	0.59	0.34	1.46	1.22					0.54	0.11	1.66	99.38	0.79	1.03	8.00	10.46	99.47
V															0.01	0.01	
Fe																	
Ni																	
Mn												0.26			0.02	0.02	0.19
Mg				0.18					0.72				0.03			0.03	
Ca				0.04					0.03				0.01				
Na				3.42									0.05				
K				0.09					3.16				4.95				
O	60.0	60.0	60.0	58.6					63.4	60.0	60.0		65.0	60.0	60.0	60.0	
Cr#	0.01	0.01	0.04	0.03					0.02	0.003	0.042		0.02	0.026	0.200	0.262	

Table 3. Analytical data for two large hopper crystals of corundum

1174C								
	corundum							
	in contact with Cr balls					cores		main
	SEM		EMP	TEM		SEM	EMP	
wt.%	n=9	stdev	n=3	low-Cr	high-Cr	n=3	n=3	n=6
SiO_2			0.01				0.00	0.01
ZrO_2			0.00				0.00	0.00
Ti_2O_3			0.00				0.00	0.01
Al_2O_3	68.6	9.0	68.90	70.4	42.2	97.0	97.08	76.80
Cr_2O_3	31.4	3.3	31.15	29.7	57.6	2.95	2.95	23.14
V_2O_3			0.02				0.00	0.02
FeO			0.00				0.00	0.00
MnO			0.04				0.02	0.05
MgO			0.01				0.00	0.01
CaO			0.00				0.00	0.02
total	100.0		100.14	100.1	99.8	100.0	100.1	100.0
at. %								
Al	30.6		30.6	31.2	20.8	39.2	39.2	33.3
Cr	9.41		9.29	8.84	19.1	0.80	0.80	6.72
V			0.01					0.01
Mn			0.01					0.02
Mg			0.01					0.01
Ca								
O	60.0		60.0	59.9	60.1	60.0	60.0	60.0
Cr#	0.24		0.23	0.22	0.48	0.02	0.02	0.17
ppm	(LA-ICPMS)							
Mg			98					17
Si			1405					1460
P			42					29
Sc			<0.9					<0.4
Ti			58					3
V			156					34
Cr			166000					13800
Fe			<28					<20
Co			<0.12					<0.03
Ni			<0.63					<0.12
Zn			<0.93					<0.75
Ga			0.22					<0.05
Zr			3.4					0.11
Nb			0.07					0.11

1174c (cont.)							
wt.%	β-alumina	spinel	% element	Cr balls		Cr nitride	
				SEM	EMP	SEM	TEM
	n=4	n=4		n=8	n=3	n=2	
			N			7.69	13.2
SiO_2	0.02	0.01	Si	0.13	0.07	0.11	
ZrO_2	0.00	0.01	Al		0.24		
Ti_2O_3	0.00	0.01	Cr	99.9	99.31	92.1	86.8
Al_2O_3	85.62	21.51	Mn		0.27		
Cr_2O_3	4.74	58.46					
V_2O_3	0.01	0.04	total	100.1	99.6	99.9	100.0
FeO	0.00	0.00					
MnO	0.02	0.14	at. %				
MgO	0.39	18.06	N			18.9	36.1

CaO	0.01	0.18	Si	0.10	0.13		
Na$_2$O	0.07	0.12	Al		0.46		
K$_2$O	9.43	0.00	Cr	99.9	99.15	81.1	63.9
total	100.30	98.53	Mn		0.27		
at. %							
Al	34.40	10.30					
Cr	1.28	18.70					
V							
Mn	0.01	0.10					
Mg	0.02	10.90					
Ca	0.03						
Na	0.10						
K	4.10						
O	60.10	60.00					
Cr#	0.04	0.65					

