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1            **Parageneses of TiB$_2$ in corundum xenoliths from Mt Carmel, Israel:**

2            **Siderophile behaviour of Boron under reducing conditions**

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14
15
16 **Abstract**

17

18    Titanium diboride (TiB$_2$) is a minor but common phase in melt pockets trapped in the

19    corundum aggregates that occur as xenoliths in Cretaceous basaltic volcanoes on Mt

20    Carmel, N. Israel.  These melt pockets show extensive textural evidence of immiscibility

21    between metallic (Fe-Ti-C-Si) melts, Ca-Al-Mg-Si-O melts and Ti-(oxy)nitride melts.  The

22    metallic melts commonly form spherules in the coexisting oxide glass.  Most of the observed

23    TiB$_2$ crystallized from the Fe-Ti-C silicide melts, and a smaller proportion from the oxide

24    melts. The parageneses in the melt pockets of the xenoliths require $fO_2 \leq \Delta IW$ -6, probably

25    generated through interaction between evolved silicate melts and mantle-derived CH$_4$+H$_2$

26    fluids near the crust-mantle boundary.  Under these highly reducing conditions boron, like

27    carbon and nitrogen, behaved mainly as a siderophile element during the separation of

28    immiscible metallic and oxide melts.  These parageneses have implications for the residence

29    of boron in the peridotitic mantle, and for the occurrence of TiB$_2$ in other less well-

30    constrained environments such as ophiolitic chromitites.

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32    **Introduction**
33
34         Boron is a "quintessential element of the Earth's upper continental crust" (Grew

35    2015).  It was not created during stellar nucleosynthesis, but was introduced into Earth's

36    mantle from the interstellar medium during planetary accretion.  It has a low abundance in

37    the Solar system and hence in the bulk Earth; the estimated concentration in the Primitive

38    Upper Mantle is ca 0.26 ppm B (Palme and O'Neill 2005). Although Dobrzhinetskaya et al.

39    (2014) described boron nitride (BN; qingsongite) in a chromitite in the Luobusa ophiolite of

40    the Yarlung-Zhangbo suture zone (Tibet), reports of B-bearing phases in mantle-derived

41    rocks are extremely rare.  The most well-known examples are the blue Type IIb diamonds,

42    with up to 8.4 ppm B in the famous Hope diamond (Gaillou et al., 2012).  As a classic

43    incompatible element, B has been concentrated into the continental crust over time by

44    magmatic and sedimentary processes, resulting in 295 known mineral species (Grew et al.,

45    2017).

46         Titanium diboride ($TiB_2$) is produced on an industrial scale using a variety of high-

47    temperature techniques, including reduction of $TiO_2$ by reaction with boron carbide, or with

48    alkali-boron hydrides.  It is valued for its extreme hardness, high melting point and high

49    thermal and electrical conductivity.  It is extremely rare in nature, but was recently

50    described as inclusions in corundum separated from ophiolitic chromitites in Tibet, and

51    given the name jingsuiite (Xiong et al.,2019a,b).

52         $TiB_2$ also was earlier reported as inclusions in skeletal corundum aggregates found as

53    ejecta from small Cretaceous volcanoes on Mt Carmel, northern Israel (Griffin et al. 2016).

54    It is part of an unusual assemblage of minerals related to highly reducing conditions,

55    interpreted as developed in magma chambers near the crust-mantle boundary (Griffin et al.

56    2016b, 2018a, 2019a; references therein). Here the $TiB_2$ occurs in several distinct

57    parageneses, reflecting crystallization from both Fe-Ti silicide melts, and coexisting silicate

58    melts.  The occurrence of the boride *in situ* in these aggregates provides textural evidence

59    and context that can give further insights into the behaviour of boron under highly reducing

60    conditions in the uppermost mantle.

61
62    **Occurrence**
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64    The material described here comprises xenoliths from the pyroclastic ejecta of at least eight

65    Cretaceous (99-85 Ma) intraplate pyroclastic basaltic volcanoes exposed on Mt Carmel, in

66    northern Israel (Griffin et al. 2016b, 2018a, 2019a; references therein). Aggregates of

67    skeletal corundum crystals (Carmel Sapphire$^{TM}$) occur in-situ as xenoliths in the tuffs, and re-

68    deposited in nearby alluvial placers, mainly in the Kishon River.  Suggestions that any of this

69    material might be of anthropogenic origin (LItasov et al. 2019a,b) have been refuted in

70    detail by Griffin et al. (2019b).

71         Melt pockets trapped within and between these rapidly-grown corundum crystals

72    can be divided into Type S (silicate melts with phenocrysts), Type A (Fe-Ti-silicides and Fe

73    alloys, representing immiscible metallic melts; Fig. 1) and Type N (dominated by Ti nitrides

74    with minor TiC) (Griffin et al. 2016b). Another paragenesis (Type DF) is represented by

75    coarser-grained xenoliths of hibonite+grossite+spinel +fluorite ± native V (Griffin et al.

76    2019a).

77
78    **Methods**
79
80    The sampling methods have been described in detail by Griffin et al. (2019a).

