MS 66733R revised 28-09-2018

1 **A terrestrial magmatic hibonite-grossite-vanadium assemblage: desilication**

2 **and extreme reduction in a volcanic plumbing system, Mt Carmel, Israel**

3

4 William L. GRIFFIN[1], Sarah E.M. GAIN[1], Jin-Xiang HUANG[1], Martin SAUNDERS[2],

5 Jeremy SHAW[2], Vered TOLEDO[3] and Suzanne Y. O'REILLY[1]

6

7 [1]*ARC Centre of Excellence for Core to Crust Fluid Systems (CCFS) and GEMOC,*

8 *Earth and Planetary Sciences, Macquarie University, NSW 2109, Australia;*

9 *bill.griffin@mq.edu.au*

10 [2] *Centre for Microscopy, Characterisation and Analysis, The University of Western*

11 *Australia, WA 6009, Australia; martin.saunders@uwa.edu.au*

12 [3] *Shefa Yamim (A.T.M.) Ltd., Netanya 4210602, Israel; vered@shefayamim.com*

13

14 **Abstract**

15 Hibonite ($CaAl_{12}O_{19}$) is a constituent of some refractory Calcium-Aluminum

16 Inclusions (CAIs) in carbonaceous meteorites, commonly accompanied by grossite

17 ($CaAl_4O_7$) and spinel. These phases are usually interpreted as having condensed, or

18 crystallized from silicate melts, early in the evolution of the solar nebula. Both Ca-Al

19 oxides are commonly found on Earth, but as products of high-temperature

20 metamorphism of pelitic carbonate rocks. We report here a unique occurrence of

21 magmatic hibonite-grossite-spinel assemblages, crystallized from Ca-Al-rich silicate

22 melts under conditions (high temperature, very low oxygen fugacity (fO_2))

23 comparable to those of their meteoritic counterparts. Ejecta from Cretaceous

24 pyroclastic deposits on Mt Carmel, N. Israel, include aggregates of hopper/skeletal

25 Ti-rich corundum, which have trapped melts that crystallized at fO_2 extending from 7

26 log units below the Iron-Wustite buffer ($\Delta IW = -7$; SiC, Ti_2O_3, Fe-Ti silicide melts) to

27 $\Delta IW \leq -9$ (native V, TiC, TiN). The assemblage hibonite+grossite+spinel+TiN first

28 crystallized late in the evolution of the melt pockets; this hibonite contains % levels of

29 Zr, Ti and REE, reflecting the concentration of incompatible elements in the residual

30 melts as corundum continued to crystallize. A still later stage appears to be

31 represented by coarse-grained (cm-size crystals) ejecta that show the crystallization

32 sequence: corundum + Liq $\rightarrow$ (low-REE) hibonite $\rightarrow$ grossite + spinel ± krotite $\rightarrow$

33 $Ca_4Al_6F_2O_{12}$ + fluorite. V^0 appears as spheroidal droplets, balls up to mm size, and

34 spectacular dendritic growths, included in hibonite, grossite and spinel. Texturally

35 late V^0 averages 12 wt% Al and 2 wt% Mn. Spinels contain 10-16 wt% V in V^0-free

36 samples, and <0.5 wt% V in samples with abundant V^0. Ongoing paragenetic

37 studies suggest that the fO_2 evolution of the Mt Carmel magmatic system reflects

38 interaction between OIB-type mafic magmas and mantle-derived CH_4+H_2 fluids near

39 the crust-mantle boundary. Temperatures estimated by comparison with 1-atm.

40 phase-equilibrium studies range from ca 1500 °C down to 1200-1150 °C. When fO_2

41 reached ca $\Delta IW = -7$, the immiscible segregation of Fe,Ti-silicide melts and the

42 crystallization of SiC and TiC effectively desilicated the magma, leading to

43 supersaturation in Al_2O_3 and the rapid crystallization of corundum, preceding the

44 development of the hibonite-bearing assemblages. Reports of Ti-rich corundum and

45 SiC from other areas of explosive volcanism suggest that these phenomena may be

46 more widespread than presently realized, and the hibonite-grossite assemblage may

47 serve as another indicator to track such activity.

48 This is the first reported terrestrial occurrence of krotite ($CaAl_2O_4$), and of at least two

49 unknown Zr-Ti oxides.

50

51 **Introduction**

52   Hibonite ($CaAl_{12}O_{19}$) was described as a new mineral in 1956 (Curien et al.,

53 1956), and is named after Paul Hibon, who found cm-sized black crystals in a placer

54 deposit in Madagascar in 1953.   It is a constituent of some refractory Calcium-

55 Aluminum Inclusions (CAIs) in carbonaceous chondrites, commonly associated with

56 grossite ($CaAl_4O_7$) and corundum (Grossman et al., 1988; Beckett et al., 2006).

57 Hibonite also occurs as microscopic grains in meteorites and it is one of the oldest

58 minerals in the solar system.

59   The type locality of hibonite is the Esiva alluvial deposits, in Tulear Province,

60 Madagascar. The material was probably derived from nearby deposits of thorianite-

61 bearing skarns, which are widespread in the Pan-African (565-515 Ma) granulite

62 belts of Madagascar and Tanzania (Rakotondrazafy et al., 1996). In these rocks,

63 early corundum + spinel + scapolite asemblages are altered to anorthite +calcite+

64 less calcic scapolite, while hibonite crystallized at the expense of corundum and

65 spinel. Hibonite also occurs as tabular crystals up to 3 cm across in calcitic marbles

66 from the Tashelga-Malzaskaya region in Siberia (Konovalenko et al., 2012). These

MS 66733R revised 28-09-2018

67 metamorphic hibonites are notably high in Fe^{3+}, and coexist with V-rich minerals

68 (goldmanite, tashelgite, mukhinite). P-T conditions are estimated at 700-800 °C, 3.5

69 kbar. The crystallization of hibonite implies a very low silica activity and, in this

70 location, probably high CO_2.

71   The type locality of grossite is the Hatrurim formation (formerly known as the

72 "Mottled Zone"), a unique rock complex exposed mainly in the Judean Desert of

73 Israel, where it was first described by Gross (1977). The formation was deposited as

74 a thin marine, bituminous chalk-marl formation of Campanian to Neogene age.

75 However, at several localities, it is metamorphosed to the sanidinite and pyroxene-

76 hornfels facies (up to 1000 °C, very low P), due to spontaneous isochemical

77 combustion of bituminous compounds. Hibonite and grossite are widespread in these

78 metamorphosed sediments.

79   All previously known terrestrial occurrences of hibonite and grossite are, to

80 our knowledge, metamorphic in origin. In contrast, the textures of hibonite-bearing

81 CAIs in CV chondrites are ambiguous; hibonite occurs as a minor phase coexisting

82 with melilite, or in coarse-grained assemblages that could be metamorphic.

83 However, CAIs from CM chondrites are dominated by assemblages such as

84 hibonite+ spinel + perovskite, some of which contain glass. Textural features are

85 consistent with crystallization of hibonite from Al-rich melts (Kurat, 1975; Grossman

86 et al., 1988; Ireland et al., 1991), condensed from the solar nebula. The predicted

87 sequence of crystallization would be corundum-hibonite-perovskite, with subsequent

88 reactions leading to mellilite and spinel. The condensation and crystallization of such

89 melts would require temperatures of *ca* 1500 - 1300 °C and would have occurred at

90 the very low oxygen fugacity (fO_2) imposed by the hydrogen-dominated composition

91 of the early solar nebula (Yoneda and Grossman, 1995; Grossman et al., 2008).

92   The apparent absence of magmatic hibonite-grossite assemblages on Earth

93 thus is understandable. However, we report here a terrestrial analog to the hibonite-

94 bearing CAIs of CM chondrites, from the Mt Carmel volcanics of northern Israel. Our

95 aimis to document these unusual parageneses; define their relationships to other

96 members of the ultra-reduced Mt Carmel volcanic system (Griffin et al., 2016, 2018;

97 Xiong et al., 2017); discuss briefly the mechanisms that can produce similar high-T,

98 low-fO_2 environments on Earth and indicate its implications for the behaviour of

99 carbon in deep-seated volcanic systems.

100

MS 66733R revised 28-09-2018

101

Background

103   Several years of exploration for placer gemstone deposits in the drainage of

104   the Kishon river, which enters the sea near Haifa in northern Israel (Fig. SD1), have

105   provided this unusual occurrence of hibonite and grossite.

106   Upper Cretaceous (98-80 Ma, Turonian-Cenomanian) mafic to ultramafic

107   pyroclastic rocks (vent breccias, tuffs) exposed in the Mt Carmel area, northern

108   Israel, represent a series of small explosive volcanoes that erupted on a shallow

109   carbonate shelf (Sass, 1980). Black pyroclastics occur in eruptive vents, while

110   variegated pyroclastics occur as layers of various thickness interbedded with

111   carbonates, indicating repeated explosive eruptions. Analyses of fine-grained, but

112   possibly altered, lapilli suggest that the magmas were tholeiitic to alkali picrites

113   (Griffin et al., 2016). The pyroclastic rocks carry mantle xenoliths (peridotites,

114   pyroxenites) derived from <90 km depth (maximum P-T estimates of ca 1030 °C and

115   2.3 GPa), suggesting a thin lithosphere and a high thermal gradient (Esperanca and

116   Garfunkel, 1986; Mittlefehldt, 1986; Kaminchik et al., 2014; Apter, 2015). They also

117   contain a wide variety of xenocrysts: debris from garnet/spinel peridotites and

118   pyroxenites, and megacrysts of clinopyroxene, ilmenite, zircon and corundum.

119   Aggregates of hopper-formed corundum crystals (Carmel Sapphire^{TM}) are

120   common in the pyroclastic ejecta of the volcanoes exposed on Mt Carmel, and in

121   associated alluvial deposits. Melt pockets trapped within and between the skeletal

122   corundum crystals contain mineral assemblages including moissanite (SiC), Fe-Ti-Zr

123   silicides/ phosphides, Ti nitrides and borides, and native V, that require high T

124   (≥1450 to ca 1200 °C) and fO_2 from 6 to 9 log units more reducing than the Iron-

125   Wustite buffer (ΔIW = -6 to -9).

126   Paragenetic studies (Griffin et al., 2016, 2018; Xiong et al., 2017; Fig. 1)

127   suggest that the crystallization of corundum and the low fO_2 reflect the interaction of

128   basaltic magmas with mantle-derived CH_4+H_2 at high fluid/melt ratios, leading to

129   progressive reduction and desilication of the magma, and ultimately to Al_2O_3-

130   supersaturation, the rapid growth of skeletal/hopper corundum crystals, and the

131   deposition of abundant amorphous carbon. This evolution included several stages of

132   liquid-liquid immiscibility, including the segregation of Fe- and Ti-silicide melts from

4

133   silicate melts, driven by a progressive decrease in fO$_2$. The latest stage of this

134   evolution is defined by the appearance of hibonite, grossite and spinel, suggesting

135   that silica-deficient melts evolved beneath some of the volcanic centers.

136

137   **Methods**

138   The samples, collected and provided by Shefa Yamim, have been mounted in

139   epoxy discs, polished and characterized by optical microscopy, and by back-

140   scattered electron and cathodoluminescence imaging in the scanning electron

141   microscope, to identify minerals and to establish parageneses. Mineral compositions

142   were analysed by both SEM-EDS and WDS electron microprobe. Trace elements

143   were analysed by LA-ICPMS. Selected samples were examined by TEM using FIB

144   foils, and TEM-EDS and TEM-XRD were used to obtain chemical analyses and

145   crystallographic parameters of specific phases. 3D-μCT scans of individual grains

146   and aggregates were taken to examine structures in three dimensions. Details of

147   each of these methods are given in the Supplementary Data.

148

149   **Petrography**

150   HIbonite from the primary pyroclastic deposits and in placer samples from the

151   Kishon and Yoqneam Rivers occurs in two parageneses. Paragenesis A comprises

152   inclusions in and between skeletal corundum crystals, and paragenesis B the

153   granular aggregates of hibonite+grossite+spinel.

154

155   **Paragenesis A: hibonite in corundum**

156   Hibonite occurs in pockets of trapped melt interstitial to, or included in,

157   corundum crystals within the corundum aggregates (Figs 2, 3). The melt pockets in

158   the corundum aggregates have been described by Griffin et al. (2016; 2018) and

159   Xiong et al. (2017). The earliest parageneses consist of tistarite (Ti$_2$O$_3$) ± a Ti-Al-Zr

160   oxide (informal name: TAZ) ± Mg-Al spinel in a matrix of Ca-Mg-Al-Si-O glass. The

161   earliest trapped melts represent considerable modification of assumed primary

162   silicate melts (probably basaltic), including progressive desilication by the exsolution

163   of immiscible Fe-Ti oxide melts and Fe-Ti-Zr-silicide melts, and the crystallization of

164   moissanite and khamrabaevite (TiC), at fO$_2$ = ΔIW-6 or less. This process continued,

165   producing progressively lower fO$_2$, witnessed especially by the appearance of Ti^{2+}-

MS 66733R revised 28-09-2018

166 bearing phases (TiB_2, TiN, TiC, TiO). The earliest appearance of hibonite in the melt

167 pockets is in association with TAZ, spinel, TiN, Fe-Ti silicides, TiC and glass,

168 interstitial to corundum crystals (Fig. 2). This hibonite is locally associated with

169 grossite, but appears also to be in textural equilibrium with corundum. In some

170 pockets hibonite is intergrown with or crosscut by at least two unknown Zr-Ti oxides.

171 (Table 1; Fig. 3). These phases and others (Table 1) appear to reflect the

172 continuous concentration of incompatible elements in the silicate melts (percent

173 levels of Ti, Zr, La, Ce; Table 2) as the trapped melt volumes were progressively

174 reduced by the growth of corundum, in parallel with the decrease in fO_2.

175

176 **Paragenesis B: hibonite-grossite aggregates**

177   Rounded to angular grains ranging from millimeters up to 2.5 cm across

178 consist of flattened hexagonal prisms (a:c = 7-17) of hibonite in a matrix of grossite

179 and Mg-Al spinel (Fig. 4). The rough material typically is purplish in colour (Fig. 4a),

180 but in polished, more transparent grains some has a yellow-orange colour. The

181 hibonite displays orange cathodoluminescence, while that of grossite is blue to

182 purple. A characteristic feature is the occurrence of balls and dendrites of native

183 vanadium, included in hibonite and grossite, and more rarely in spinel.

184   The major paragenesis of these intergrowths is shown in Figures 5-7.

185 Hibonite occurs as tabular crystals up to 1 cm across, in a matrix of granular grossite

186 and spinel (commonly as euhedral octahedra); fluorite is the last phase to crystallize.

187 Resorbed remnants of corundum in some hibonite laths (Figs 5,6) indicate that

188 corundum crystallized before the Ca-Al-oxides and that hibonite crystallized via the

189 peritectic reaction corundum (Cor) + liquid/melt (L) → hibonite. This was followed by

190 the cotectic precipitation of grossite, hibonite and spinel, and finally the assemblage

191 grossite + spinel + $CaAl_2O_4$ (krotite) + fluorite.

192   Grossite commonly is euhedral against interstitial fluorite. The oxyfluoride

193 phase $Ca_4Al_6F_2O_{12}$ (widely synthesised, but not previously reported in nature)

194 appears to precede fluorite in the crystallization sequence and to coexist with

195 grossite. Rare grains of perovskite ($CaTiO_3$) also appear to coexist with grossite (Fig.

196 5c; Table 1) or intergrown with fluorite (Fig. 5d).

197   Most of the hibonite-grossite aggregates show little or no preferred orientation

198 of the hibonite crystals, but some have radiating structures. In the example shown in

199 Figure SD2, the hibonite + grossite + spinel + fluorite assemblage appears to have

6

MS 66733R revised 28-09-2018

200   grown from a substrate of coarse-grained grossite; the width of the hibonite tablets

201   increases with distance from the contact, suggesting a quench-related structure.