	1175A					
	β-alumina	corundum				
		"core"		spinel	Cr-spin	CrN?
wt%	n=4	n=3	"rim"		SEM	SEM
			n=4	n=5	n=1	n=3
SiO$_2$	0.02	0.03	0.01	0.02		N=17
ZrO$_2$	0.00	0.02	0.00	0.02		
Ti$_2$O$_3$	0.01	0.00	0.00	0.03		
Al$_2$O$_3$	74.89	99.18	92.80	48.95	3.44	
Cr$_2$O$_3$	9.83	0.73	8.23	26.51	76.4	Cr=83
V$_2$O$_3$	0.00	0.01	0.00	0.03		
FeO	0.02	0.00	0.01	0.00		
MnO	0.05	0.00	0.01	0.12		
MgO	7.12	0.02	0.01	21.16	20.1	
CaO	0.16	0.01	0.01	0.05		
Na$_2$O	0.40	0.01	0.02	0.02		
K$_2$O	8.41	0.00	0.00	0.08		
total	100.91	100.00	101.09	97.0	99.9	
at.%						
Si	0.01			0.01		
Al	32.11	39.80	37.75	20.91	1.71	
Cr	2.82	0.19	2.25	7.60	25.6	56.8
Mg	3.78			11.43	12.7	
Na	0.35					
K	3.90					
O	56.97	60.0	60.0	60.1	60.1	
N						43.2
Cr#	0.081	0.005	0.06	0.27	0.94	

Table 4. Individual Cr-ruby grains with Cr inclusions

	1210A-1					1210A-2			1210B-1	
	β-alumina	corundum			Cr-alloy	β-alumina	corundum		β-alumina	
		cores	inner rims	outer rims	(metal %)		cores	rims	laths	overgrowths
wt %	$n=3$	$n=3$	$n=4$	$n=3$	$n=2$	$n=1$	$n=4$	$n=7$	$n=6$	$n=5$
SiO_2	0.01	0.00	0.01	0.01	0.09	0.15	0.01	0.03	0.01	0.09
ZrO_2	0.01	0.01	0.00	0.00		0.02	0.00	0.00	0.01	0.00
Ti_2O_3	0.00	0.00	0.00	0.02		0.00	0.00	0.00	0.00	0.00
Al_2O_3	86.32	98.00	77.03	60.26	0.05	79.20	98.51	81.73	89.74	71.17
Cr_2O_3	1.87	2.22	22.64	39.74	99.45	6.63	0.74	16.70	1.83	17.64
V_2O_5	0.01	0.01	0.03	0.03		0.00	0.01	0.01	0.00	0.02
FeO	0.00	0.00	0.00	0.02		0.00	0.01	0.01	0.01	0.01
MnO	0.01	0.00	0.05	0.09	0.32	0.06	0.00	0.03	0.00	0.06
MgO	0.07	0.01	0.02	0.01		1.57	0.01	0.02	0.08	0.78
CaO	0.01	0.00	0.00	0.01		0.06	0.00	0.00	0.01	0.07
Na_2O	0.03	0.00	0.00	0.01		0.17	0.00	0.00	0.02	0.04
K_2O	12.65	0.00	0.00	0.00		13.09	0.00	0.00	8.05	10.75
total	100.99	100.24	99.78	100.19	99.91	100.96	99.27	98.54	99.78	100.63
at.%										
Ti				0.02						
Al	34.04	39.37	33.36	27.68		31.57	39.79	35.15	35.16	29.78
Cr	0.49	0.6	6.58	12.24		1.77	0.20	4.82	0.52	4.90
V	0.00		0.01	0.01						
Fe										
Mn			0.02	0.03		0.02		0.01		0.02
Mg	0.03		0.01	0.01		0.79	0.01	0.01	0.39	0.41
Ca						0.02				0.02
Na	0.02					0.11			0.02	0.02
K	5.40					5.96			3.86	4.82
O	60.00	60.00	60.00	60.00		59.8	60.00	60.00	60.10	60.00
Cr#	0.00	0.015	0.165	0.307		0.05	0.005	0.121	0.015	0.141

	1210B-1 (cont.)			1210B-2				
	corundum		Cr-Fe alloy	corundum			Cr-alloys	
wt%	cores	rims	SEM	cores	rims	outermost	(metal %)	
	$n=4$	$n=6$	$n=5$	$n=4$	$n=4$	$n=2$	$n=5$	$n=1$
SiO_2	0.01	0.00	(metal %)	0.01	0.03	0.01	0.24	0.12
ZrO_2	0.04	0.00		0.01	0.01	0.01	0.00	0.00