81    *SEM, FE-SEM, EMP*

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

83    EVO MA15 scanning electron microscope (SEM) at the Geochemical Analysis Unit (GAU),

84    Macquarie University, Sydney, Australia was used to capture Backscattered Electron (BSE)

85    images and Energy Dispersive X-ray spectrometry (EDS) was used to map the elemental

86    composition of the samples, and to analyze phases of interest. An accelerating voltage of 15

87    keV and a beam current of 1 nA was used. Images and qualitative EDX data also were

88    collected on an FEI Teneo Field Emission Scanning Electron Microscope equipped with

89    secondary and backscattered-electron detectors and a pair of integrated Bruker Energy

90    Dispersive X-ray Spectroscopy analyzers (Bruker XFlash Series 6).

91         Major and minor elements were determined by electron microprobe (EMP) using a

92    CAMECA SX100 equipped with five wavelength-dispersive spectrometers at the Macquarie

93    University GeoAnalytical (MQGA; formerly GAU), Macquarie University, Sydney, Australia.

94    Analyses were performed using a focused beam (1-2 μm) with an accelerating voltage of 15

95    keV and a beam current of 30 nA. Calibration standards were a suite of natural and

96    synthetic minerals, including synthetic $TiB_2$, TiC and TiN. B, C, N and O were measured using

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97    a PC2 crystal (on Spectro 4). Peak counting was 30 s, and background was counted for 15 s

98    on either side of the peak. Oxygen and carbon were corrected for blank effects (carbon

99    coating) by analysis of the synthetic Ti phases; matrix corrections were carried out by the

100    ZAF software.

101

102    *Transmission Electron Microscopy (TEM)*

103    Focused Ion Beam (FIB) foils from the region of interest were prepared for TEM using

104    two dual-beam FIB systems, an FEI Nova NanoLab 200 at UNSW and an FEI Helios G3 CX at

105    the Centre for Microscopy Characterisation and Analysis (CMCA), The University of Western

106    Australia, Perth, Australia.  High Angle Annular Dark Field - Scanning Transmission Electron

107    Microscopy (HAADF-STEM) imaging and element mapping were carried out using an FEI

108    Titan G2 80-200 TEM/STEM with ChemiSTEM Technology operating at 200 kV at the Centre

109    for Microscopy Characterisation and Analysis (CMCA), The University of Western Australia,

110    Perth, Australia. The element maps were obtained by EDS using the Super-X detector on the

111    Titan with a beam size ~1 nm and a probe current of ~0.25 nA. Total acquisition times of 20-

112    30 minutes were used to obtain good signal-to-noise ratios. Electron diffraction was carried

113    out using a field limiting aperture that selected an area approximately 400nm in diameter.

114    Electron energy-loss spectroscopy (EELS) was carried out using a Gatan Enfinium

115    spectrometer at the same beam size and beam current as the EDS, and at a dispersion of 0.1

116    eV/pixel.

117

118

119    *X-ray diffraction*

120    A small $TiB_2$ fragment was handpicked from the polished section under a reflected

121    light microscope and mounted on a 5 μm diameter carbon fiber, which was, in turn,

122    attached to a glass rod. Then, the fragment was tested by single-crystal X-ray diffraction.

123    Single-crystal X-ray studies were carried out at the Dipartimento di Scienze della Terra,

124    Università di Firenze using a Bruker D8 Venture diffractometer equipped with a Photon III

125    CCD detector, with graphite-monochromatized Mo$K\alpha$ radiation (λ = 0.71073 Å), and with 70

126    s exposure time per frame; the detector-to-sample distance was 7 cm.

127    The structure was solved by direct methods in the space group *P*6/*mmm* and then

128    refined using the program Shelxl-97 (Sheldrick 2008). The site occupancy factor (s.o.f.) at the

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129   Ti and B sites was allowed to vary (Ti and B versus structural vacancy) using scattering

130   curves for neutral atoms taken from the International Tables for Crystallography (Wilson

131   1992). Both the sites were found to be fully occupied by Ti and B, respectively and then

132   fixed in the subsequent refinement cycles. At the last refinement stage, with anisotropic

133   atomic displacement parameters, the residual value settled at $R_1(F)$ = 0.0517 for 46 unique

134   reflections and 5 parameters. Crystallographic data are available as supplementary

135   material[1].

136

137   **Petrography and Parageneses**

138

139         Petrographic observations reveal two main parageneses of $TiB_2$ in the melt pockets

140   trapped in corundum aggregates from the Mt Carmel volcanic rocks.

141

142   *Metallic paragenesis*

143         In most occurrences, $TiB_2$ is closely associated with Fe-Ti silicides, TiC

144   (khamrabaevite) and TiN (osbornite; typically with O±C in solid solution), as well as the Ca-

145   Al-Mg silicate glass.  The silicides typically occur as spherical bodies enclosed in corundum

146   (Fig. 1) and have sharp contacts to the silicate glasses or to phases crystallized from them

147   (Figs 2-4), consistent with an origin as metallic melts, immiscible with the Ca-Al-Mg silicate

148   melts of the Type S melt pockets.  Coarser crystals of $TiB_2$ may contain lamellar inclusions of

149   TiN and/or TiC, as well as blobs of Fe-Ti silicides (Fig. 3a).  Euhedral crystals are intergrown

150   with silicides (Fig. 3b) or surrounded by silicides and TiN (Fig. 3c).  Smaller grains appear to

151   have crystallized along with TiC from spherical inclusions of Fe-Ti silicides in the corundum

152   aggregates (Fig 4); TiN commonly occurs on the rims of such silicide balls.

153         A FIB foil was prepared to examine the contact between an Fe-Ti-Cr silicide and an

154   unidentified oxide phase (nominally $Mg(Al,Ti)_6(Si,Zr)O_{12}$) that crystallized together with

155   carmeltazite from the associated silicate melt; the images revealed a crystal of $TiB_2$ that

156   clearly has grown from the silicide melt (Fig. 5).  The original silicide has broken down into

157   three coexisting phases, enriched respectively in Cr, Ti and Fe (Fig. 5b; Table 2); the wavy

158   outlines between the three phases suggest that they were still molten at the time of

159   eruption. The $TiB_2$ crystal is zoned from a high-Cr core to a low-Cr rim (Fig. 6).  The outer rim

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160   contains an inclusion of a Cr,Fe-rich silicide, similar to the silicide phase in which that part of

161   the TiB$_2$ crystal was growing (Table 2).  The negative-crystal form of this inclusion suggests

162   that it was trapped as a melt.  The TiB$_2$ crystal also encloses scattered tiny (100 nm)

163   hexagonal (i.e. negative-crystal) inclusions of an Fe-Cr silicide, each containing a small

164   bubble (Fig. 6b). In a second FIB foil (Figure 7) the contact between a TiB$_2$ crystal and a TiN

165   melt is decorated with a thin film of a vanadium silicide.