202   Small drop-like grains of native vanadium (V^0) are common in hibonite and

203   grossite (Fig. 5a,b), indicating the lowering of fO_2 to $\Delta IW \leq -9$, where V^0 becomes

204   stable (Fig. 1). It occurred roughly at the temperature of the peritectic reaction cor + L

205   = hibonite, although there is no obvious reason for the two reactions to be linked.

206   Native V also occurs as balls up to 500 μm across, either isolated within hibonite, or

207   together with grossite and fluorite in complex pockets among hibonite grains (Fig.

208   8a). These larger balls contain percent levels of Cr and Mn, and have exsolved into

209   laths of V^0 with higher and lower levels of these two elements (Fig. 8b,c; Table 1).

210   Some of these balls are altered to mixtures of fluorite and carbonates (Fig. 8d)

211   related to cracks, some of which are filled with an Al-hydroxide, possibly gibbsite.

212   Larger cracks contain pockets with a geode-like zoned filling of this phase, including

213   terminated crystals extending into open voids. Since the assemblage V^0 + CaF_2

214   apparently is stable in other situations (Fig. 8a), this alteration is interpreted as a

215   post-eruption phenomenon.

216   In some cases, vanadium in hibonite develops from drop-like balls with worm-

217   like protuberances (Fig. 8), into spectacular 3D dendritic growths (Fig. 9; Fig. SD3),

218   growing sub-parallel to the c axis of the hibonite crystals.

219

220   **Mineral chemistry**

221   ***Major and minor elements***

222   Hibonite included in corundum (paragenesis A) contains significant levels of

223   Si, Zr, Ti, Cr, Sr, Mg and LREE (up to >6% Ce_2O_3; Table 1), but does not contain

224   measurable levels of V. TEM imaging shows a hexagonal cell with c = 22.73 Å,

225   compared to 22.29 Å in the type material; the a axis is 4.8 Å, shorter than in the type

226   material (5.6 Å). Calculation of the structural formula on the basis of 19 oxygens

227   indicates that essentially all of the Ti is present as Ti^{3+}. The apparent deficit in

228   trivalent ions in the formula (Table 1) probably reflects the levels of other REE (see

229   below) that are below the detection limit of the EMP (ca 0.1 wt%). In contrast,

230   hibonite in the granular aggregates (paragenesis B) contains percent levels of V, and

231   minor levels of Mg, but all other elements are below detection for the EMP.

MS 66733R revised 28-09-2018

232 Calculation of the structural formula (Table 1) suggests that V is present as V^{3+}, or

233 even partly as V^{2+}.

234   Grossite is essentially stoichiometric $CaAl_4O_7$ with no minor elements at the

235 EMP level. The Raman spectrum of the stoichiometric phase $CaAl_2O_4$ (Table 1)

236 identifies it as the low-pressure form krotite, rather than the high-pressure form

237 dimitryivanovite. This is consistent with available pressure constraints (see below)

238 that suggest crystallization at around 1 GPa, while dimitryivanovite is stable above 2

239 GPa (Mikouchi et al., 2011). To our knowledge, this is the first natural terrestrial

240 occurrence of krotite, originally described from a CAI in a CV3 carbonaceous

241 chondrite (Ma et al., 2011).

242 Spinels occurring in melt pockets with hibonite (paragenesis A) are essentially pure

243 Mg-Al spinels, with a deficit in Mg and an excess of Al. This feature is common to

244 spinels in the less-evolved melt pockets without hibonite (our unpublished data),

245 suggesting that either Ti or Al substitutes for Mg, but it is not clear from the analyses

246 how charge balance would be achieved. Spinels in the hibonite-grossite aggregates

247 (paragenesis B) show a range of compositions, related to the presence of native V.

248 Spinels in aggregates with no visible V^0 contain 9-16 wt% V (4.5-8 at%), and 1.7-8%

249 wt% Mn; with a few exceptions, the contents of V and Mn are positively correlated,

250 while both MgO and Al_2O_3 show negative correlations with V_2O_3 (Figure SD4).

251 Detailed studies of the related phase dellagiustaite (ideally AlV_2O_4; Camara et al.,

252 2018), show all vanadium is ordered in the octahedral sites, with Al in the tetrahedral

253 site; $^AAl^B(V^{2+}V^{3+})O_4$ (where A are tetrahedral sites and B are octahedral sites). It

254 seems likely that this is also the case in the high-V spinels reported here.

255   Spinels in aggregates with scattered small beads of V^0 contain 2-5 wt% V and

256 0.3-1.3 wt% Mn. In aggregates with abundant V^0, the spinels mostly contain <0.5

257 wt% V and Mn. These less V-rich spinels have 2.0 Al ions per formula unit,

258 suggesting that all of the V substitutes for Mg.

259   The Ca-Al oxyfluoride in the hibonite-grossite-spinel aggregates (Figs 5, 6)

260 has the formula $Ca_4Al_6O_{12}F_2$; it is known from experimental studies on the CaO-

261 Al_2O_3-F system (Kim, 2011). F. Cámara, R. Pagano, A. Pagano, L. Bindi and F.

262 Nestola have described this phase in similar material from Sierra de

263 Comechingones, San Luis, Argentina, and have proposed the name calfidine (IMF

264 proposal number 2018-093; not yet approved).

MS 66733R revised 28-09-2018

265   All EDS analyses of fluorite contain carbon, and may fit a formula $CaF_{2-x}C_x$.

266   The EMP analyses did not include carbon, but the deficiency in the sums suggests

267   the presence of a missing component such as carbon.

268   The perovskite phase has the formula $CaTiO_3$, implying that the Ti is present

269   as Ti^{4+}; this anomalous at the fO_2 implied by its coexistence with V^0. It also contains

270   1.6 wt% V and 1.3 wt% F.

271   The only Zr-Ti oxide grain large enough to analyse by EMP (Fig. 3) contains

272   minor amounts of Al, Mn, Mg and Ca; the structural formula of the mean analysis

273   (Table 1) can be simplified as Zr_3TiO_8, implying that Ti is present as Ti^{4+}. However,

274   the large standard deviations on the mean analysis indicate that this "phase" is very

275   heterogeneous. Multiple SEM-EDS analyses which sample smaller volumes (Table

276   1) suggest the presence of several other oxides with variable ratios of (Zr+Ti)/O, in

277   which Ti appears to be present as Ti^{3+}. These may represent breakdown products of

278   the Zr_3TiO_8 phase shown in Figure 3, but most occur as discrete grains. Further

279   TEM studies will be required to confirm the nature of these phases.

280   The smallest vanadium spheres are nearly pure V^0, with 0.5-2 wt% Si and 1.5-

281   2.5 wt% Mn. As these are inclusions are in hibonite or corundum, the Si is assumed

282   to substitute in the alloy, rather than being a matrix contamination. Most larger V

283   inclusions have lower Si, but contain 1-2% Cr and 0.5-3.5% Mn, and may have up to

284   ca 4 wt% Al (V_9Al; Table 1; Figure 9). The latest to form are irregular balls with drop-

285   like protruberances, that occur in nests of grossite surrounded by laths of hibonite

286   (Fig. 8). These are similar in form to the drops that develop into the spectacular

287   dendrites (Figs 9, SD3). They contain even higher levels of Al, with up to 15 wt%

288   and a mean of 12% (V_4Al; Table 1); single-crystal XRD has confirmed a cubic

289   structure (L. Bindi, pers. comm., August 2018).

290

291   ***Trace elements***

292   Mean trace-element data for the major phases, from LA-ICPMS analysis, are

293   given in Table 3 and shown in Figure 10.

294   Hibonite in the corundum aggregates (paragenesis A) is extremely enriched in

295   the REE (ΣREE = 2.7 wt%) with a moderate enrichment in LREE over HREE. It

296   shows small negative anomalies in Sr, Eu and Y, and a positive anomaly in Yb. Ti

297   reaches 1.7 wt%, Sr 1 wt% and Zr 0.35 wt%. Th + U are also enriched (0.3 and 0.04

MS 66733R revised 28-09-2018

298   wt%), while vanadium is very low (2 ppm). CHECK against Table, which shows

299   higher values? Fe is absent, although minor Mn (34 ppm) is present; the only other

300   transition element is Ni (3.5 ppm).

301   Hibonite in the hibonite-grossite aggregates (paragenesis B) shows LREE

302   enrichment, and a mild depletion in HREE relative to chondrites; Ba is depleted

303   relative to Ce and La. The extended REE pattern is essentially parallel to that of the

304   mean hibonite in paragenesis A (Fig. 10b), but lower in most elements by *ca* two

305   orders of magnitude, and shows a relative depletion in Zr. One grain (982-2c-01)

306   shows an unusual depletion in the lighter elements (Sr to Ce, Ba) while the other

307   REE levels are similar to those in the mean hibonite. Most grains show negative Eu

308   anomalies (Eu/Eu* = 0.2-0.82, mean 0.46, n=9), but the other anomalies seen in the

309   interstitial-hibonite pattern are absent. Ti contents in the hibonites of paragenesis B

310   range from 70-720 ppm, and are roughly correlated with V contents, which range

311   from 1100-13300 ppm. The highest V contents are found in grains with small

312   inclusions of V^0, although care was taken to avoid these during analysis. The next

313   most abundant transition element is Mn (50-580 ppm) and most grains carry low

314   levels of Fe and/or Cr. Th and U contents are scattered (1-17 ppm and 1.4-4 ppm,

315   respectively) but Th/U ratios show less spread (3.8 ± 2.1(1σ)). Most Na values are

316   around 20 ppm, but K is <0.02 wt% in most grains. B is reported at levels of 20-50

317   ppm (but is <2 ppm in one); we cannot be confident of these values, but note that the

318   Mt Carmel system does contain boride minerals (TiB$_2$; Griffin et al., 2016).

319   *Grossite* in paragenesis B has generally chondritic to subchondritic levels of

320   the REE, and low levels of most other trace elements (Fig. 10c). The high standard

321   deviations relative to the absolute values suggest that many of these elements reside

322   in tiny inclusions of other minerals, or melt, inside the grossite. Most grains show a

323   pattern with relatively flat HREE and MREE, and depleted LREE; the patterns and

324   absolute abundances of Y and the HREE are similar to those of coexisting hibonite

325   (Fig. 10b,c). However, some grains do not show the LREE depletion. Ba is elevated

326   relative to La and Ce, and all grains show high levels of Sr and Y compared to the

327   MREE, although the absolute levels are similar to those in hibonite. In contrast to

328   the hibonite, most grains of grossite show a small positive Eu anomaly. Ti (30-120

329   ppm) contents are lower than in hibonite, but contents of V (850-2750 ppm) and Mn

330   (0-510 ppm) overlap the ranges seen in hibonite, and Fe levels (mostly 100-250

10

MS 66733R revised 28-09-2018

331   ppm) are higher. There is no obvious correlation between Ti and V. In marked

332   contrast to the hibonites, contents of Th and U in grossite are typically <0.05 ppm.

333   *Large spinel* grains in paragenesis B contain ca 2.5% V; Mn contents range

334   from 3100-6400 ppm, while Cr, Ti and Zn values average 77, 150 and 10 ppm,

335   respectively. Ga contents are < 0.2 ppm, giving very high Al/Ga ratios. Ca contents

336   are unusually high for spinels, at 1100-4300 ppm.

337   A single LA-ICPMS analysis of a large *vanadium* sphere in hibonite gave

338   values of 490 ppm Zn, 21 ppm Cu, and 69 ppm Nb.

339

340   **DISCUSSION**

341   ***Conditions of formation***

342   *Temperature*

343   The temperatures during the crystallization of the Mt Carmel super-reduced

344   assemblages can be estimated from experimental data, which are mainly from 1-atm

345   experiments. Therefore the estimated temperatures may represent minimum values

346   in the individual simple systems. The major phases all lie within the simple and well-

347   studied system CaO-MgO-Al2O3-SiO2; the coexisting melts consist mainly of these

348   oxides, though with significant levels of Ti, Zr and REE.

349   Hibonite crystallizes from $CaO-Al_2O_3$ melts (Fig. 11a) *via* the peritectic

350   reaction Crn + Liq → hibonite; different experimental or theoretical studies place this

351   reaction at 1850-1880 °C; in more SiO_2-rich systems (Fig. 12) the peritectic extends

352   down to ca 1475 °C. There is disagreement in the literature as to the nature of

353   lower-temperature phase transitions on this binary. Some studies (e.g. Guo et al.,

354   2015; Azof et al., 2017) show both grossite and krotite melting congruently,

355   producing the binary eutectics Hbn + Gros + Liq and Gros + Krot + Liq. Others (e.g.

356   Mao et al 2004) show both phases melting incongruently, in peritectic reactions Hbn

357   → Gros + Liq and Gros → Krot +Liq. Still others show singularities in which the

358   peritectic reactions correspond to the congruent melting points of grossite and

359   krotite, respectively. The older experimental work is more consistent with the

360   modeling of Mao et al. (2004; Fig. 12). In the aggregates of Paragenesis B, there is

361   no obvious reaction relationship between hibonite and grossite, but the grossite

362   +spinel assemblage does appear to crystallize after hibonite.

363   Grossite (Gros) appears at 1750-1780 °C in the binary system, and krotite at

364   ca 1600 °C. In the 1-atm. $CaO-MgO-Al_2O_3$ system (Fig. 11c) the Hbn+Gros+Liq

365 peritectic descends to the Gros+Spl+Liq cotectic at ca 1690 °C. In the 1-atm.

366 liquidus diagram two intermediate Ca-Al-Mg oxides appear through peritectic

367 reactions just above this temperature (Fig. 11b), but these phases have not been

368 recognised in the Mt Carmel system. Their apparent absence may be a pressure

369 effect (see below), or it may reflect the presence of abundant fluorine in the system,

370 effectively sequestering Ca. Alternatively, they may have been consumed in

371 peritectic reactions. The presence of krotite as an interstitial late phase implies that

372 the residual melts evolved further, toward the peritectic Gros + Liq (±spinel) → krotite

373 at ca 1520 °C (Fig. 11b). Krotite + Spn + Liq coexist along a cotectic leading to more

374 Ca-rich compositions, not seen in our samples, at ca 1350 °C

375 The presence of fluorine may lower these liquidus temperatures. The fluorite-

376 grossite assemblage precipitates at ca 1375 °C in the 1-atm. CaF_2-$CaAl_2O_4$ system

377 and the $Ca_4Al_6O_{12}F_2$ phase crystallizes from *ca* 1480 °C to a eutectic with fluorite at

378 1375 °C (Fig. SD5; Kim, 2011). $Ca_4Al_6O_{12}F_2$ is unstable at T <1150 °C, providing a

379 lower limit for the cooling of the system before eruption terminated the evolution of

380 the melts. The presence of this phase implies that F^{1-} had replaced a significant

381 amount of the O^{2-} in the melt (Peng et al., 2011).

382 One spinel has been found coexisting with hibonite in the melt pockets (Table

383 1). Like spinels coexisting with tistarite and the TAZ phase in the earlier stages of

384 the melt evolution, it has a large excess of Al_2O_3 and a deficit in divalent cations; by

385 comparison with the experimental MgO-Al_2O_3 system (e.g. Bhaduri and Bhaduri,

386 1999; Callister, 2008) it gives a T close to 1400 °C, within the range of temperatures

387 derived from spinels in other melt pockets (1600 °C to 1200 °C, with a mean of 1400

388 °C; our unpublished data). In contrast, the spinels in the hibonite-grossite

389 aggregates are nearly stoichiometric (Mg, V)Al_2O_4, which yields a temperature

390 around 1200 °C.