Ti$_2$O$_3$	0.00	0.03	0.11	0.02	0.09	0.03	0.00	0.00
Al$_2$O$_3$	93.91	64.01	82.5	97.50	85.36	61.66	99.39	88.46
Cr$_2$O$_3$	5.96	35.63	16.2	2.99	14.23	36.66	0.00	0.00
V$_2$O$_5$	0.01	0.02	1.06	0.00	0.01	0.02	0.00	0.01
FeO	0.02	0.00	99.97	0.00	0.00	0.00	0.00	11.00
MnO	0.00	0.06		0.01	0.02	0.06	0.26	0.00
MgO	0.00	0.01		0.01	0.01	0.01	0.00	0.00
CaO	0.00	0.00		0.00	0.00	0.01	0.00	0.23
Na$_2$O	0.00	0.01		0.00	0.01	0.02	0.00	0.00
K$_2$O	0.00	0.03		0.00	0.01	0.02	0.00	0.00
total	99.96	99.80		100.54	99.76	98.48	99.89	99.82
at.%								
Zr	0.01							
Ti		0.01	0.21		0.03	0.01		
Al	38.1	29.09	83.6	39.16	35.94	28.56	99.50	
Cr	1.51	10.86	15.3	0.81	4.02	11.39	0.19	
V			0.80			0.01		
Fe								
Mn		0.02			0.01	0.02		
Mg								
Ca								
Na								
K								
O	60.4	60.0		60.03	60.00	60.01		
Cr#	0.038	0.272		0.020	0.101	0.285		

	1210B-3				1210B-5		
	β"-alumina	Corundum		Cr alloy	corundum		β"-alumina
wt%		cores	rim	metal %	cores	rims	
	n=4	*n*=6	*n*=1	*n*=1	*n*=6	*n*=4	*n*=6
SiO$_2$	0.00	0.01	0.02				
ZrO$_2$	0.00	0.01	0.01				
Ti$_2$O$_3$	0.00	0.00	0.00			0.02	
Al$_2$O$_3$	80.22	99.49	93.36			0.01	
Cr$_2$O$_3$	5.38	0.72	6.98	99.6	99.96	94.98	79.05
V$_2$O$_5$	0.01	0.00	0.01		0.41	5.64	5.23
FeO	0.00	0.00	0.00		0.02		0.02
MnO	0.00	0.01	0.02	0.31	0.02		0.05
MgO	6.16	0.00	0.02		0.01		7.95
CaO	0.01	0.00	0.00				0.01
Na$_2$O	0.01	0.00	0.00				0.01

K$_2$O	8.46	0.00	0.00				8.49
total	100.21	100.25	100.41	99.89	100.37	100.81	100.81
at.%							
Al	31.83	39.73	38.08		39.87	38.45	31.03
Cr	1.43	0.26	1.91		0.11	1.53	1.38
V					0.01	0.01	0.01
Fe					0.01	0.01	0.01
Mn			0.01			0.01	0.01
Mg	3.09		0.01				3.95
Ca							
Na	0.01						0.01
K	3.63						3.61
O	60.01	60.01	59.99		60.00	59.99	59.99
Cr#	0.043	0.007	0.048		0.003	0.038	0.043

Figure 1

a)

1500°C, 1atm

SiC
SiO$_2$ + C

Solar nebula

Ni^0 ← ● → Ni^{2+}

Fe^0 ← ● → Fe^{2+} ← ● → Fe^{3+}

Cr^0 ← ● → Cr^{2+} ← ● → Cr^{3+}

V^0 ← ● → V^{2+} ← ● → V^{3+} ← ● → V^{4+} ← ● → V^{5+}

Mn^0 ← ● → Mn^{2+}

Ti^{2+} ← ● → Ti^{3+} ← ● → Ti^{4+}

IW   EMOD   QFM

-14 -12 -10 -8 -6 -4 -2 0 2 4 6 8 10

Log fO$_2$ Δ(IW)

b)

CH$_4$ + H$_2$

CO$_2$ + H$_2$O

H$_2$

H$_2$

CO$_2$ + H$_2$O

Syentic magma

CH$_4$ + H$_2$

Hibonite, grossite, fluorite and native vanadium | Al super-saturation --> hopper corundum | Moissanite (SiC) | Cr-ruby with Cr^0 | Fe metal-oxide melts | High Mg calcite (ca 1400°C) | Wustite | reduced, Fe-depleted peridotite wall-rocks Fo$_{93-94}$