166

167   *Oxide paragenesis*

168          The observations above define a paragenesis of TiB$_2$ + TiC + Fe-Cr-Ti silicides (melts)

169   ± TiN (melts); the illustrated microstructures indicate that these melts are immiscible with

170   the Al-Ca-Mg silicate melts of the Type S pockets.  Since immiscible melts are by definition in

171   mutual equilibrium, phases in one melt should be in equilibrium with phases crystallizing

172   from the coexisting melt, and a phase that crystallizes from both melts will have the same

173   major-element composition in each melt.  Therefore, in principle, TiB$_2$ should also be able to

174   crystallize from the silicate melts, and coexist with the early-crystallizing tistarite,

175   carmeltazite and Mg-Ti-Al spinel.  While rare, such parageneses have been observed.  Figure

176   8 shows a large Type S melt pocket in which spinel (with oriented lamellae/needles of an

177   unidentified Ti-rich phase in the inner parts) has crystallized before tistarite. It includes an

178   irregular mass of platy TiB$_2$ which appears to have crystallized earlier, making it the first

179   phase to crystallize from the silicate melt.   Figure 3a shows a large TiB$_2$ crystal in a silicate

180   melt pocket together with carmeltazite and tistarite. The TiB$_2$ appears to have grown in the

181   silicate melt, but contains inclusions of both TiN and FeTiSi; this may represent a case in

182   which TiB$_2$ was simultaneously in equilibrium with the silicate melt, the TiN melt and a

183   silicide melt.  In another example, the crystal of TiB$_2$ in Figure 9a appears to have crystallized

184   from the silicate melt together with TiC and ZrP, which also are part of the metallic

185   paragenesis. The large TiB$_2$ crystal and the attached ball of Fe-Ti silicide in Figure 9b appear

186   to coexist in a melt that also contains abundant blebs of Ti(N,O). Similarly, while the TiB$_2$ in

187   the examples shown in Figure 4 appears to have crystallized from the silicide melt, it is

188   euhedral against the silicate glass, and thus also appears to have been in equilibrium with

189   the surrounding silicate melt.  Finally, Figure 10 shows an oxide assemblage in which TiB$_2$

190   coexists with a Ti-rich hibonite and a phase with the composition MgAl$_8$O$_{13}$, which was

191   shown by single-crystal X-ray diffraction to exhibit the spinel structure. Its probable formula

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192 is $(Al_{0.56}Mg_{0.34}\square_{0.10})(Al_{1.88}\square_{0.12})O_4$, a Mg-bearing $\gamma$-$Al_2O_3$. This may correspond to the recently

193 described mineral deltalumite $(Al_{0.67}\square_{0.33})Al_2O_4$; Pekov et al. 2019), with Mg occupying

194 vacant sites in the spinel structure.

195

196 **Chemistry**

197 Table 1 gives electron microprobe (EMP) data on $TiB_2$ from a variety of parageneses;

198 Table 2 gives the compositions of phases in the images of Figures 3-11. EMP data are given

199 where available, SEM data where necessary because of small grain sizes, and

200 semiquantitative TEM-EDS in the case of the FIB foils described above. While some

201 examples of $TiB_2$ are essentially pure, others show solid solution of transition elements that

202 also are present in the coexisting silicide melts: Cr up to 1.9 wt %; V to 11.7 wt%; Fe to 0.9

203 wt%. These "extra" elements are unlikely to reflect overlap of the electron beam onto the

204 coexisting silicides, on three grounds. (1) V contents in $TiB_2$ are all higher than the V

205 contents of the coexisting silicides. (2) The partitioning of Cr and V between $TiB_2$ and

206 coexisting silicides is generally consistent across the available analyses, but the ratios of the

207 two elements are different in the two phases; $TiB_2$ contains 20-50% as much Cr as coexisting

208 silicide, and 1.2-7 times as much V. (3) The zoning of the $TiB_2$ shown in the FIB foil (Fig. 5c),

209 where interference is unlikely because of the thin target and small beam size, demonstrates

210 that elements such as Cr enter the $TiB_2$ lattice in the presence of silicide melts that carry

211 those elements. The mean of 16 EMP analyses, regardless of the variable presence of

212 transition elements, gives an average formula of $TiB_2$ (B/Ti = 1.99). Where the transition

213 elements are present, they substitute for Ti, giving a more general formula of $(Ti,V,Cr,Fe)B_2$.

214 The high level of oxygen in grain #5 (Table 1) may reflect overlap onto adjacent silicate glass;

215 however, the B/Ti of this analysis is low (1.80), which could suggest that the O is substituting

216 for B. Similarly, the C content of the $TiB_2$ shown in Figure 9 (Table 2) may reflect

217 interference from coexisting TiC.

218 EELS spectra for Ti in $TiB_2$, TiC and TiN from these samples are similar (Fig. 12), and

219 consistent with the presence of Ti as $Ti^{2+}$ (Stoyanov et al. 2007); this implies that boron is

220 present as $B^{1-}$.