391

392 *Pressure*: There are no independent constraints on the pressure of formation for the

393 hibonite-grossite assemblage; it crystallized at very low pressure in the Solar nebula

394 (Beckett et al., 2006), at ca 1-2 km depth in the Hatrurim Formation (Gross,1977),

395 and at ca 10-30 km depths in the granulite-facies occurrences (Rakotondrazafy et

396 al., 1996). Dmisteinbergite, the metastable high-T hexagonal polymorph of anorthite,

397 occurs as a quench phase in many melt pockets (Xiong et al., 2017). In

398 experiments, this phase can be produced by rapid cooling of the melt to ca 1200 °C

MS 66733R revised 28-09-2018

399 (Davis and Tuttle, 1952). In the present case, this reflects the peritectic reaction Crn

400 + Liq→ An, which is constrained experimentally to P_{min} > 0.9 GPa and T ca 1450 °C

401 (Goldsmith, 1980). The parageneses in the hibonite-grossite aggregates (Figs 5, 6)

402 document crystallization across the peritectic Liq + Crn → hibonite, followed by

403 crystallization along the hibonite-grossite cotectic to where it joins the cotectic   Gros

404 + Spl +Liq. Ottonello et al. (2013) modelled the CaO-Al_2O_3-SiO_2 liquidus at

405 pressures to 2 GPa, and argued that grossite is not a liquidus phase at P ≥1 GPa

406 (Fig. 13). The presence of $CaAl_2O4$ as krotite, rather than the higher-P polymorph

407 dmitryivanovite, also limits P to <2 GPa (Mikouchi et al., 2009). If these constraints

408 are accepted, the Mt Carmel corundum-SiC system was crystallizing at P= *ca* 1 GPa

409 (depths of 25-30 km) near the crust-mantle boundary in the area (Segev and

410 Ryabkov, 2011), when the host basalts erupted.

411

412 *Oxygen fugacity (fO$_2$)*: Hibonite is stable over a wide range of oxygen fugacity. The

413 Mt Carmel assemblages described here require very reducing conditions, consistent

414 with the occurrence of tistarite (Ti_2O_3) and SiC as inclusions in corundum. The

415 presence of a positive Yb anomaly in the hibonite of paragenesis A is consistent with

416 this low fO_2, as Yb^{2+} will substitute for Ca in the hibonite more readily than Yb^{3+}. In

417 the hibonite-grossite aggregates of paragenesis B, the coexistence of native V

418 requires fO_2 <ΔIW-8 (Fig. 1). As noted above, low oxygen fugacity is not a pre-

419 requisite for the crystallization of the hibonite-grossite-spinel assemblage. However,

420 it was the progressive lowering of fO_2 during the evolution of the magmatic system

421 that led to the immiscibility of silicide melts, driving the desilication of the magma that

422 ultimately allowed the crystallization of the oxide assemblage hibonite-grossite-spinel

423 (Griffin et al., 2016; Xiong et al., 2017).

424   In summary, the crystallization of the hibonite-grossite assemblage in the Mt

425 Carmel system probably occurred at depths of 25-30 km, temperatures falling from

426 ca 1500 °C to ca 1200 °C prior to eruption, and fO_2 between ΔIW -6 and ΔIW -9.

427

428 **Melt Evolution**

429   For a rough estimate of the composition of the bulk crystallization products,

430 element maps of eight hibonite-grossite aggregates were point-counted to determine

431 the modal abundances of the analysed phases, and bulk compositions were

432 calculated. These proved to show little variation in composition (Table 2); the mean

433 contains ca 80 wt% Al_2O_3, 16 wt% CaO, 2 wt% MgO and 1 wt% F, while other

434 components are present at levels of ≤0.5%.   This composition lies close to the

435 hibonite-grossite boundary on the CA binary (Fig. 11a), and the CAS ternary plot

436 (Fig. 12), but in the field of corundum in the CMA ternary (Fig. 11b).

437   The major-element composition of a melt coexisting with the average hibonite

438 in paragenesis A (24 analyses) was calculated using the D values of Kennedy et al.

439 (1994), based on 1-atm. experimental studies, and our own values derived from a

440 single hibonite-glass pair (Fig. 2). There are obvious hurdles in this approach, in

441 terms of concetration levels and non-ideality of melts, but the data may be useful on

442 a comparative basis. The value for $D_{Si}^{h/m}$ given by Kennedy et al. (1994) is clearly

443 not applicable to the Mt Carmel material, as it would predict >100 wt% SiO_2 in the

444 melt. A value for $D_{Si}^{h/m}$ derived from our analysis of the glass coexisting with one

445 hibonite in corundum would predict 28 wt% SiO_2 in the melt coexisting with the mean

446 interstitial hibonite. The actual analysed melt contains 38.3 wt% SiO_2, while the

447 interstitial hibonite coexisting with it has higher SiO_2 than the mean value.

448   As expected, the melt predicted using both approaches is very high in Al_2O_3

449 and CaO (Table 3). MgO contents predicted by the data of Kennedy et al. (1994) are

450 higher than our calculated values. The levels of Zr and Ti predicted by both sets of

451 distribution coefficients are similar. This composition lies near the corundum-

452 anorthite cotectic on the CaO-Al_2O_3-SiO_2 (CAS) liquidus phase diagram at 1 atm

453 pressure (Fig. 12), but close to the corundum-hibonite peritectic at 1 GPa (Fig. 13;

454 Ottonello et al., 2013). Glasses coexisting with hibonite in meteoritic spherules,

455 interpreted as melts condensed from the solar nebula (Ireland et al., 1991) are

456 broadly similar in being essentially CMAS melts, but have lower Al and higher Si, Ca

457 and Mg than those calculated for the interstitial hibonite.

458   The calculated major-element composition of the melt in equilibrium with the

459 mean hibonite composition of paragenesis B (Table 3) suggests a further evolution to

460 higher CaO/Al_2O_3, but lower MgO. SiO_2 and TiO_2 are below detection limits in the

461 hibonite, and this may suggest SiO_2 contents ≤20 wt% and TiO_2 contents ≤0.5 wt%

462 in the melt. This composition, though poorly constrained, lies within the CAS liquidus

463 field of corundum at one atm. and at 1 GPa (Figs 12, 13).

464   If the melts calculated for the two parageneses are linked by the evolution of

465 the trapped melts beyond the corundum-hibonite peritectic, that evolution is unlikely

466   to have been driven only by fractional crystallization of the observed assemblages,

467   which would increase SiO_2 but decrease Al_2O_3 in the melt. However, such an

468   evolution would be broadly consistent with the overall trend seen in the Mt Carmel

469   system, of continued desilication of the silicate melts by immiscible separation of

470   silicide melts and crystallization of SiC, with falling fO_2 (Fig. 13)

471   The Fe-Ti silicide melts that separated from the parental melts earlier in their

472   evolution contain <0.5 wt% V (our unpublished data), suggesting that V did not

473   partition strongly into the metallic melts. This is consistent with the generally

474   lithophile nature of V, and the observation that the partition coefficient

475    $D_V^{metallic\ melt/silicate\ melt}$ decreases (i.e. V becomes more lithophile) with increasing Si

476   content in the metallic melt (Tuff et al., 2011). However, $D_V^{metallic\ melt/silicate\ melt}$ should

477   be higher at low fO_2; this may indicate that most of the separation of silicide melts

478   occurred at high enough fO_2 (ΔIW -6 to -7) to hinder a stronger uptake of V, leaving

479   enhanced levels of V in the residual melts.

480   During the further evolution of the melts, there were few crystallizing phases

481   that accepted significant levels of V, until the appearance of the hibonite-related

482   spinels described here. At that point, fO_2 may have been low enough for the stability

483   of both V^{3+} and V^{2+}, allowing substitution for Mg and Al in the first spinels, up to 8

484   at.% (Table 1). XANES analysis of V in fassaitic pyroxenes from refractory CAIs has

485   found V^{2+}/V^{tot} ratios as high as 0.7, consistent with a solar gas (i.e. H-dominated;

486   Simon et al., 2007). The presence of Ti^{2+}-bearing phases (e.g. TiC) and V^0 suggest

487   that the minimum fO_2 during the late stages of the Mt Carmel system was at least

488   this low (Fig. 1), and thus that H_2 may have been the main volatile species present.

489   Righter et al. (2006; see also Papike et al., 2013) studied the partitioning of V

490   between silicate melts and Al-spinels over a wide range of oxygen fugacity and

491   composition. Using their equation (2) and the constants they calculated from the

492   low-fO_2 experiments, we estimate $D_V^{spinel/silicate\ melt}$ to be in the range of 43-45 for the

493   spinels in the hibonite-grossite aggregates. This approach suggests that the melt

494   coexisting with the high-V spinels (Table 1) contained on the order of 1000-1500

495   ppm V. The concentration of V in the late Ca-Al-Si-O melts thus represents only a

496   moderate (5x) enrichment relative to a proposed mafic parental melt (200-300 ppm;

497   Fig. 2). The melt that crystallized the medium-V spinels contained about 400 ppm V,

498   and the melt with the low-V spinels, which crystallized in the presence of V^0,

499 contained only about 35 ppm V. This trend partly reflects the rapid sequestration of

500 V into its own melt phase, which is clearly immiscible with the silicate melt.

501

502 ### *Composition of coexisting melts –Trace Elements*

503   The $D^{hibonite/melt}$ values for a range of trace-elements published by Kennedy et

504 al. (1994; K94 below), Ireland et al. (1991; I91 below) and Drake and Boynton (1988;

505 DB88 below) allow calculation of the trace-element patterns of the melts that would

506 have equilibrated with the analysed hibonites (Fig. 14a; Table 3). The melts

507 calculated from the interstitial hibbonites in the corundum aggregates (paragenesis

508 A) have relatively flat HREE-MREE and mild enrichment in the LREE. The LREE

509 patterns calculated with I91 have lower MREE-HREE than those calculated from the

510 K94 data. The D_{Eu} value of K94 is >1 and produces a negative Eu anomaly, whereas

511 those of I91 and DB88 produce positive Eu anomalies. The three sets of D_{Yb} values

512 all produce a marked positive Yb anomaly in the melts with the interstitial hibonite of

513 paragenesis A. The calculated melts have much higher contents of the REE and

514 other trace elements than melts coexisting with hibonite in meteoritic glass spherules

515 (Ireland et al., 1991; Fig. 14c). However, the meteoritic glasses do not show LREE

516 enrichment, nor any Yb anomaly.

517   The calculated melts in equilibrium with the hibonite of paragenesis B are, as

518 might be expected, much more depleted in most trace elements (except Th, U and

519 Ba), in general rougher (a function of low count rates) and more spoon-shaped than

520 the pattern of the paragenesis-A melt. The melts calculated from the hibonite of

521 paragenesis B have REE levels similar to those of meteoritic glasses, but the

522 patterns are more spoon-shaped than those of the meteoritic glasses.

523   LA-ICPMS analyses of glasses in the melt pockets in the corundum

524 aggregates define three prominent populations, ranging from a high-Ce, low-Ba type

525 to a lower-Ce, higher-Ba type (Fig. 14b; Table 3); all three types have strongly

526 negative Sr anomalies. While the high-Ce glasses have flat HREE-MREE and

527 LREE-enrichment, the lower-Ce glasses have a more concave-upwards pattern. The

528 higher-Ce, lower-Ba glasses are broadly similar to the calculated melt in equilibrium

529 with the interstitial hibonites (paragenesis A).   In the pyroclastic ejecta, many

530 fragments of the corundum aggregates are coated in the low-Ce, high-Ba glass,

531 which has patterns even more upward-concave than those of the higher-Ce glasses

532 (Fig. 14b). These glasses are broadly similar to the calculated melt in equilibrium

533 with the mean hibonite of paragenisis B, but also show many differences.

534   For comparison with the partitioning data of Kennedy et al. (1994), Ireland et

535 al. (1991) and Drake and Boynton (1988), we have calculated the distribution

536 coefficients between the interstitial hibonites (paragenesis A) and the high-Ce, low-

537 Ba glass, and between the aggregate hibonites (paragenesis B) and the low-REE,

538 high-Ba glasses (Table 3).   The D values calculated from the interstitial hibonite *vs*

539 the high-Ce glasses in general agree within a factor of 2 with those of I91 and DB88.

540 Notable exceptions are D_{Sr}, D_V, D_{Zr} and D_{Ba}; for the latter two the K94 D values look

541 more appropriate. The D values proposed here may be useful in further studies of

542 meteoritic hibonite associations, especially for elements where no D values are

543 otherwise available. The D values calculated by pairing the hibonite of paragenesis

544 B with the high-Ba glass do not provide a good match with any of the other datasets,

545 suggesting that the high-Ba glass, although apparently formed late in the magmatic

546 evolution, was not in equilibrium with the hibonite-grossite-spinel aggregates.

547

548 **SUMMARY**

549 1. The assemblage hibonite+grossite+spinel of paragenesis A crystallized from

550 evolved, FeO-free, highly-reduced silicate melts trapped within aggregates of

551 hopper/skeletal corundum, found as ejecta in the late Cretaceous mafic-ultramafic

552 explosive-pyroclastic volcanic rocks exposed on Mt Carmel, N. Israel. Coexisting

553 minerals indicate $fO_2 \leq \Delta IW$ -6. These highly reducing conditions are attributed to

554 interaction between mantle-derived CH_4+H_2 fluids and mafic magmas near the base

555 of the crust (25-30 km).

556

557 2. Coarse-grained aggregates of hibonite + grossite + spinel + fluorite ± krotite ±

558 perovskite ± $Ca_4Al_6O_{12}F_2$ (paragenesis B) appear to represent the further evolution of

559 the silicate melts. Textural evidence shows that hibonite crystallized via the

560 peritectic reaction Crn + Liq $\rightarrow$ Hbn, and was succeeded by Hbn + Gros + Spl.

561

562 3. Native vanadium occurs as rounded inclusions in the hibonite, grossite and spinel

563 of the coarse aggregates; some of these inclusions develop into spectacular

564 dendritic clusters roughly parallel to the c axis of hibonite crystals. The presence of

565 V^0 requires $fO_2 \leq \Delta IW$ -9, suggesting a decline in fO_2 by ca 3 log units during the

566 crystallization of this assemblage.

567

568 4. Spinels in the hibonite + grossite +spinel aggregates contain 9-15 wt% V; those

569 coexisting with minor V^0 contain 3-5 wt% V, and those coexisting with abundant V^0

570 contain ≤0.5 wt% V. In high-V spinels, vanadium appears to be present as both V^{2+}

571 and V^{3+}, while in lower-Al spinels it may be present as V^{2+}; these spinels are

572 essentially stoichiometric $(Mg,V)Al_2O_4$, and are consistent with crystallization

573 temperatures around 1200°C.

574

575 5. The late crystallization of the previously-unreported phase $Ca_4Al_6O_{12}F_2$ together

576 with fluorite in the hibonite-grossite-spinel aggregates (paragenesis B) suggests that

577 crystallization of the aggregates began at T >1400 °C, cooled to the pseudo-eutectic

578 Gros + Fl + $Ca_4Al_6O_{12}F_2$ + Liq at ca 1375 °C, and remained at T >1150 °C until

579 crystallization was terminated by the volcanic eruption. This is consistent with the

580 appearance of dmisteinbergite as a quench phase in melt pockets in corundum.

581

582 **IMPLICATIONS**

583 This is the first reported terrestrial example of the crystallization of hibonite and

584 grossite from high-T silicate melts, the first terrestrial occurrence of krotite, and the

585 first report of native vanadium melts. The Mt Carmel assemblages described here

586 are analogous in many ways to those observed in many CAI inclusions in

587 carbonaceous chondrites. The inferred conditions of crystallization of the Mt Carmel

588 assemblages are similar to those of the CAIs in terms of temperature and fO_2, but

589 appear to have formed at higher pressures, ca 1 GPa. The analogies suggest that

590 the Mt Carmel system also formed in the presence of abundant H_2 and carbon.