Figure 2

a) Eurasian Plate · TURKEY · Tauride Block · CYPRUS · Kyrenia Range · Lamaca Ridge · Latakia Ridge · Cyprus active margin · Eratosthenes Seamount · Mediterranean Sea · Levant Basin · Iskenderun Basin · Coastal Maqualaia · Ghab basin · SYRIA · Aleppo High · Mardin High · Al Furat Fault · Sinjar Trough · Euphrates Graben · Palmyra fold belt · Rutba High · LEBANON · Beirut · Yammouneh F. · Damascus · Carmel F. · Sea of Galilee · JORDAN · Amman · Jerusalem · Dead Sea · ISRAEL · Ramon · Dead Sea Transform · Azraq - Sirhan Graben · Al Jawf Graben · Arabian Plate · Sinai Plate · EGYPT · Eastern Desert · Suez Graben · Gulf of Suez · Gulf of Elat · Red Sea · African Plate

b) N · BO · HA · MAK · MUH · RMC · KM · O · BS · T · S · Kishon River · Migdal Ha-Emeq · Ein Hashofet 1 Drill · Ramot Menashe · Umm El Fahm

Volcanics / Sediments
- Quaternary
- Pliocene
- Miocene
- Oligocene
- Eocene
- Paleocene
- Cretaceous

Mt. Carmel Magmatic Bodies - Legend:
- **HA** = Har Alon
- **BO** = Beit Oren
- **RMC** = Rackefet
- **MUH** = Muhraka
- **MAK** = Makure
- **BS** = Bat Shlomo
- **T** = Tavassim
- **O** = Ofer
- **S** = Shefeya

0 1.05 2.1 4.2 6.3 8.4 Km

Inset: N · 1125 · 1210 · 1174 · Legend: Ruby Samples · Streams and tributaries · 250m · 500m

Figure 3

Figure 4

a)

b)

4 mm

Lorem ipsum

Figure 5

a) BSE image

Mg-Al-Cr
Spl

high Cr

low Cr

Crn

500 μm

b) layered
EDS map

Si Na Mg Cr Al O Ca Electron

Al

Mg

Figure 6

Figure 7

a) BSE
Na-β-alumina
Crn
Cr-Fe alloy
500 μm

b) BSE
Crn
Cr⁰
K-β-alumina
250 μm

c) BSE
Crn -core
-rim
K-β-alumina
1 mm

EDS
Al
Cr
K

Figure 8

a)

BSE K-β-alumia

Cr⁰

low
Cr Crn

high
Cr Crn

250 µm

b) EDS

Cr⁰

Crn 100 µm

c) EDS

Crn
low --> high Cr Cr⁰

Al

50 µm

d)

Crn Cr⁰

Cr₂N

HAADF
Map data 1282
HAADF MAG: 7100x HV: 200kV
2 µm

Cr
Map data 1282
HAADF MAG: 7100x HV: 200kV
2 µm

N
Map data 1282
HAADF MAG: 7100x HV: 200kV
2 µm

Al
Map data 1282
HAADF MAG: 7100x HV: 200kV
2 µm

Figure 9

a) Cr-L$_{2,3}$ Edge

High Cr Corundum
Low Cr Corundum
Cr Metal
CrN
Reference spectrum
Cr$_2$O$_3$
(Mcbride & Brydson 2004)

Energy-Loss (eV)

b) O-K Edge

Energy-Loss (eV)