221

222 **Crystallography**

223   The structure of the $TiB_2$ has been determined by both electron diffraction (TEM)

224 and single-crystal X-ray diffraction, on two samples with different parageneses.  The

225 electron diffraction was carried out on the hexagonal plate shown in Figure 6a, representing

226 the silicide paragenesis; the diffraction pattern is shown in Figure 6b.  The diffraction spots

227 form a hexagon; the planar spacing of the spots nearest the center of the pattern is *ca* 0.26

228 nm.  This pattern is perfectly consistent with the [0001] zone axis of the known hexagonal

229 structure of synthetic $TiB_2$ (Villars and Calvert 1991).

230   The X-ray diffraction study was done using the grain illustrated in Fig. 10,

231 representing the oxide paragenesis. The structure (hexagonal, space group *P*6/*mmm*) is of

232 the $AlB_2$-type (Villars and Calvert 1991) and consists of a simple-hexagonal lattice in which

233 HCP Ti layers alternate with graphite-like B layers. Unit cell parameters (in hexagonal

234 setting) are: *a* = 3.0218(6) and *c* = 3.2197(8) Å.

235

236 **Discussion**

237 *Relationships to Ti-nitrides*

238   The microstructural relationships among the silicides and $TiB_2$ on the one hand, and

239 the Ti-oxynitrides on the other, are ambiguous.  The detailed chemistry and occurrences of

240 the nitrides will be discussed elsewhere.  For the purposes of this report it is sufficient to say

241 that the nitrides appear to have been molten and highly mobile at the time of eruption, and

242 they commonly appear to fill skeletal cavities in the corundum, surrounding and

243 interpenetrating other phases (Figs 3a, 9b, 11) including the $TiB_2$, although in other cases

244 (e.g. Fig. 3c) they appear to be in textural equilibrium with $TiB_2$, or possibly exsolving from

245 silicide melts that were crystallizing $TiB_2$ (e.g. Fig. 4a).  However, in Figure 11, the nitride

246 melt appears to post-date the $TiB_2$, in which case their spatial relationship would be simply

247 coincidental, though we might still ask if the $TiB_2$ actually crystallized from the oxynitride

248 melt.  Thus there is not at present enough evidence to define a separate $TiB_2$ + Ti(N, O)

249 paragenesis.

250

251 *Conditions of formation*

252   It is clear from the petrography that most of the observed $TiB_2$ crystallized from a

253 range of Fe-Ti-Cr-V silicide melts, rich in enough in carbon to precipitate abundant TiC as

254 well as the $TiB_2$.  The textural relationships also indicate that some of the $TiB_2$ crystallized

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255    directly from the silicate melts now represented by the Ca-Al-Mg-Silicate glasses, while

256    those that crystallized from silicide melts were simultaneously in equilibrium with the

257    silicate melt and coexisting Ti(N,O) melts.

258            The overall picture is one of a close relationship between silicate melts, silicide

259    melts, nitrides and $TiB_2$.  The petrography, and especially their subspherical morphology,

260    indicate that the silicide melts were immiscible with the dominant Ca-Al-Mg-Si oxide melt

261    from which corundum was crystallizing.  The scarcity of boron-bearing phases in the silicate

262    melt pockets, contrasted with the relative abundance of $TiB_2$ associated with metallic melts,

263    suggests that B behaved as a siderophile element ($B^0$) during immiscible-melt separation

264    under these reducing conditions.  It partitioned strongly (though not completely) into

265    silicide melts, and then crystallized as $TiB_2$ either on cooling, or because immiscibility

266    concentrated B and C to an extent that forced the crystallization of borides and carbides.

267            The initial crystallization of the silicate melts formed $Ti^{3+}$-bearing phases such as

268    tistarite and carmeltazite at estimated temperatures of 1400-1450 °C, and the implied $fO_2$ of

269    the magmatic system at this point was $ca$ $\Delta$IW-7, the approximate $fO_2$ of the $2TiO_2 \rightarrow Ti_2O_3$

270    + O buffer reaction (1500 °C, 1 atm; Griffin et al. 2016).

271            The buffer reaction $Ti_2O_3 \rightarrow 2TiO + O$ requires much lower $fO_2 \leq \Delta$IW -11.5 (1500 °C,

272    1 atm), whereas the lowest $fO_2$ recorded in the Mt Carmel xenolith assemblage is $ca$ $\Delta$IW -

273    10, in a hydrogen-dominated atmosphere (Griffin et al. 2019).  $Ti^{2+}$ phases normally would

274    not be stable in equilibrium with the local silicate melt ($\Delta$IW-7 to -8).  This suggests that

275    crystallisation of $TiB_2$ was driven by saturation in boron, in an atmosphere dominated by

276    $CH_4+H_2$ and with little oxygen available with which to form more conventional boron-

277    bearing phases.  It may have involved a structurally-driven reaction in which $Ti^0$ dissolved in

278    the silicide melt was oxidized to $Ti^{2+}$ and $B^0$ was reduced to $B^{1-}$. A similar mechanism would

279    apply to the crystallisation of $Ti^{2+}C$ from the same Fe-Ti-Si melts that precipitated $TiB_2$ (Fig.

280    1), and to the inferred separation of apparently immiscible TiN melts (Figs 2b,7).

281            In the examples shown here, $TiB_2$ is crystallizing at temperatures well below its

282    melting point.  However, it is interesting to note that both $TiB_2$ and TiC have been grown

283    from molten aluminum at temperatures of 1500-1450 °C (Higashi and Atoda, 1970; Higashi

284    et al., 1976).