591 These unusual mineral assemblages thus reflect a magmatic environment in which

592 fO_2 was reduced to levels that imply coexistence with fluid phases dominated by

593 hydrogen. Such environments have not previously been reported on Earth. Their

594 existence suggests previously unrecognised processes, which may be widespread in

595 connection with deepseated magmatism (Griffin et al., 2018). The observations

596 presented here emphasise the importance of immiscibility between silicate melts and

597 metallic melts under conditions of low fO_2, and this may be a significant factor in

MS 66733R revised 28-09-2018

598 element fractionation and partial melting in a metal-saturated mantle. The depth(s)

599 of origin of the CH_4-dominated volatile fluxes identified here remains to be

600 determined, but the proposed transfer of such volatiles to shallow depths by deep-

601 seated magmatism implies a deep source, and may represent an underappreciated

602 part of the deep carbon cycle

603

Acknowledgements

614

References

616 Apter, D.B., 2014. High pressure indicator minerals from the Rakefet magmatic complex
617   (RMC), Mt.Carmel, Israel. Abstracts Kimberley Diamond Symposium, Kimberley,
618   South Africa.
619 Beckett, J.R., Connolly, H.C., Ebel, D.S. (2006) Chemical processes in igneous Calcium-
620   Aluminum-rich inclusions: A mostly CMAS view of melting and crystallization. *In*
621   Lauretta, D.S., McSween,H.Y. (eds) Meteorites and the Early Solar SystemII.
622   University of Arizona Press. pp. 389-429.
623 Bhaduri, S., Bhaduri, S., 1999. Phase and microstructural evolution of heat treated
624   nanocrystalline powders in Al2O3-MgO binary system. Nanostructured materials,
625   11(4): 469-476.
626 Callister, W.D.J., 2007. Materials Science and Engineering: An introduction (7th ed.). John
627   Wiley and Sons, Inc.
628 Cámara, F., Pagano, R., Pagano, A., Bindi, L. (2018) Dellagiustaite, IMA 2017- 101. CNMNC
629   Newsletter No. 42, April 2018, page 446; Mineralogical Magazine, 82: 445–451.
630 Curien, H., Guillemin, C., Orcel, J., Steinberg, M., 1956. La hibonite, nouvelle espece
631   minerale. Compte Rendu Academie Scientifique Paris, 242: 2845–2847 (In French).
632 Davis, G.L., Tuttle, O.F., 1952. Two new crystalline phases of the anorthite composition,
633   CaO.Al2O3.2SiO2. American Journal Science, Bowen 250A: 107-114.
634 Drake, M.J., Boynton, W.V., 1988. Partitioning of Rare Earth Elements Between Hibonite and
635   Melt and Implications for Nebular Condensation of the Rare Earth Elements.
636   Meteoritics, 23(1): 75-80.

MS 66733R revised 28-09-2018

637 Esperança, S., Garfunkel, Z., 1986. Ultramafic xenoliths from the Mt. Carmel area (Karem
638   Maharal Volcano), Israel. Lithos, 19(1): 43-49.

639 Gentile, A.L., Foster, W.R., 1963. Calcium hexaluminate and its stability relations in the
640   system CaO-Al2O3-SiO2. Journal American Ceramics Society, 46:74-76.

641 Goldsmith, J.R., 1980. The melting and breakdown reactions of anorthite at high pressures
642   and temperatures. American Mineralogist, 65(3-4): 272-284.

643 Griffin, L.W. et al., 2018. Super-reducing conditions in ancient and modern volcanic systems:
644   Sources and behaviour of carbon-rich fluids in the lithospheric mantle. Mineralogy
645   and Petrology, https://doi.org/10.1007/s00710-018-0575-x.

646 Griffin, W. et al., 2016. First terrestrial occurrence of tistarite (Ti_2O_3): Ultra-low oxygen
647   fugacity in the upper mantle beneath Mount Carmel, Israel. Geology: G37910.

648 Gross, S., 1977. The Mineralogy of the Hatrurim Formation Israel. Geological Survey of Israel,
649   80 pp.

650 Grossman, J.N., Rubin, A.E., MacPherson, G.J., 1988. ALH85085: a unique volatile-poor
651   carbonaceous chondrite with possible implications for nebular fractionation
652   processes. Earth and Planetary Science Letters, 91(1): 33-54.

653 Grossman, L., Beckett, J.R., Fedkin, A.V., Simon, S.B., Ciesla, F.J., 2008. Redox conditions in
654   the solar nebula: Observational, experimental, and theoretical constraints. Reviews
655   in Mineralogy and Geochemistry, 68(1): 93-140.

656 Guo , C., Shang,S.,Du, Z.,Jablonski, P.D.,Gao, M.C., Liu, Z-K., 2015. Thermodynamic modeling
657   of the CaO-CaF2-Al2O3 system aided by first-principles calculations. CALPHAD,
658   48:113-122.

659 Ireland, T.R., Fahey, A.J., Zinner, E.K., 1991. Hibonite-bearing microspherules: A new type of
660   refractory inclusions with large isotopic anomalies. Geochimica et Cosmochimica
661   Acta, 55(1): 367-379.

662 Jerebtsov, D.A., Mikhailov, G.G., 2001. Phase diagram of CAO-Al2O3 system. Ceramica
663   International, 27,:25-28.

664 Kaminchik, J., Segev, A., Katzir, Y., 2014. The origin of intraplate alkaline mafic magmatism in
665   continental shelves: lavas and xenoliths from the Upper Cretaceous volcanos of Mt
666   Carmel. Unpublished MSc thesis, Beer Sheva University, Israel.

667 Kennedy, A.K., Lofgren, G.E., Wasserburg, G.J., 1994. Trace-element partition coefficients for
668   perovskite and hibonite in meteorite compositions. Chemical Geology, 117(1): 379-
669   390.

670 Kim, D.-G., 2011. Experimental Study and Thermodynamic Modelling of the CaO-SiO2-
671   Al2O3-CaF2 System. Master Thesis, McGill University Libraries.

672 Konovalenko, S.I., Ananyev, S.A., Garmayeva, S.S., 2012. Rare and new minerals of the
673   Tashelga-Maizaskaya zone of Gornaya Shoriya, their peculiarities and nature. Journal
674   of Siberian Federal Univeristy—Engineering and Technologies, 5: 301-310.

675 Ma, C. et al., 2011. Krotite, CaAl2O4, a new refractory mineral from the NWA 1934
676   meteorite. American Mineralogist, 96(5-6): 709-715.

677 Mikouchi, T. et al., 2009. Dmitryivanovite: A new high-pressure calcium aluminum oxide
678   from the Northwest Africa 470 CH3 chondrite characterized using electron
679   backscatter diffraction analysis. American Mineralogist, 94(5-6): 746-750.

680 Mittlefehldt, D.W., 1986. Petrology of high pressure clinopyroxenite series xenoliths, Mount
681   Carmel, Israel. Contributions to Mineralogy and Petrology, 94(2): 245-252.

682 Osborn, E.F., Muan, A., 1964. In: Levin, E.M., Robbins, C.R., McMurdie, H.F. (Eds.),
683   Phase Diagrams for Ceramists. The American Ceramic Society, Columbus, OH.

MS 66733R revised 28-09-2018

684   Vol. 1, 219 pp.

685 Ottonello, G. et al., 2013. Thermodynamic investigation of the CaO–Al2O3–SiO2 system at
686   high P and T through polymer chemistry and convex-hull techniques. Chemical
687   Geology, 346: 81-92.

688 Papike, J. et al., 2013. Developing vanadium valence state oxybarometers (spinel-melt,
689   olivine-melt, spinel-olivine) and V/(Cr+ Al) partitioning (spinel-melt) for martian
690   olivine-phyric basalts. American Mineralogist, 98(11-12): 2193-2196.

691 Peng, K.W., Zhang, P., Xie, J.G., Ma, H.L., 2012. Study on Properties of Al2O3 -CaO-SiO2-CaF2
692   Slag System. Advanced Materials Research, 396-398: 786-790.

693 Rakotondrazafy, M.A., Moine, B., Cuney, M., 1996. Mode of formation of hibonite
694   (CaAl12O19) within the U-Th skarns from the granulites of S-E Madagascar.
695   Contributions to Mineralogy and Petrology, 123(2): 190-201.

696 Righter, K., Sutton, S.R., Newville, M., Le, L., Schwandt, C.S., Uchida, H., Lavina, B., Downs,
697   R.T., 2006. An experimental study of the oxidation state of vanadium in spinel and
698   basaltic melt with implications for the origin of planetary basalt. American
699   Mineralogist, 91: 1643-1656.

700 Sass, E., 1980. Late Cretaceous volcanism in Mount Carmel, Israel. Israel Journal of Earth
701   Sciences, 29(1-2): 8-24.

702 Segev, A., Rybakov, M., 2011. History of faulting and magmatism in the Galilee (Israel) and
703   across the Levant continental margin inferred from potential field data. Journal of
704   Geodynamics, 51(4): 264-284.

705 Simon, S.B., Sutton, S.R., Grossman, L., 2007. Valence of titanium and vanadium in pyroxene
706   in refractory inclusion interiors and rims. Geochimica et Cosmochimica Acta, 71(12):
707   3098-3118.

708 Tuff, J., Wood, B.J., Wade, J., 2011. The effect of Si on metal-silicate partitioning of
709   siderophile elements and implications for the conditions of core formation.
710   Geochimica et Cosmochimica Acta, 75: 673-690.

711 Xiong, Q. et al., 2017. Super-reduced mineral assemblages in "ophiolitic" chromitites and
712   peridotites: the view from Mount Carmel. European Journal of Mineralogy, 29(4): 57-
713   570.

714 Yoneda, S., Grossman, L., 1995. Condensation of CaO-MgO-Al2O3-SiO2 liquids from cosmic
715   gases. Geochimica et Cosmochimica Acta, 59(16): 3413-3444.

716

717 **Figure Captions**

718 Figure 1. (a) Schematic evolution of a mafic magmatic system progressively reduced

719 by interaction with mantle-derived CH_4+H_2 fluids. Boxes illustrate the reconstructed

720 sequence of mineral assemblages; the relative variations in major elements through

721 this process are not to scale, but are intended to emphasize the effects of reduction,

722 crystallization and the immiscibility of silicide melts. (b) relative positions of relevant

723 fO_2 buffers at 1500 °C, 1 atm. (after Papike et al., 2016).

724

MS 66733R revised 28-09-2018

725   Figure 2. Hibonite in corundum. (a) BSE image of hibonite and associated phases in

726   melt pocket in corundum; (b) closeup BSE image of hibonite; note euhedral

727   terminations on corundum crystals, and residual glass in outermost thin wedge.

728

729   Figure 3. Zr_3TiO_8 "phase" with irregular borders crosscutting hibonite in melt pocket

730   in corundum; note presence of spinel. The Zr_3TiO_8 phase is heterogeneous on a

731   small scale, as reflected in its speckled appearance, and breaks up in contact with

732   Ca-Mg-Al-oxide glass (black), suggesting that both were melts during emplacement

733   of the Zr_3TiO_8 phase.

734

735   Figure 4. Hibonite-grossite aggregates. (a) large grain of hibonite-grossite aggregate

736   with mm-size spheres of native V (V^0); (b) transmitted-light photo of transparent

737   specimen, enclosing black spinel grain and rods of V^0; (c) phase map of (b) showing

738   paragenesis of aggregates. Comparison of (b) and (c) shows that each tiny V^0

739   inclusion represents the end of a long rod or dendrite branch.

740

741   Figure 5. Hibonite-grossite aggregate illustrating crystallization sequence. (a-e)

742   resorbed corundum in hibonite reflects peritectic reaction L + Cor → Hib, followed by

743   grossite+ spinel ± krotite; fluorite and $Ca_4Al_6F_2O_{12}$ crystallize last. V^0 appears to

744   separate from melt at temperatures near the peritectic reaction, as few inclusions of

745   V^0 are found in the corundum; (f) aggregate showing late crystallization of the F-

746   bearing perovskite phase; (g-h) BSE image and phase distribution map showing

747   intergrowth of perovskite and fluorite.   Dark grey phase in BSE image is ?gibbsite,

748   which replaces fluorite and leaves geode-like open cavities.

749

750   Figure 6. (a) Phase map of aggregate showing randomly-oriented hibonite plates,

751   with narrow resorbed corundum cores, and hibonite+grossite intergrowths at edges

752   of plates. Grossite (light green) is euhedral against CaF_2 (orange), the last phase to

753   crystallize. Spinels (blue-green) are euhedral. (b) Element-distribution maps for Ca

754   and Al.

755

756   Figure 7. Parageneses of vanadium "balls". (a) vanadium spheroids with spinel,

757   grossite and fluorite; (b) BSE image of spheroid #1 in (a), showing intergrowth of Mn-

758   rich and Mn-poor V; (c) BSE image and map of V distribution in spheroid #2 in (a),

22

MS 66733R revised 28-09-2018

759 showing intergrowth of native V with V-Mn alloy; (d) V spheroid partially altered to

760 unidentified Ca-V phase(s).

761

762 Figure 8. High-Al (mean 15 wt%) V balls in nest of grossite between hibonite laths,

763 with outlines suggesting they were fluid when trapped. Note euhedral $Ca_4Al_6O_{12}F_2$

764 protruding into fluorite, the last phase to crystallize. The coexistence of $Ca_4Al_6O_{12}F_2$

765 with grossite and fluorite constrains the crystallization of the assemblage to >1150 °C

766 (Kim, 2011); see Fig. SD5.

767

768 Figure 9. 3D-µCT images of dendritic native V in hibonite. (a) low-resolution image

769 of two dendrite clusters in a hibonite grain. (b) magnified view, looking parallel to

770 (0001) face; red to orange, vanadium; green, open cavities; (c) view from starting

771 point, toward crystal face along c axis. Tendrils radiate off irregular clumps of V^0.

772 Some consist of a series of joined balls that extend toward the crystal surface, then

773 sprout into 3-D dendritic networks with clear breaks and restarts at intermediate

774 crystal planes. The patterns suggest nucleation of V melts on the surface of growing

775 crystals. (See animated version in Figure SD3).

776

777 Figure 10. Chondrite-normalized trace-element abundances. (a) hibonite in hibonite-

778 grossite aggregates; (b) mean hibonite in aggregates *vs* mean hibonite included in

779 corundum; (c) coexisting hibonite-grossite pairs, linked by colour.

780

781 Fig 11. Phase diagrams constraining temperatures of crystallization. (a) two "end-

782 member" versions of the $CaO-Al_2O_3$ binary, showing reactions as eutectics (Guo et

783 al., 2015; black lines) or peritectics (Jerebtsov and Mikhailov, 2001; red lines); red

784 star shows average bulk composition of hibonite-grossite aggregates (Table 1); (b)

785 Al-corner of $CaO-MgO-Al_2O_3$ liquidus diagram (after data from FactSage);

786 intermediate Ca-Mg-Al oxides (1-4) have not been identified in this study.

787

788 Figure 12. $CaO-Al_2O_3-SiO_2$ liquidus diagram at 1 atm. pressure (after Osborne and

789 Muan,1960; Gentile and Foster,1963), showing compositions of hibonite-grossite-

790 spinel aggregates, and calculated and analysed melts; red arrows show the effects

791 of desilication, and crystallization of hibonite+grossite aggregates.

792

MS 66733R revised 28-09-2018

793 Figure 13. Calculated liquidus diagrams of CaO-Al_2O_3-SiO_2 system at 3 pressures,

794 after Ottonello et al. (2013). Trd/Cr, tridymite/cristobalite; Qz, quartz; Wo,

795 wollastonite; An, anorthite; Mul, mullite; Rk, rankinite; Gh, gehlenite; Crn, corundum;

796 Hbn, hibonite; Gros, grossite, Grs, grossular; Krt, krotite; Lrn, larnite. Note the

797 shrinkage of the fields of anorthite and gehlenite, and the expansion of the krotite

798 and hibonite fields, with increasing P, and disappearance of the liquidus field of

799 grossite above ca 1 GPa.

800

801 Figure 14. Analyzed glasses and calculated melts. (a) trace-element spectra of

802 melts calculated using distribution coefficients of Kennedy et al. (1994; K94), and the

803 analyzed glass coexisting with hibonite in Paragenesis A; (b) trace-element spectra

804 of glasses described in text; (c) comparison of calculated melts with hibonite-bearing

805 glasses from Lance and Murchison meteorites (Ireland et al., 1991).