Figure 10

Figure 11

a) BSE

Crn w/
10-12wt% Cr

Cr⁰

Crn w/
<0.5wt% Cr

500 µm

b) BSE

K-β-alumina

Crn
<1wt% Cr

Cr⁰

Crn
10-11.5wt% Cr

250 µm

c) BSE

K,Mg-β-alumina

Cr⁰

Crn
0.6wt% Cr

Crn
7wt% Cr

250 µm

Figure 12

Cr - N

Data from SGTE 2007 alloy database

T(°C) vs mole N/(Cr+N)
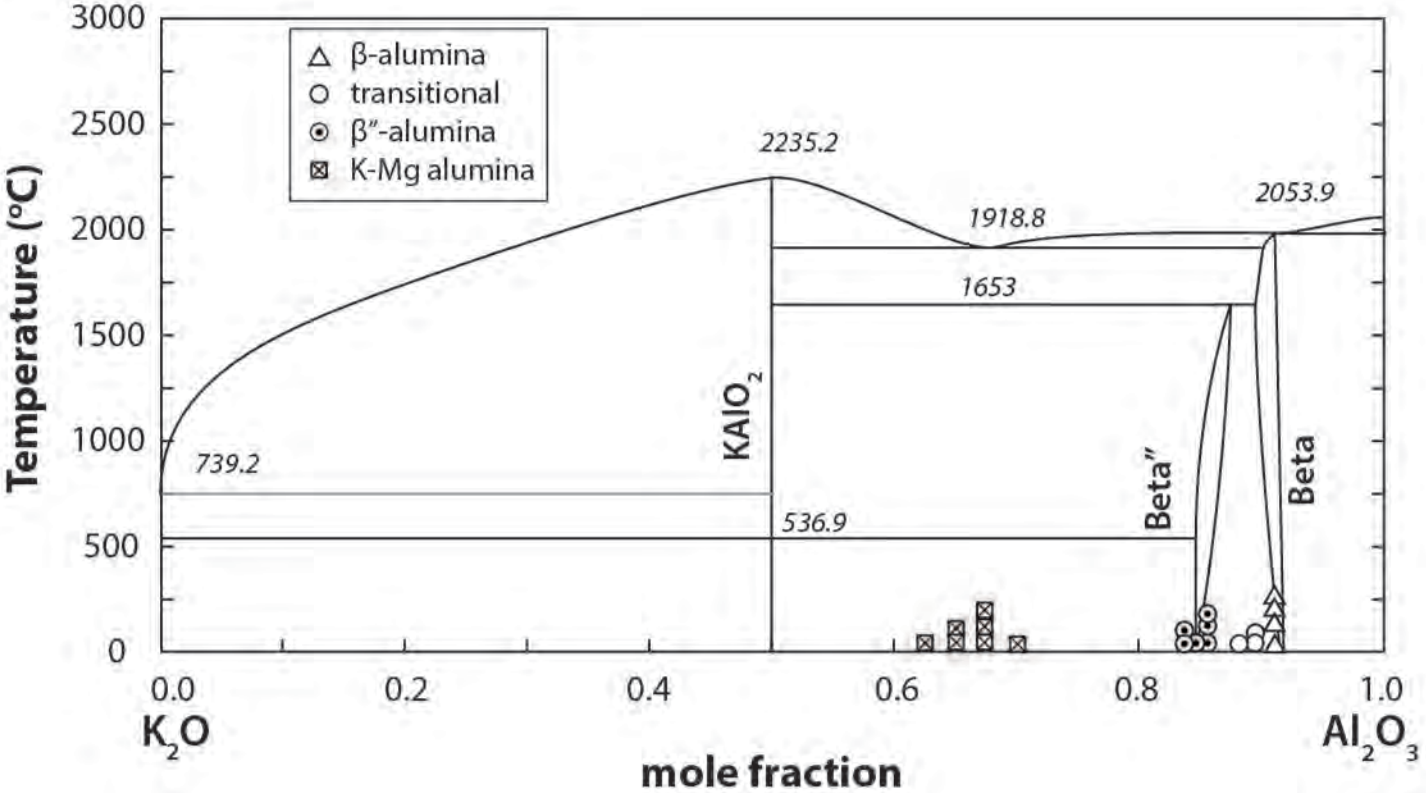
BCC

HCP

FCC

Liquid

Cr⁰ + Cr₂N

Cr₂N + CrN

CrN + Liq

Figure 13

Figure 14

Figure 15

Figure 16

a) $P_{O_2} = 10^{-3}$ atm

b) $P_{O_2} = 10^{-5}$ atm

c) $P_{O_2} = 10^{-7}$ atm

d) $P_{O_2} = 10^{-9}$ atm

Liquid

$(Al,Cr)_2O_3$ Solid

core   rim   overgrowth