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286    *Crystallization environment*

287    The earliest paragenesis in the melt pockets of these xenoliths is corundum +

288    tistarite ($Ti_2O_3$) + carmeltazite ($ZrAl_2Ti_4O_{11}$; Griffin et al., 2018b) + Mg-Al-Ti spinel, in a Ca-

289    Mg-Al-Si-O glass.  The crystallization of these $Ti^{3+}$-bearing phases requires $fO_2$ at least 6 log

290    units below the Iron-Wustite buffer ($\Delta$IW-6; Griffin et al. 2016).  Paragenetic studies (Griffin

291    et al. 2018a, 2019; Xiong et al. 2017) suggest that both the low $fO_2$ and the crystallization of

292    skeletal corundum reflect the interaction of differentiated mafic to syenitic magmas with

293    $CH_4+H_2$ at high fluid/melt ratios. The skeletal form of the corundum crystals in the

294    aggregates implies rapid crystallization from a melt supersaturated in $Al_2O_3$, and probably

295    growth from a substrate.  We have suggested (Xiong et al. 2017; Griffin et al. 2018a) that

296    this supersaturation was achieved by the rapid desilication of a parental melt, driven by the

297    exsolution of immiscible Fe-Ti-C-silicide melts, which also occur abundantly as inclusions in

298    the corundum (Type A pockets), and in the Type S melts.  These melts crystallized

299    moissanite (SiC), $TiB_2$, TiN (osbornite) and khamrabaevite (TiC); the $Ti^{2+}$-bearing phases and

300    the presence of native vanadium in corundum-hibonite-grossite xenoliths suggest still lower

301    $fO_2$ (Griffin et al. 2016b, 2018a, 2019a).  These fluid-melt systems were sampled by eruption

302    of the host basalts, but were not directly genetically related to them; they represent much

303    shallower, pre-existing systems.

304    The P-T conditions of these melt-fluid systems are broadly constrained by

305    mineralogy, observed reactions and thermodynamic modelling.  Dmisteinbergite is a

306    hexagonal to trigonal (depending on degree of Si-Al ordering) polymorph of anorthite (An;

307    Zolotarev et al. 2019).  In the $CaO-Al_2O_3-SiO_2$ system, it crystallizes metastably at

308    temperatures ca 150 °C below the anorthite solidus during rapid cooling (Abe et al. 1991).

309    In the Type-S melt pockets dmisteinbergite occurs as needles and narrow laths in the $Al_2O_3$-

310    $SiO_2$-CaO glasses.  The microstructures strongly suggest a quench reaction, with

311    crystallization occurring under rapid decompression and cooling during the explosive

312    eruption of the host magma.  This reflects the peritectic reaction Liq + corundum (Crn) $\rightarrow$

313    An, which is the reverse of the incongruent melting of anorthite (An $\rightarrow$ Liq + Crn). This well-

314    studied reaction is constrained experimentally to pressures (*P*) >0.9 GPa and temperatures

315    (*T*) of ca 1550 °C (Goldsmith 1980). Thermodynamic modelling in the $CaO-Al_2O_3-SiO_2$ system

316    (Ottonello et al. 2013) shows that the melt-pocket glasses, which clearly were crystallizing

317    corundum (Griffin et al. 2016b, 2018a), would not be in equilibrium with corundum at *P* <1

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318    GPa, consistent with the crystallization of dmisteinbergite during decompression.  However,

319    the same modelling suggests that grossite ($CaAl_4O_7$), which is found together with

320    corundum and hibonite ($CaAl_{11}O_{19}$) in some highly reduced xenoliths from Mt Carmel

321    (Griffin et al. 2019a) may not be stable at $P$ >1 GPa.  It therefore is probable that the

322    corundum aggregates crystallized at pressures near 1 GPa.

323        Comparisons of mineral parageneses in the melt pockets with experimental studies

324    suggest that $T$ decreased from >1450°C to $ca$ 1200°C as $fO_2$ dropped from ΔIW-6 to ΔIW≤-9

325    (Griffin et al. 2018a, 2019a; references therein).  These $P$-$T$ estimates ($ca$ 1 GPa, 1450-1200

326    °C) place the proposed site of fluid-melt interaction in the uppermost mantle, near the

327    crust-mantle boundary in the area, which is geophysically estimated to lie at 25-30 km

328    depth (Segev and Rybakov 2011).

329        One possible model for the crystallization environment is a magma chamber that

330    was being infiltrated from below by abundant highly reducing fluids derived from a metal-

331    saturated mantle.  If this active percolation of reducing fluids results in an $fO_2$ gradient, with

332    lowest $fO_2$ at the base, this could result in the growth of a forest (or mush) of skeletal

333    corundum crystals at the bottom, where melt pockets trapped in the mush evolved under

334    progressively decreasing $fO_2$.  Silicide and nitride melts typically coexist with tistarite +

335    spinel + carmeltazite + Ca-Al-Mg silicate glass, the assemblage that represents the earliest

336    stage in the crystallization sequence in these melt pockets. This seems to be consistent with

337    a relatively rapid process, in which the onset of silicide-melt immiscibility desilicated the

338    silicate melt and drove it into supersaturation in $Al_2O_3$, and the rapid crystallization of the

339    corundum.

340

341    *Boron in the mantle*

342        Boron may be a "quintessential crustal element" but the boron in the crust must

343    ultimately have been derived from the mantle.  Several recent studies of Type II (low-N)

344    diamonds conclude that they have formed in the sublithospheric mantle, at depths ranging

345    down to 700-800 km (Motasami et al. 2018; Korolev et al. 2018; Smith et al. 2016, 2018).