806

807 **Tables**

808 Table 1. Major-element compositions of selected phases, and bulk aggregates

809

810 Table 2. Trace-element compositions of selected phases

811

812 Table 3. Calculated melts and estimated partition coefficients

813

814

815 **Supplementary Data**

816 Figure SD1. Location map showing position of the study area within the Levant-

817 Arabia context (a) and geological map (b) with sample localities. Volcanic centres on

818 Mt Carmel are marked by yellow dots.

819

820 Figure SD2. Aggregate showing apparent quench structure; thin hibonite tablets

821 radiate from coarse crystals of grossite + spinel, suggesting crystallization from a

822 substrate into liquid.

823

824 Figure SD-3. 3D-CT video of vanadium dendrites in hibonite crystal. Red-orange,

825 vanadium; green, open cavities.

826

827 Figure SD4. Interelement correlations in V-rich spinels of paragenesis B.

828

829 Figure SD5. CaF_2-$CaAl_2O_4$ binary (after Kim, 2011) showing crystallization of

830 $Ca_4Al_6F_2O_{12}$ from ca 1500 °C to 1390 °C, and instability of $Ca_4Al_6F_2O_{12}$ + grossite +

831 CaF_2 below *ca* 1150°C. Red arrow shows possible evolution of the late melts in the

832 hibonite-grossite-spinel aggregates.

833

834

835 **Methods**

836

837 Samples were mounted in epoxy blocks, polished and coated with carbon. A Zeiss

838 EVO MA15 scanning electron microscope (SEM) at the Geochemical Analysis Unit

839 (GAU), Macquarie University, Sydney, Australia was used to capture Backscattered

840 Electron (BSE) images and Energy Dispersive X-ray spectrometry (EDS) was used

841 to map the elemental composition of the samples. An accelerating voltage of 15 keV

842 and a beam current of 1 nA was used.

843 Major elements were determined by electron microprobe (EMP) using a CAMECA

844 SX100 equipped with five wavelength-dispersive spectrometers at the Macquarie

845 University GeoAnalytical (MQGA; formerly GAU), Macquarie University, Sydney,

846 Australia. Analyses were performed using a focused beam (1-2 μm) with an

847 accelerating voltage of 15 keV and a beam current of 20 nA. Standards were a suite

848 of natural and synthetic minerals. Peak counting varied between 10 – 20 s, and

849 background was counted for 5 – 10 s on either side of the peak. Oxygen and carbon

850 were measured directly; matrix corrections were carried out by the ZAF software.

851 Major elements also were determined by electron microprobe (EMP) using a JEOL

852 8530F electron microprobe equipped with five wavelength dispersive spectrometers

853 at the Centre for Microscopy Characterisation and Analysis (CMCA), The University

854 of Western Australia, Perth, Australia. Analyses were preformed using a fully

855 focussed beam with an accelerating voltage of 15 keV, a beam current of 15 nA.

856 Standards were a suite of natural and synthetic minerals. On-peak counting times

857 were 30 seconds for all elements. X-ray intensity data was corrected for Time

858 Dependent Intensity (TDI) loss (or gain) using a self-calibrated correction for Si k☐,

859 Ti k☐, Mn k☐, Na k☐, K k☐ and mean atomic number (MAN) background corrections

860 were used throughout (Donovan & Tingle, 1996; Donovan et al., 2016). Unknown

861 and standard intensities were corrected for deadtime. Oxygen was measured, matrix

862 corrections and ZAF correction were applied throughout.

863 Trace elements were obtained using a Photon Machines Excite 193 nm ArF

864 EXCIMER laser system coupled to an Agilent 7700x ICP-MS at the GAU, Macquarie

865 University, Sydney, Australia. Detailed method descriptions have been given by

866 (Jackson et al., 2004). The ablation conditions included beam size (50 μm), pulse

867 rate (5Hz) and energy density (7.59 J/cm2). Ablation was performed in an HelEx II

868 cell and helium was used as the carrier gas at a total flow rate of 0.825L/min.

869 Average analytical runs comprised of 20 analyses, 2 analyses of reference materials

870 and 10 analyses of unknowns, bracketed by two analyses of NIST610 standard glass

871 at the beginning and end of each run. Analyses consisted of 60 second of

872 background and 120 seconds of ablation. Trace element concentrations were

873 calculated from the raw signal data using the on-line software package GLITTER

874 ((Griffin et al., 2008); www.mq.edu.au/GEMOC). GLITTER calculates the element

875 concentrations and relevant isotopic ratios for each mass sweep and displays them

876 as time-resolved data. This allows homogeneous segments of the signal to be

877 selected for integration. GLITTER then corrects the integrated ratios for ablation-

878 related fractionation and instrumental mass bias by calibration of each selected time

879 segment against the identical time-segments of the standard glass (NIST610 using

880 the GeoReM values). An appropriate major element was used as an internal

881 standard to quantify trace element concentrations and the synthetic BCR2 and

882 NIST612 glasses were used as reference materials (GeoReM).

883 FIB foils from the region of interest were prepared for TEM using a dual- beam FIB

884 system (FEI Nova NanoLab 200). High Angle Annular Dark Field Scanning

885 Transmission Electron Microscopy (HAADF- STEM) imaging and element mapping

886 were carried out using an FEI Titan G2 80- 200 TEM/STEM with ChemiSTEM

887 Technology operating at 200 kV at the Centre for Microscopy Characterisation and

888 Analysis (CMCA), The University of Western Australia, Perth, Australia. The element

889 maps were obtained by energy dispersive X- ray spectroscopy using the Super- X

890 detector on the Titan with a probe size ~1 nm and a probe current of ~0.25 nA. Total

891 acquisition times of 20- 30 minutes were used to obtain good signal- to- noise ratios.

892 Electron diffraction was carried out using a field limiting aperture that selected an

893 area approximately 400nm in diameter.

MS 66733R revised 28-09-2018

894   For X-ray micro-computed tomography (µCT), the grain was mounted on a finger of

895   rigid PVC plastic with double-sided tape and a separate tomogram was collected for

896   each grain using a µCT system (Versa 520 XRM, Zeiss) running Scout and Scan

897   software (v11.1.5707.17179, Zeiss) at the CMCA. Samples were scanned at 50 kV

898   and 77 µA with the source detector positions set to -17.7 and 117 mm, respectively.

899   An LE1 source filter was applied to screen out low energy X-rays. A 0.4X objective

900   lens was used together with 2x camera binning to achieve an isotropic voxel

901   resolution of 9 µm. Each scan comprised 2501 projections through 360o with an

902   exposure of 3s for each projection. Raw data were reconstructed using

903   XMReconstructor software (v11.1.5707.17179, Zeiss) following a standard centre

904   shift and beam hardening correction. The standard 0.7 kernel size recon filter setting

905   was also used. The visualization and analysis of data generated from µCT scans

906   were performed using Avizo (v8.1.1, FEI) software

907

Table 1. EDS and EMP analyses of selected phases

	hibonite							
	hibonite in corundum				hibonite in aggregates			
	SEM-EDS		EMP		SEM-EDS		EMP	
wt%	n=24	stdev	n=6	stdev	n=48	stdev	n=13	stdev
SiO2	0.43	0.38	0.16	0.12			0.03	0.04
ThO2			0.15	0.05				
ZrO2	0.59	0.59	0.46	0.26				
HfO2								
Ti2O3	2.95	1.59	2.61	1.5			0.02	0.02
Al2O3	83.2	1.38	82.8	4.52	90.1	0.72	89.80	0.99
Cr2O3	1.00	0.56					0.02	0.01
La2O3	0.19	0.1	n/a					
Ce2O3	1.18	1.16	3.46	2.9				
Sc2O3			0.01	0.02				
P2O5								
Y2O3			0.06	0.05				
VO			0.01	0.01	0.90	0.71	0.60	0.39
FeO			0.01	0.01				
MnO			0.06	0.06				
MgO	2.07	0.21	1.88	0.65	0.51	0.20	0.66	0.19
CaO	6.49	0.74	5.78	1.56	8.31	0.15	8.30	0.11
F							0.20	0.05
C								
Totals	98.07		97.45		99.82		99.63	

Atomic Prop.								
Si	0.15		0.06	0.04				
Th			0.01	0.004				
Zr	0.10		0.08	5				
Hf								
Ti	0.78		0.79	0.41				
Al	34.40		35.4	1.13	36.9	0.25	37.31	0.56
Cr	0.26							
La	0.02							
Ce	0.15		0.47	0.40				
V					0.21	0.16	0.17	0.11
Fe								
Mn			0.02	0.02				
Mg	1.04		1.02	0.37	0.31	0.11	0.35	0.1
Ca	2.45		2.23	0.55	3.10	0.06	3.13	0.06
F							0.20	0.10
O	60.65		59.9	0.52	59.4	0.14	58.91	0.56

C

	grossite				w/ Hbn+Crn	spinels			
	SEM-EDS		EMP		SEM-EDS	high-V spinel		medium-V-spinel	
			EMP			EMP		EMP	
	n=41	stdev	n=12	stdev	n=1	n=9	stdev	n=10	stdev
			0.01	0.01		0.04	0.02		
					3.9	0.40	0.50	0.03	0.03
	78.5	0.26	77.02	0.47	72.1	60.92	1.96	69.84	1.2
						1.40	0.18	0.22	0.08
			0.10	0.12					
			0.15	0.10		16.41	2.60	3.95	1.01
					3.0	3.68	2.55	0.86	0.41
			0.05	0.02	20.6	19.75	0.89	23.95	0.63
	21.4	0.18	21.24	0.18		0.25	0.06	0.2	0.04
	99.9		98.57		99.6	102.85		99.05	
						0.02	0.01		
			0.01	0.01	1.13	0.13	0.16		
	33.3	0.09	33.0	0.39	29.43	29.30	0.15	29.63	0.77
						0.47	0.00		
			0.05	0.02		6.27	0.99	1.21	0.4
					0.88	1.31	0.91	0.26	0.12
					10.63	12.16	0.48	12.85	0.22
	8.30	0.07	8.21	0.11		0.11	0.03	0.07	0.03
	58.4	0.03	58.7	0.49	57.92	50.55	1.52	58.0	0.51

‖ | |

low-V spinel		perovskite		$Ca_2Al_6O_{13}F_2$		fluorite		
EMP		EMP		EMP		SEM-EDS		EM
n=10	stdev	n=3	stdev	n=10	stdev	n=20	stdev	n=6
0.02	0.03							
		1.78	0.2					
0.12	0.28	48.00	0.29					
71.81	0.84	2.68	0.09	54.3	1.1			
0.02	0.02	0.15	0.01					
		0.39	0.01	0.40	0.04			0.68
0.24	0.27	1.58	0.03					
		0.01	0.01					
0.46	0.39	0.11	0.02	0.04	0.04			
26.90	0.83			26.9	0.83			
0.18	0.05	39.49	0.20	38.2	0.6	50.6*	0.74	51.34*
		1.27	0.14	6.54	0.11	43.3		46.71
						5.43		
99.8		95.46		99.56		100.0		98.7

* Ca wt %

low-V spinel		perovskite		$Ca_2Al_6O_{13}F_2$		fluorite		
		0.39	0.05					
		17.45						
29.33	0.32	1.43	0.05	24.3	0.42			
0.01	0.01	0.05	0.01					
0.07	0.07	0.58	0.01					
		0.01	0.01					
0.13	0.11	0.04	0.01	0.01	0.01			
13.90	0.42							
0.07	0.02	19.23	0.16	15.55		35.4		34.16
		1.83	0.21	7.85		63.8		65.57
58.27	0.06	58.87	0.4	52.11	0.29			

| | || | || | || 11.3 | |

IP stdev	Zr-Ti oxides						
	(Zr,Al)TiO3		Zr3TiO7		ZrTiO3		(Zr,Ti
	SEM-EDS		SEM-EDS		SEM-EDS		SEM-
	n=5	stdev	n=8	stdev	n=12	stdev	n=12
	1.01	1.54					
	49.1	5.41	66.1	4.33	78.2	1.53	92.3
	0.24	0.54	0.43	0.64	1.38	0.25	1.48
	34.4	2.66	25.2	2.43	16.2	1.31	4.68
	3.33	1.64	2.89	1.70	0.89	0.16	0.21
0.02	2.03	1.85	0.86	0.18	0.27	0.49	
			1.50	1.34	0.48	0.39	
	1.33	0.7	0.77	0.37	0.44	0.17	
1.36	3.26	2.15			0.68	0.27	0.13
	94.7		97.8		98.5		98.8
	0.70	0.97					
	15.2	1.83	23.7	2.07	29.4	1.02	37.2
			0.09	0.13	0.20	0.16	0.35
	18.3	1.37	15.5	1.17	10.5	0.84	3.27
	2.48	1.21	2.34	1.37	0.81	0.14	
			0.58	0.78	0.31	0.25	
	1.33	0.33	0.63	0.31	0.51	0.19	
0.71	2.21	1.45	0.55	0.15	0.56	0.22	0.11
0.72	58.5	1.59	56.2	0.69			

|| || || ||

Vana

)2O3		Vanadium				V9(M	
-EDS		SEM-EDS		EMP		SEM-EDS	
stdev		n=28	stdev	n=5	stdev	n=4	stdev
	Si	0.49	0.48	0.42	0.22	0.67	0.25
	Ti						
2.78	Zr						
0.23							
1.39				0.01	0.02		
0.29	Al			0.32	0.5	4.28	0.1
	Cr	1.60	0.39	*1.6*		0.71	0.77
	V	96.2	1.3	95.2	3.23	88.7	2.83
	Fe			0.03	0.01		
	Mn	1.53	0.99	1.21	0.63	5.12	1.92
	Mg						
0.18	Ca	0.19	0.22	0.09	0.06	0.54	0.41
		100.0		98.9		100.0	

0.59
0.06
0.91

0.16

||

dium						reconstructed
n,Al)			V4Al			aggregates
EMP		SEM-EDS		EMP		
n=5	stdev	n=7	stdev	n=7	stdev	n=9
0.52	0.11	0.43	0.06	0.38	0.04	0.02
0.01	0.01					
0.15	0.11			0.20	0.03	
3.94	1.27	11.8	0.40	11.58	0.25	79.5
0.71		0.44	0.50	*0.44*		
79.83	6.86	85.2	0.66	83.37	0.76	0.50
0.01	0.01					
12.20	6.55	2.19	0.39	2.09	0.07	
						2.1
0.41	0.35			0.21	0.17	16.2
						1.0
97.78		100.1		98.28		99.3

Table 2. Trace elements (LAM-ICPMS)

	Hibonite A		Hibonite B		Grossite B		Spinel B	
	mean	stdev	mean	stdev	mean	stdev	mean	stdev
	n=2		n=9		n=7		n=4	
Li	59.1		<1.5				7.46	0.98
Be	10.0		<0.2				<0.3	
B	19.2		30.0	16.7	27.9	19.0	29.9	5.83
Na	45		24.0	13.3	90.7	12.0	332	267
Mg	11863		3700	875	542	49	149364	14403
Si	4777		1302	540	1017	676	1135	185
P	3.4		55.1	23.6	31.6	22.4	55.8	14.4
K	104		<5		<5		48.2	63.2
Sc	171		<0.5		0.22	0.37	<0.7	
Ti	16777		291	206	58.4	32.1	152.3	24.3
V	1.8		6002	3358	1804	748	25517	2437
Cr	0.2		13.9	9.30	6.55	5.0	76.5	20.2
Mn	34		207	192	249	139	4361	1402
Fe	<20		67.4	23.1	166	49	<30	
Co	<0.1		<0.1		0.05	0.06	<0.2	
Ni	3.5		<0.5		0.24	0.26	<0.5	
Cu	<0.2		<0.2		0.01	0.02	<0.3	
Zn	0.02		<1		0.60	0.75	9.60	2.0
Ga	7.6		0.42	0.4	0.03	0.05	<0.2	
Rb	<0.5		<0.2		<0.15		<0.2	
Sr	9889		76.4	26.9	34.7	10.1	<7	
Y	407		3.10	0.6	3.89	0.77	0.06	0.01
Zr	3468		5.21	3.7	0.12	0.24	<0.1	
Nb	<0.1		0.12	0.1	<0.01		<0.05	
Cs	<0.1		<0.1		<0.01		<0.1	
Ba	153		10.8	3.7	6.18	1.31	1.54	2.1
La	5758		7.73	5.1	0.09	0.11	<0.04	
Ce	15222		20.7	16.5	0.24	0.29	<0.05	
Pr	1181		3.38	4.7	0.03	0.04	<0.04	
Nd	3716		5.80	4.0	0.07	0.20	<0.02	
Sm	493		1.45	1.2	0.09	0.08	<0.3	
Eu	54		0.22	0.1	0.09	0.03	<0.06	
Gd	277		0.69	0.5	0.06	0.09	<0.3	
Tb	30.7		0.14	0.2	0.02	0.02	<0.05	
Dy	136		0.55	0.3	0.31	0.15	<0.2	
Ho	19.9		0.11	0.2	0.05	0.05	<0.03	
Er	42		0.13	0.1	0.27	0.08	<0.1	
Tm	3.5		0.01	0.02	0.03	0.03	<0.04	
Yb	46		0.05	0.08	0.18	0.14	<0.2	
Lu	1.5		<0.03		0.02	2.00	<0.04	
Hf	227		0.21	0.2	0.01	0.02	<0.2	
Ta	<0.1		0.17	0.1	<0.01		<0.15	
Pb	<0.2		<0.12		<0.15		<0.2	

Th	2807		10.5	9.5		<.05			<0.04
U	443		2.35	1.2		0.04	0.01		<0.04

Table 3. Analyzed glasses and calculated melts

Major Elements

	hibonite in corundum n=24	Calc. Melt Kennedy	Calc. Melt this work	Melt analyzed n=6	hibonite in aggregates n=48	Calc. Melt Kennedy	Calc. Melt this work
SiO2	0.43	*215*	27.8	31.0	0.3		15
ZrO2	0.59	1.5	2.5	0.4			
Ti2O3	2.95	2.3	2.2	0.5	0.03		0.02
Al2O3	83.2	42	44.8	40.6	90.1	45	38
Cr2O3	1.00						
La2O3	0.19	0.03					
Ce2O3	1.18	0.24					
Sc_2O_3				0.69			
V2O5					0.90		
FeO							
MnO							
MgO	2.07	4.1	1.7	0.8	0.51	1.0	0.3
CaO	6.49	20	21.0	19.2	8.31	26	21
BaO				0.9			
SrO	0.6	0.8					
K2O				3.2			
Na2O				1.0			
SO2				0.7			
sum	98.7		100.0	99.0	100.2	72.0	73.7

Trace elements

| | Hbn in Crn | Hbn in agg | Hbn in Crn | hib in agg | Partition coefficients hibonite/melt | | |
	n=2	n=8	hi-Ce glass	hi-Ba glass	Kennedy	Ireland	Dr/Boyn
Li	59.1	<0.5	0.25				
Be	10.0	0.1	0.32	0.13			
B	19.2	34.0	0.005	0.003			
Na	45	24.8	0.018	0.002			
P	3.4	57.5	0.018	0.90			
K	104	15.2	0.100	0.012			
Sc	171	<0.2	0.67		0.31	1.4	
Ti	16777	238	0.20	0.071	1.25		
V	1.8	5092	0.010	128		0.30	
Cr	0.2	11	0.007	0.32			
Mn	34	159	0.082	7.08			
Fe	<20	70		0.078			
Co	<0.1	0.1		0.13			
Ni	3.5	0.8	0.098	0.047			
Cu	<0.2	<0.2					
Zn	0.02	1.02	0.000	0.001			
Ga	7.6	0.62	0.41	0.090			
Rb	<0.5	0.31		0.27			
Sr	9889	72.9	8.28	0.36	0.63	0.86	0.53
Y	407	3.10	0.53	0.041		1.1	
Zr	3468	4.32	0.35	0.000	0.36	1.2	
Nb	<0.1	0.13		0.03	0.18	0.19	
Cs	<0.1	0.08		0.66			
Ba	153	10.2	0.084	0.001	0.03	2.5	
La	5758	7.86	7.34	0.35	6.20	6.0	7.2
Ce	15222	20.5	9.66	0.46	5.15	4.5	
Pr	1181	3.55	7.63	0.76	4.35	4.5	
Nd	3716	5.80	6.65	0.35	3.55	4.0	
Sm	493	1.45	4.49	0.41	1.70	2.9	2.7
Eu	54	0.22	2.47	0.24	1.30	0.4	0.53
Gd	277	0.86	2.85	0.20	0.92	3.0	1.49
Tb	30.7	0.16	1.86	0.17	0.64	2.2	
Dy	136	0.54	1.18	0.061	0.38	1.4	
Ho	19.9	0.18	0.78	0.07	0.26	1.1	
Er	42	0.19	0.56	0.019	0.20	0.58	
Tm	3.5	0.04	0.30	0.022	0.12	0.34	
Yb	46	0.16	0.56	0.010	0.06	0.22	0.1
Lu	1.5	<0.2	0.13		0.04	0.22	
Hf	227	0.26	0.91	0.0004	0.73	4.0	
Ta	<0.1	0.15		0.30			

Pb	<0.2	<0.2			
Th	2807	9.75	3.94	0.41	1.15
U	443	2.14	3.29	0.11	0.07

	meteoritic glasses with hibonite (Ireland et al., 1991)			Calculated melts - trace elemer			melt w/
	Lance	Mur 7-228	Mur 7-753	melt with Hbn in Crn			
				Kennedy	Ireland	Dr/Boyn	Kennedy
SiO2	36.7	40.2	40.1				
Ti2O3	1.3	1.6	2.7				
Al2O3	29.2	27.7	27				
MgO	6.8	7.3	7.3				
CaO	25.5	22.9	22.6				
sum	99.5	99.7	99.7				
Trace elements							
Sc	81	37	6.6	552	122		
Ti				13421			190
V	848	864	1154		6		
Sr	307	37	27	15697	11499	18658	116
Y	18	28	2.7		370		
Zr	169	83	16	9633	2890		12.0
Nb	8.6	8.9	9.8				0.74
Ba	27	0.59	5.9	5116	61		341
La	6.4	1.8	0.25	929	960	800	1.27
Ce	17	5.6	1.2	2956	3383		3.98
Pr	2.5	0.86	0.16	271	262		0.82
Nd	13	4.7	0.71	1047	929		1.63
Sm	4.3	1.8	0.71	290	170	183	0.85
Eu	0.49	0.66	25	41	128	102	0.17
Gd	4.4	2.9	0.18	302	92	186	0.93
Tb	0.83	0.6	0.07	48	14		0.25
Dy	5.8	4.5	0.41	357	97		1.43
Ho	0.99	1.02	0.11	78	18		0.71
Er	2.8	4.3	0.41	209	72		0.94
Tm	0.45	0.76	0.26	30	10		0.36
Yb	3.0	5.9	3.4	761	208	457	2.61
Lu	0.16	0.89	0.08	39	7		
Hf	1.24	0.68		310	57		0.36
Th				2441			8.48
U				6336			30.6

analyzed glasses Mt Carmel			
hi-Ce glass		hi-Ba glass	
n=65	stdev	n=25	stdev
45.0	2.8	43.6	2.2
1.94	1.3	8.24	1.9
1.95	1.2	1.24	0.3
26.3	6.1	34.0	2.3
0.42	0.7		
1.72	1.3		
4.6	3.0	0.12	0.2
14.0	3.2	4.38	0.7
		4.04	0.5
1.22	1.2	0.41	0.1
0.41	0.3	3.76	1.1
1.34	0.9		
97.6		99.8	

n=6	n=22
239	14.7
31	1.1
4076	9928
2466	11672
189	64
1040	1319
256	34
84731	3357
175	40
28	34
418	23
3032	898
3.9	1.1
35	17
2.6	1.0
1035	1145
18.7	6.9
2.5	1.2
1194	204
763	75
9838	26409
13.0	3.8
0.14	0.12
1826	12920
785	22
1576	45.0
155	4.7
559	16.8
110	3.5
22	0.9
97	4.3
16	1.0
115	8.9
26	2.5
75	9.9
11	1.9
82	16.4
12	3.0
249	627
1.2	0.5

3.9	8.3
712	23.7
135	19.4

	ıts	
	Hbn in aggregates	
	Ireland	Dr/Boyn
	16973	
	85	138
	2.8	
	3.6	
	0.70	
	4.1	
	1.31	1.09
	4.56	
	0.79	
	1.45	
	0.50	0.54
	0.51	0.41
	0.29	0.58
	0.07	
	0.39	
	0.16	
	0.32	
	0.12	
	0.71	1.56
	0.07	

Figure 1

Figure 2
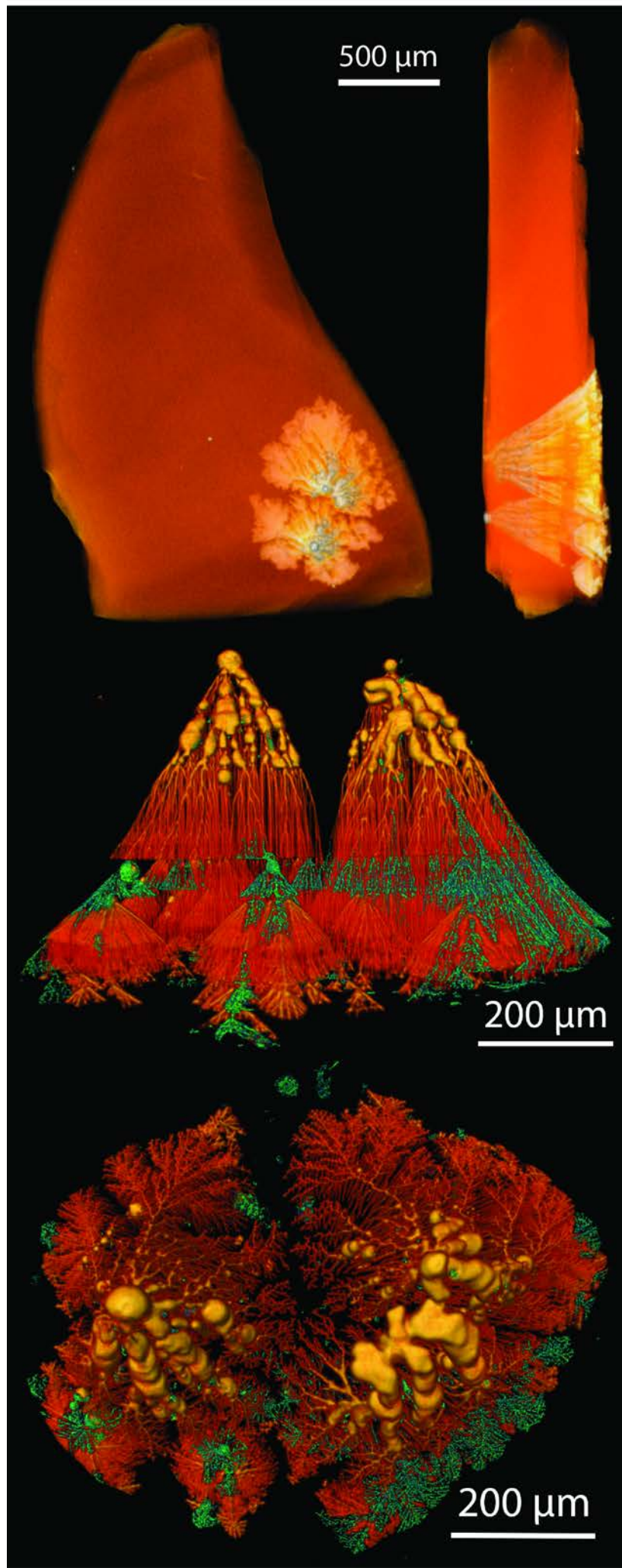
a)

FeTiSi

100 μm

hibonite

b)

Glass

50 μm

Figure 3

Corundum

Ti Nitride

Spinel

Zr_3TiO_8

Hibonite

50 μm

Figure 4

a) — 2 mm — V balls

b) — 250 μm

c) grossite — spinel 2.5% V — CaF₂ — hibonite — V inclusions — 250 μm

Figure 5

a) 250 µm

b) corundum (resorbed)
grossite
CaF$_2$
Ca$_4$Al$_6$F$_2$O$_{12}$
spinel
hibonite

c) Ca

d) Al

e) Mg V

f) perovskite
grossite
fluorite
spinel 15% V
hibonite
500 µm

g) grossite
50 µm

h) Al F Ti
perovskite
fluorite

Figure 6

a)