346    The CLIPPIR (Cullinan-type, large, inclusion-poor, pure, irregularly-shaped and resorbed) IIa

347    diamonds commonly carry Fe-rich metallic inclusions, which are jacketed by $CH_4$+$H_2$ fluids,

348    implying an $fO_2$ ≤IW.  Smith et al. (2016) therefore argued that these large diamonds grew in

349    pools of metallic melt.  The observations presented here suggest that such low-$fO_2$ metallic

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350  melts would scavenge boron and carbon from surrounding mantle peridotites, only to lose

351  both to form diamond on cooling.  However, given the low mean B content of the mantle

352  (<0.3 ppm), this mechanism probably would provide too little B to form blue Type IIb

353  diamonds with several ppm B. These contain oxide and silicate inclusions indicative of a

354  lower-mantle origin, but only rare metallic inclusions (Smith et al. 2018).  However, in 28%

355  of the samples studied, Raman spectroscopy identified thin layers of fluid ($CH_4 \pm H_2$),

356  probably formed as hydrogen escaped the inclusions and reacted with the enclosing

357  diamond, again implying an $fO_2$ of ≤IW, and the probable presence of metallic melts.  In the

358  lower mantle, subducted crustal rocks could provide more boron, as argued by Smith et al.

359  (2018).  If large Type IIb diamonds also grew in pools of metallic melt derived from crustal

360  rocks, those melts may have been able to scavenge enough boron and carbon to drive the

361  process of growing large blue diamonds.

362          $TiB_2$ has also been found as inclusions in corundum separated from ophiolitic

363  chromitites in Tibet (Xiong et al. 2019a,b).  We have previously suggested (Griffin et al.

364  2016a; Xiong et al. 2017) that the occurrences of super-reduced assemblages with

365  corundum in ophiolitic peridotites reflect processes similar to those invoked to understand

366  the Mt Carmel assemblages.  The Tibetan ophiolites also contain evidence of subduction

367  into the mantle transition zone (Griffin et al. 2016a; Zhang et al. 2017; Bindi et al. 2018;

368  references therein) prior to their rapid excavation during slab rollback.  Such a scenario

369  clearly offers opportunities for the large-scale transfer of mantle-derived reduced volatiles

370  to shallow levels, accompanying partial melting of the upwelling mantle.

371
372  **Implications**
373
374          $TiB_2$ is widespread in the corundum aggregates that occur as xenoliths in Cretaceous

375  explosive basaltic volcanoes on Mt Carmel, N. Israel.  The $TiB_2$ crystallized mainly from

376  metallic (Fe-Ti-C-Si) melts but also from immiscible coexisting Al-rich silicate melts. The

377  parageneses in the melt pockets of the xenoliths require $fO_2 \leq \Delta IW$ -6, probably generated

378  through interaction between evolved silicate melts and mantle-derived $CH_4 + H_2$ fluids, near

379  the crust-mantle boundary.  Under these highly reducing conditions boron, like carbon and

380  nitrogen, behaved mainly as a siderophile element during the separation of immiscible

381  metallic and oxide melts.

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382    These parageneses have implications for the residence of boron in the

383    sublithospheric mantle; if the oxygen fugacity of that mantle is controlled by the presence of

384    metallic Fe, the bulk of the mantle's B budget may reside in small fractions of metallic melts.

385    In that case the behaviour of boron during partial melting may depend strongly on the

386    oxygen fugacity at the point of melting, and its transfer to the crust as an incompatible

387    element might be more complex than currently assumed.  The parageneses observed in the

388    corundum aggregates from Mt Carmel bear many similarities to those found in some

389    ophiolitic chromitites, and may offer a guide to the interpretation of the occurrence of $TiB_2$

390    in such less well-constrained environments.

391

392    **Acknowledgements**

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515
516
517

**Figure captions**

519

520    Figure 1.  BSE images of typical Fe-Ti silicide balls, enclosed in melt pockets within corundum
521    aggregates in the ejecta of Cretaceous volcanoes on Mt Carmel, N. Israel.  In each case the
522    original metallic melts have unmixed into mutually immiscible Ti-rich (dark) and Ti-poor
523    (light) members prior to or during eruption.

524

525    Figure 2.  Multi-element phase map showing immiscibility between Fe-Ti silicide melt and
526    silicate melt, which has partially crystallized as a complex Mg-Al-Ti-Zr silicate and
527    carmeltazite.  Small grains of $TiB_2$ are scattered within the FeTiSi phase.  Black areas
528    represent vesicles; orange phase is Ti(N,O).

529

530    Figure 3.  BSE images of $TiB_2$ associated with Fe-Ti-silicide melts.  a, crystal of $TiB_2$ with
531    inclusions of TiN and FeTiSi.  Associated phases, crystallized from the silicate melt, are
532    tistarite and carmeltazite.  b, euhedral crystal of $TiB_2$ is rimmed by $TiFe_2$(Si,P) and Ti(N,O),
533    separated from the host corundum by a high-K glass. c, euhedral crystal of $TiB_2$ enclosed in a
534    complex silicide $(Fe,Mn,Ti,Cr)_3Si$, which is surrounded by a large blob of Ti(N,O) that is also
535    in contact with a ball of $(Fe,Ti)_2Si$. The wavy contacts between the silicides and the nitride,
536    and between the nitride and the silicate melt or the host corundum, suggest that the
537    silicides and the nitride were trapped as melts between growing corundum crystals.  The
538    bright phases at top are $(Zr,Ti)_2O_3$, in a silicate glass

539

540    Figure 4. BSE images of $TiB_2$ on the rims of silicide balls.  a, FeTiSi ball (unmixing into at least
541    3 mutually immiscible components) has crystals of $TiB_2$ and blobs of Ti(N,O) on the rim. b,
542    FeTiSi ball with crystals of $TiB_2$ embedded in rim.  c, ball of $(Fe,Cr,V)_2Si$ with V-bearing $TiB_2$ on
543    the rim, surrounded by silicate glass.  d, closeup of top of image (c), illustrating the euhedral
544    nature of $TiB_2$ crystals toward both glass and silicide.

545

546    Figure 5.  STEM-EDS and HAADF maps of FIB foil showing a euhedral $TiB_2$ crystal in Fe-Ti-Cr
547    silicide in contact with an unidentified oxide phase.  a, amorphous Ca-rich phase and TiS
548    associated with a vein of amorphous carbon along the contact.  b, element maps illustrating
549    unmixing of the silicide into Ti-rich, Fe-Cr-rich and Fe-rich components (Table 2).