Laths = hibonite

Dark cores = corundum

500 µm

b) **Al** **Ca**

Figure 7

a)
#1
hibonite
fluorite
grossite
#2
50 μm

b)
10 μm

c)
10 μm

d)
grossite
fluorite
spinel
hibonite
corundum
100 μm

Al V

Ca

Figure 8

Figure 9

Figure 10
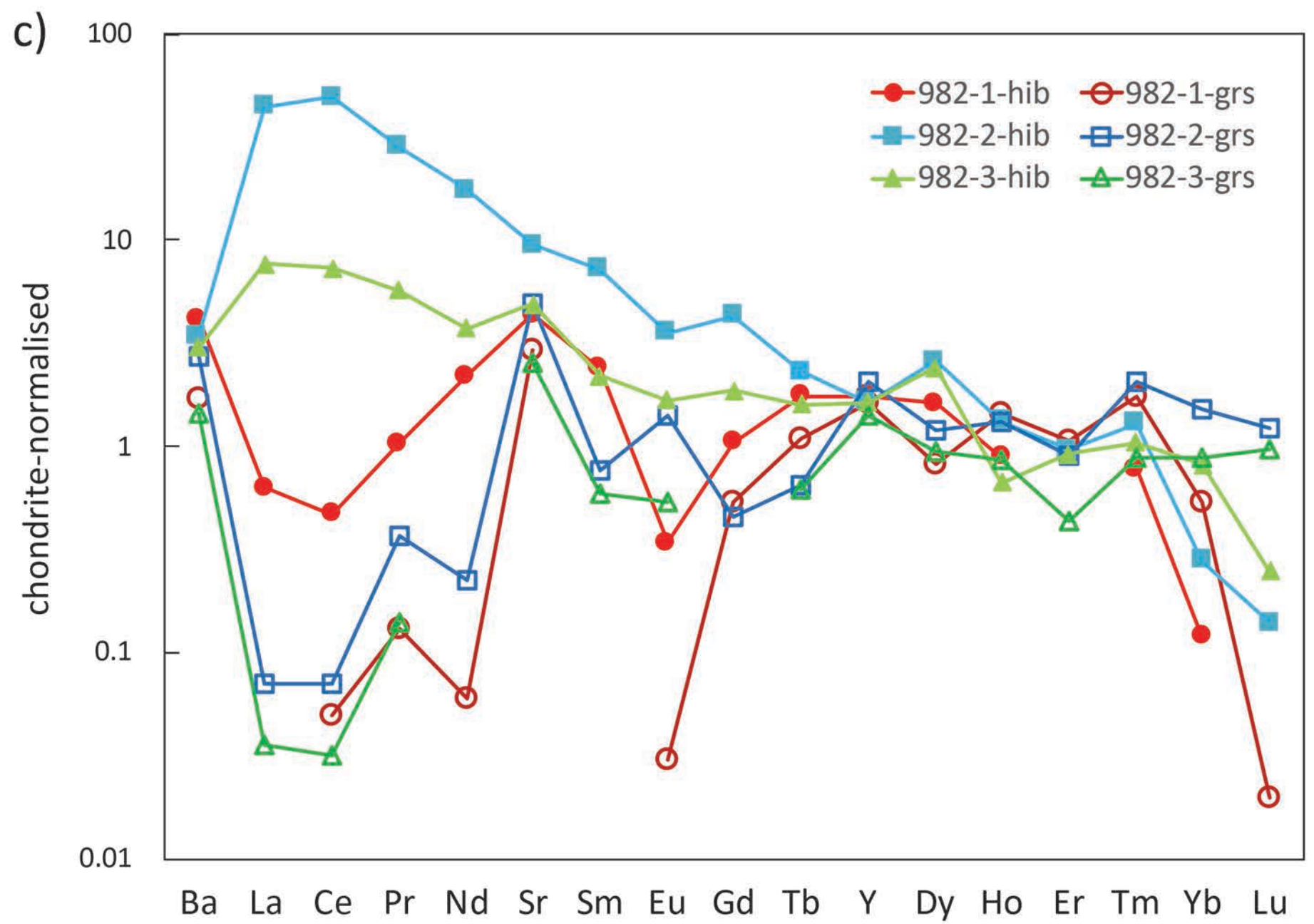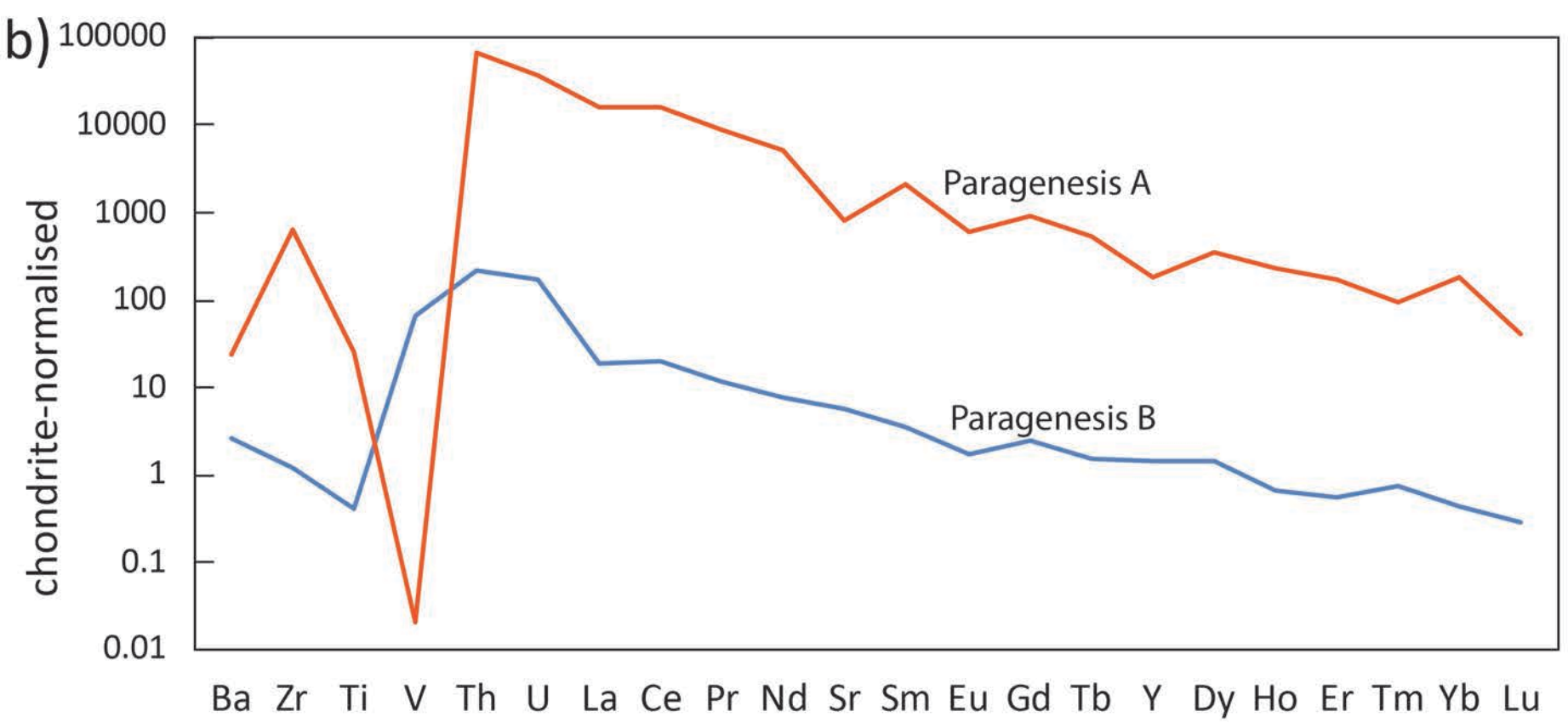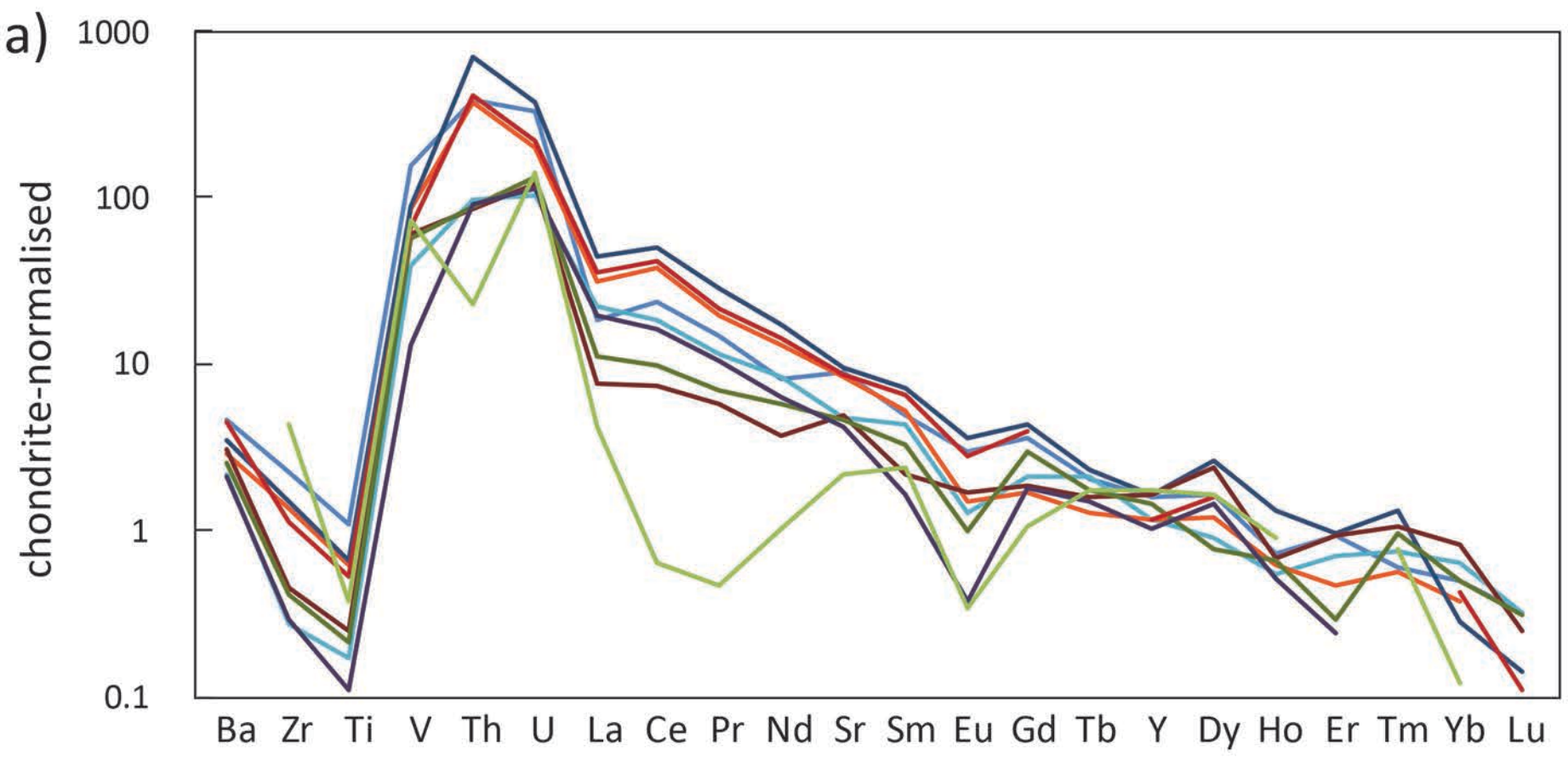
Figure 11
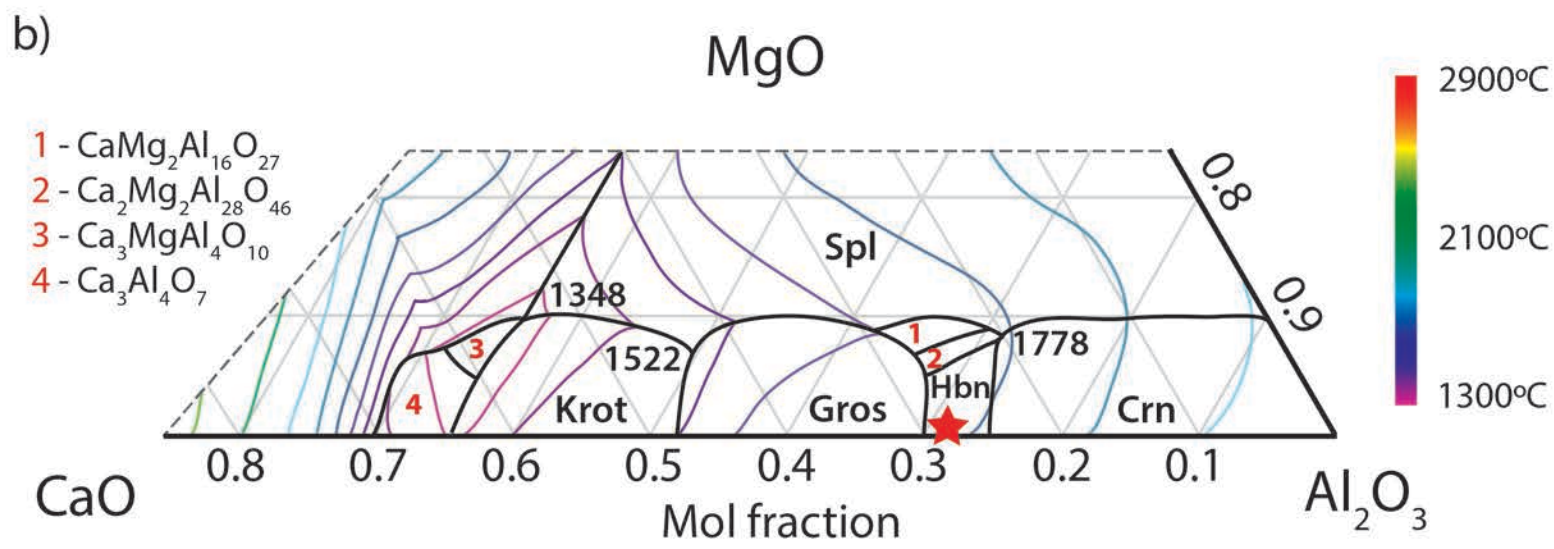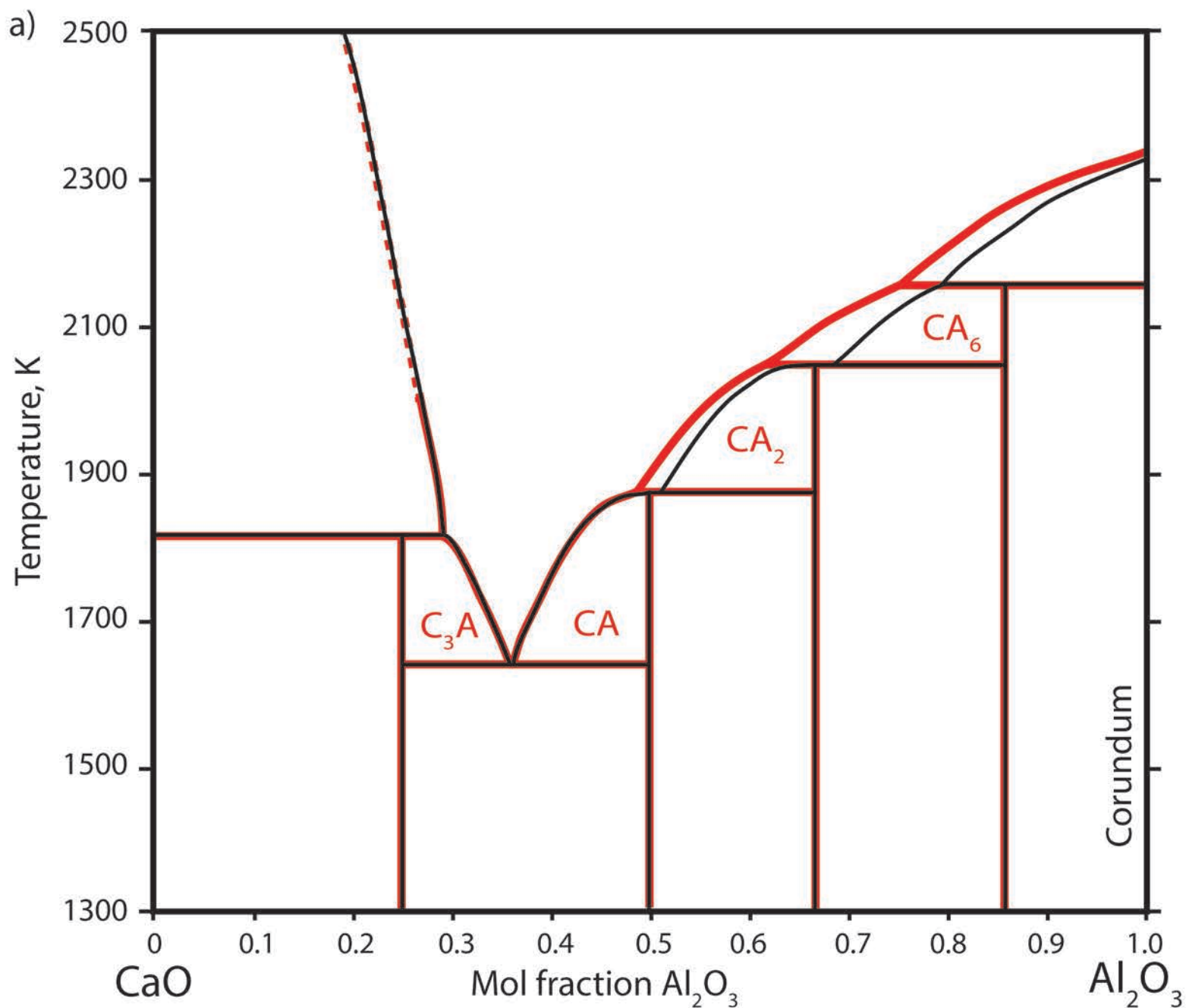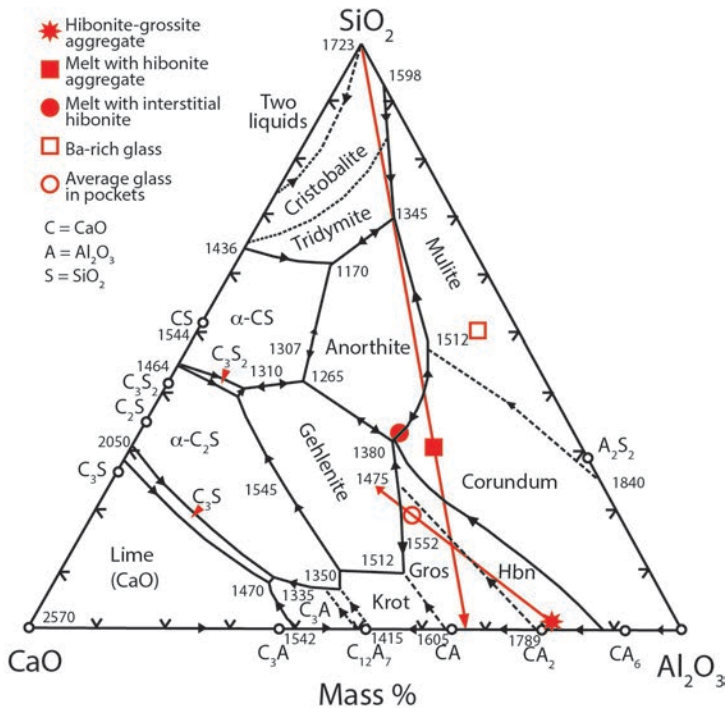