550

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551 Figure 6.  Details of the foil shown in Figure 5.  a, HAADF and STEM-EDS maps showing
552 zoning of $TiB_2$ crystal from Cr-rich core to Ti-rich rim.  Note small inclusion of Cr-rich silicide
553 in rim of $TiB_2$, indicating that unmixing of the silicide melt occurred before or coevally with
554 growth of the $TiB_2$ rim; also note a train of minute inclusions cutting across the top of the
555 crystal.  b, electron-diffraction pattern from the $TiB_2$ crystal and closeup of one of the small
556 inclusions, consisting of a hexagon of Fe-Cr-rich silicide and a void.
557
558 Figure 7.  FIB-TEM image and element maps of contact between $TiB_2$ and Ti(N,O), showing a
559 thin vein of a vanadium silicide along the contact.
560
561 Figure 8. BSE images of $TiB_2$ included in spinel.  a, Type S melt pocket with large spinel grain
562 with oriented Ti-rich needles in core, and large inclusion of $TiB_2$.  Spinel rim overgrows
563 abundant tistarite.  Quench crystals of dmisteinbergite (a polymorph of anorthite) in a
564 matrix of silicate glass reflect the Ca-Al rich nature of the silicate melt. b, closeup showing
565 lamellar crystal of $TiB_2$ in spinel with unidentified Ti-rich needles.  Light bands in the $TiB_2$ are
566 a Ti-nitride phase.
567
568 Figure 9. BSE images of $TiB_2$ parageneses.  a, $TiB_2$ crystal in silicate glass, accompanied by
569 TiC, $Ti_2Si$ and ZrP.  b, a compound grain of $TiB_2$ and a silicide alloy that has unmixed into Fe-
570 rich and Ti-rich components. The silicate glass in the right-hand end of the melt inclusion is
571 full of amoeboid blobs of Ti(N,O).
572
573 Figure 10.  BSE image of a melt inclusion in corundum, containing a crystal of $TiB_2$
574 embedded in a Mg,Ti-rich variety of hibonite, and a crystal of the phase $MgAl_8O_{13}$, a possible
575 analog to deltalumite.  Small bright blebs in a central vein are ZrP.
576
577 Figure 11.  BSE image of an irregular crystal of $TiB_2$ (dark grey) inside a skeletal crystal of
578 corundum (black); the skeletal cavities are filled by a mixture of Ti(N,O) (white) and silicate
579 glass (pale grey).  The nitride phase appears to intrude the $TiB_2$ grain.
580
581 Figure 12.  EELS spectra of Ti in $TiB_2$, TiC and TiN.
582

Table 1. Electron microprobe analyses (wt% of elements) and atomic proportions of $TiB_2$

| Sample | 1124C | 1124E | 1124E | 1124E | NGC #12 | 1124E | mean |
|---|---|---|---|---|---|---|---|
| | $n=1$ | $n=4$ | $n=1$ | $n=1$ | $n=6$ | $n=3$ | |
| Ti | 67.49 | 63.22 | 58.87 | 60.58 | 66.56 | 67.58 | 65.12 |
| Cr | 0.02 | 0.93 | 1.89 | 0.93 | 0.25 | 0.21 | 0.54 |
| Al | 0.57 | 0.00 | 0.00 | 0.02 | 0.02 | 0.03 | 0.05 |
| V | 0.10 | 3.92 | 11.00 | 6.97 | 1.00 | 1.03 | 2.68 |
| B | 27.50 | 30.58 | 30.38 | 32.0 | 30.98 | 31.24 | 30.74 |
| Si | 0.02 | 0.00 | 0.00 | 0.15 | 0.01 | 0.00 | 0.02 |
| Mn | 0.00 | 0.45 | 0.00 | 0.03 | 0.00 | 0.00 | 0.12 |
| Fe | 0.00 | 0.90 | 0.00 | 0.74 | 0.01 | 0.00 | 0.28 |
| C | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| N | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| O | 3.70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.24 |
| Total | 99.40 | 100.00 | 102.14 | 101.42 | 98.84 | 100.27 | 99.80 |
| | | | | | | | |
| at % | | | | | | | |
| Ti | 33.50 | 30.63 | 28.65 | 28.80 | 35.13 | 32.89 | 31.60 |
| Cr | 0.01 | 0.42 | 0.85 | 0.41 | 0.12 | 0.05 | 0.24 |
| Al | 0.50 | 0.00 | 0.00 | 0.00 | 0.02 | 0.04 | 0.04 |
| V | 0.05 | 1.82 | 5.03 | 3.11 | 0.50 | 0.47 | 1.23 |
| B | 60.43 | 66.57 | 65.47 | 67.36 | 64.26 | 66.55 | 66.50 |
| Si | 0.02 | 0.00 | 0.00 | 0.13 | 0.01 | 0.04 | 0.05 |
| Mn | 0.00 | 0.19 | 0.00 | 0.01 | 0.00 | 0.00 | 0.05 |
| Fe | 0.00 | 0.38 | 0.00 | 0.31 | 0.01 | 0.00 | 0.11 |
| C | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| N | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| O | *5.49* | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.91 |
| Total | 100.00 | 100.00 | 100.00 | 100.10 | 100.10 | 100.00 | 99.80 |
| B/(Ti+Al+Cr+V) | 1.77 | 2.03 | 1.90 | 2.08 | 1.80 | 1.99 | 2.01 |
| description | isolated inclusion | boride xl in ball | boride xl in ball | boride xl in ball | incl. in Type S pocket | lamellar incl. in spinel | |

Typical 1s precision is 1-2 % for major elements, and 5-10% for minor elements.