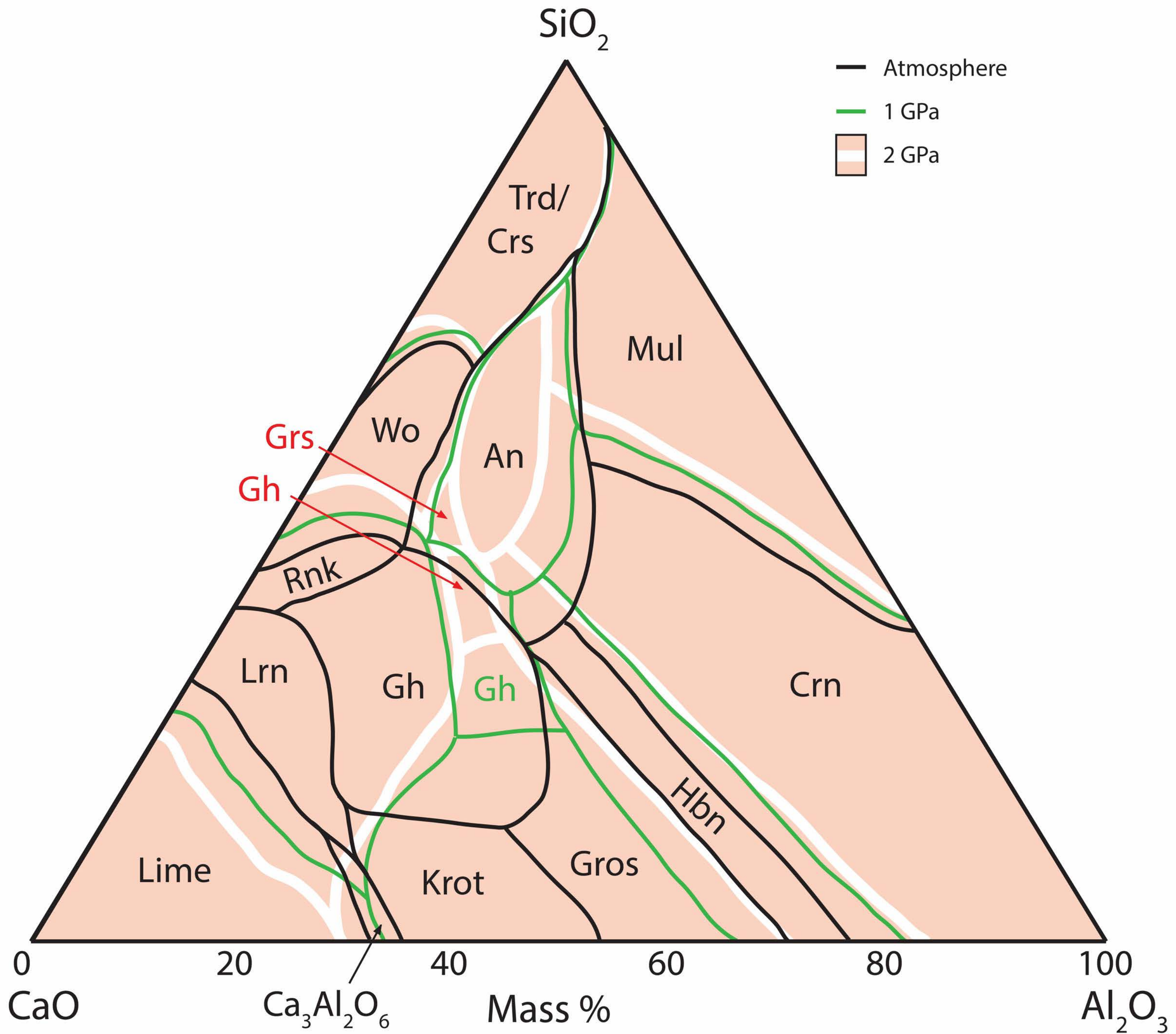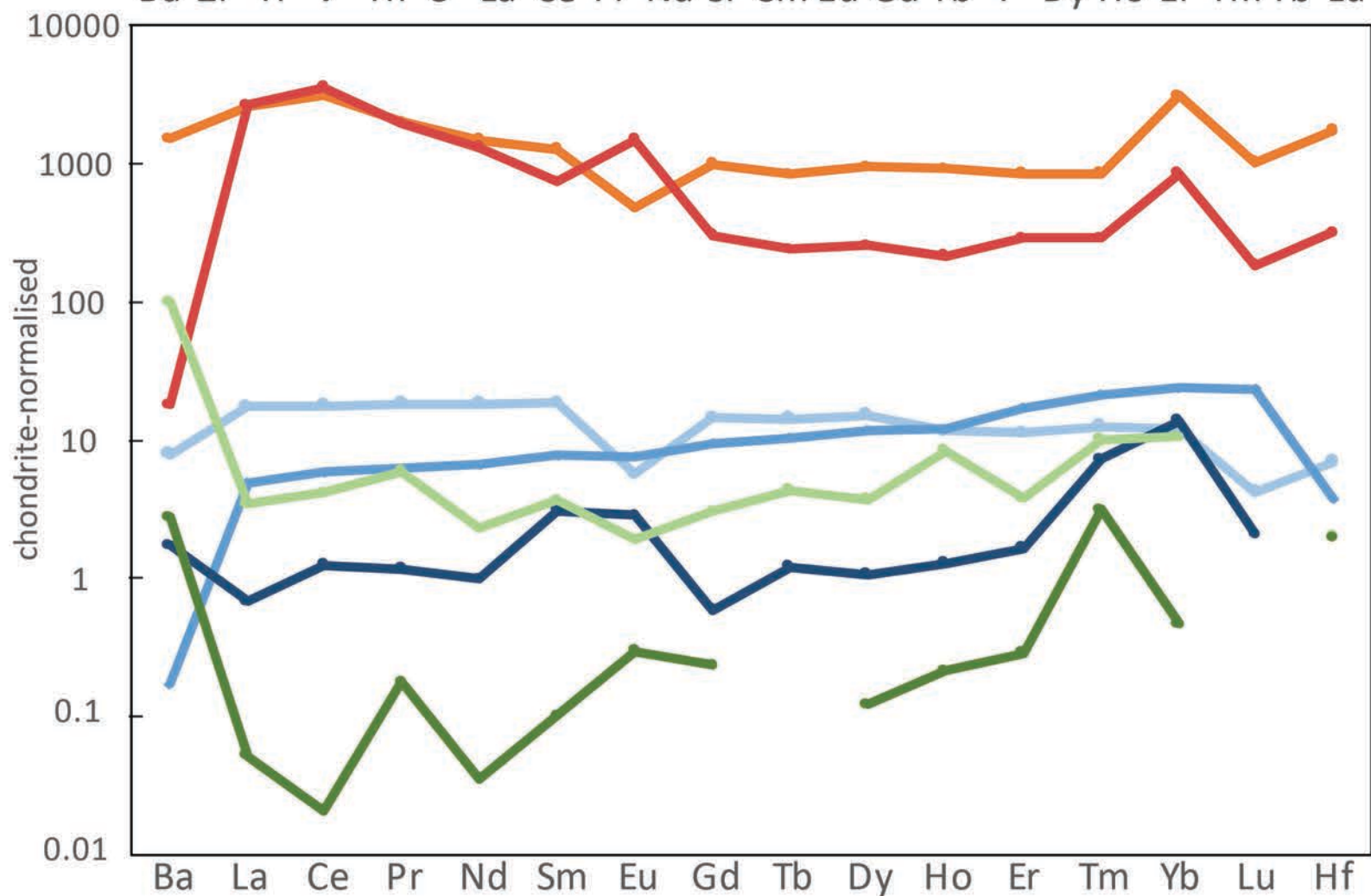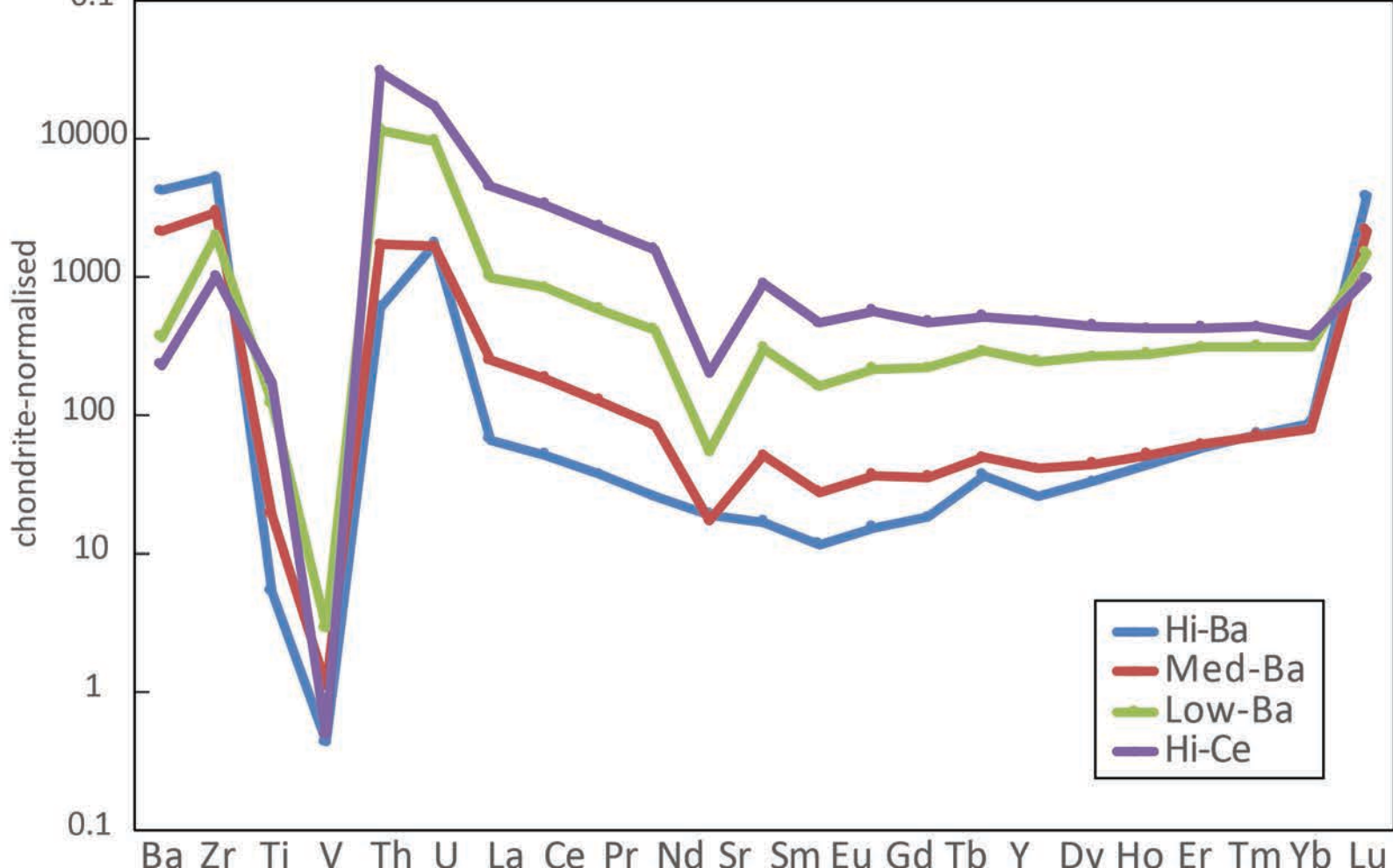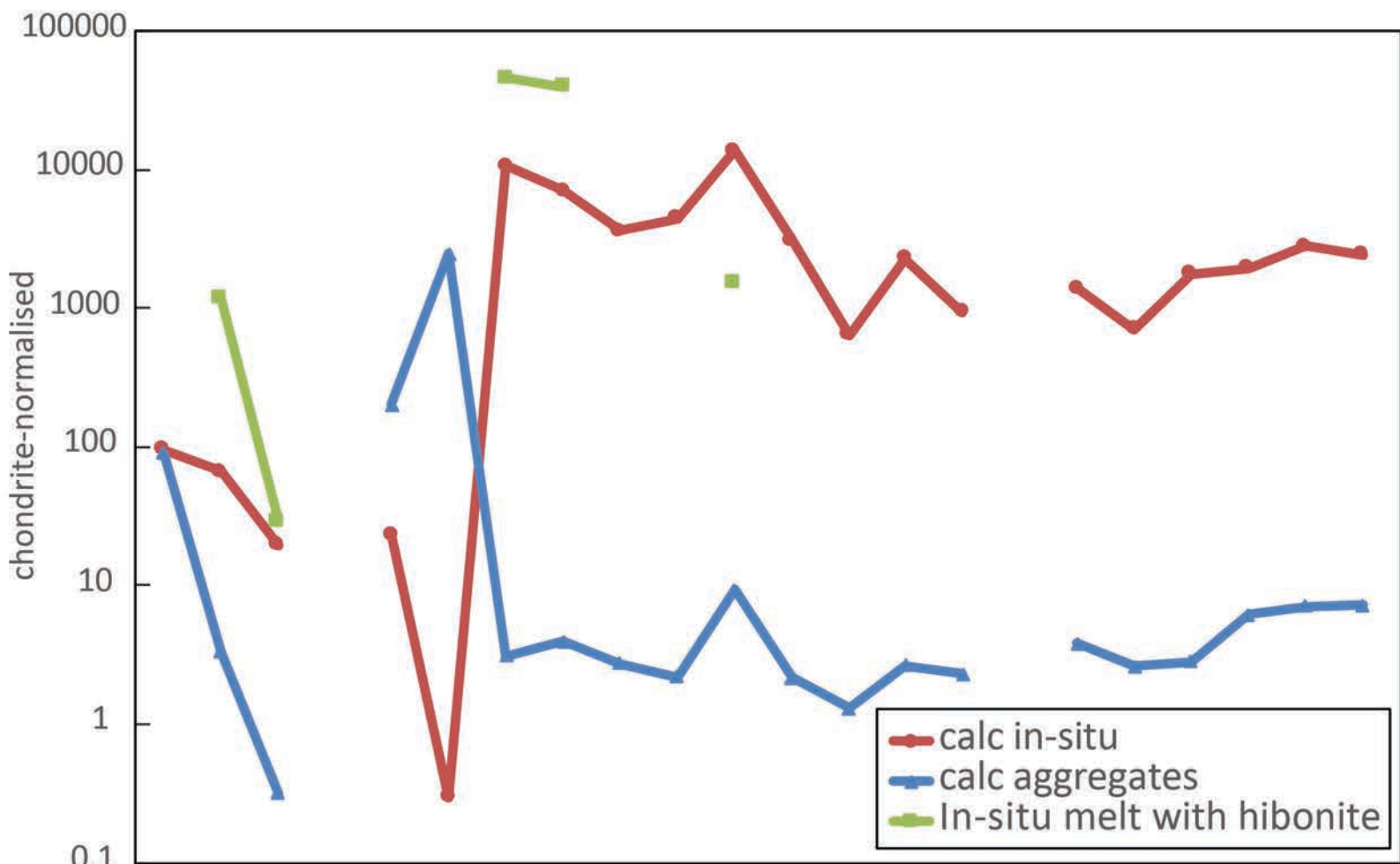
a)

b)

1 - $CaMg_2Al_{16}O_{27}$
2 - $Ca_2Mg_2Al_{28}O_{46}$
3 - $Ca_3MgAl_4O_{10}$
4 - $Ca_3Al_4O_7$

Figure 12

Legend:
- ★ Hibonite-grossite aggregate
- ■ Melt with hibonite aggregate
- ● Melt with interstitial hibonite
- □ Ba-rich glass
- ○ Average glass in pockets

C = CaO
A = Al₂O₃
S = SiO₂

Figure 13

Figure 14