**Table 2. EDS and EMP analyses of phases associated wth selected occurrences of TiB$_2$**

Analyses are EDS unless indicated as EMP

| | Fig. 2 | | | | | Fig. 3a | | | | | Fig. 3b | | | | Fig. 3c |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Figure | | | | | | | | | | | | | | | |
| Mount no. | Mount 1 | | | | | WLG1124E | | | | | NGC-S5 | | | | Corundum-479G-03 |
| Sample no. | 49-50/9 | | | | | 1124E/12 | | | | | 1124 | | | | |
| | TiB$_2$ | MgTi$_2$Al$_4$(Si,Zr)O$_{12}$ | silicide 1 (Fe,Ti,Al)$_2$Si | silicide 2 FeTiSi | TiS | TiB$_2$ | TiB$_2$ | Ti(N,O,C) | silicide 1 (Fe,Mn,Cr)$_3$Si | silicide 2 FeTiSi | TiB$_2$ | silicide 1 FeTi(Si,P) | silicide 2 (Ti,Fe,Cr)$_3$Si | Ti(N,O) | TiB$_2$ |
| wt% | n=3 | EMP n=2 | | | n=3 | n=3 | EMP n=1 | EMP n=3 | | | n=2 | | | | |
| Si | 1.21 | 5.00 | 23.9 | 20.7 | | | 0.15 | | 13.4 | 18.4 | | 14.8 | 14.7 | | |
| Zr | | 4.32 | | | | 0.25 | | | | | | | | | |
| Ti | 56.5 | 20.77 | 40.7 | 31.7 | 54.6 | 71.1 | 61.58 | 75.01 | 5.3 | 29.3 | 71.1 | 30.2 | 56.6 | 77.0 | 70.0 |
| Al | | 21.29 | 8.3 | 4.0 | | | 0.02 | | | | 0.1 | | | | |
| Cr | 2.1 | | 3.2 | 2.3 | | 2.0 | 0.92 | | 4.5 | 3.0 | | 3.9 | 1.3 | | |
| V | 4.1 | | | | | 2.1 | 6.97 | | 0.41 | 0.84 | | 1.6 | 0.8 | | |
| P | | | 0.09 | 0.27 | | | | | | 0.58 | | 4.7 | 0.4 | | |
| W | | | | | | | | | | 0.93 | | | | | |
| Fe | 1.31 | 0.02 | 22.6 | 40.0 | | 0.33 | 0.74 | | 66.4 | 41.1 | | 41.0 | 22.7 | | |
| Ni | | | | | | | | | | | | | | | |
| Mn | | 0.03 | 1.2 | 1.1 | 0.7 | | | | 7.8 | 4.2 | | 0.7 | 0.4 | | |
| Mg | | 5.28 | | | | | | | | | | | | | |
| Ca | | 0.01 | | | | | | | | | | | | | |
| Ba | | | | | | | | | | | | | | | |
| Na | | | | | | | | | | | | | | | |
| K | | | | | | | | | | | | | | | |
| S | | | | | 38.9 | | | | | 0.23 | | | | | |
| F | | | | | | | | | | | | | | | |
| B | 34.3 | | | | | 23.9 | 29.51 | | | | 30.8 | | | | 30.9 |
| N | | | | | | | | 14.9 | | | | | | 18.1 | |
| C | | | | | | | | 2.5 | | | | | | | |
| O | | 40.49 | | | 4.0 | | | 8.57 | | | | | | 8.5 | |
| sum | 99.5 | 97.2 | 100.0 | 100.1 | 98.2 | 99.7 | 99.9 | 101.0 | 97.8 | 98.6 | 102 | 96.9 | 96.9 | 103.6 | 100.9 |
| other phases* | | | | | | | | | | | Ti*, CTAZ | | | | |
| DCr Tib/silic | 0.66 | | | | | 0.44 | 0.31 | | | | | | | | 0 |
| DV Tib/silic | >4 | | | | | 5.12 | 8.30 | | | | | | | | 0 |
| atomic % | | | | | | | | | | | | | | | |
| Si | 0.95 | 4.24 | 34.04 | 31.7 | | | | | 23.70 | 30.08 | | 24.36 | 24.08 | | |
| Zr | | 1.13 | | | | 0.08 | | | | | | | | | |
| Ti | 26.0 | 10.32 | 34.01 | 28.34 | 48.4 | 39.3 | 30.75 | 46.32 | 5.50 | 28.11 | 29.7 | 29.17 | 54.41 | 46.9 | 33.9 |
| Al | | 18.78 | 12.31 | 6.34 | | | | | | | | | | | |
| Cr | 0.89 | | 2.46 | 1.89 | | 1.02 | 0.42 | | 4.30 | 2.65 | | 3.49 | 1.15 | | |
| V | 1.77 | | | | | 1.09 | 3.27 | | 0.40 | 0.76 | | 1.46 | 0.72 | | |
| P | | | 0.12 | 0.37 | | | | | | 0.86 | | 7.02 | 0.59 | | |
| W | | | | | | | | | | 0.23 | | | | | |
| Fe | 0.52 | 0.01 | 16.19 | 30.65 | | 0.16 | 0.32 | | 59.05 | 33.8 | | 33.94 | 18.7 | | |
| Ni | | | | | | | | | | | | | | | |
| Mn | | 0.01 | 0.87 | 0.86 | | | | | 7.05 | 3.51 | | 0.59 | 0.34 | | |
| Mg | | 5.18 | | | | | | | | | | | | | |
| Ca | | | | | | | | | | | | | | | |
| Ba | | | | | | | | | | | | | | | |
| Na | | | | | | | | | | | | | | | |
| K | | | | | | | | | | | | | | | |
| S | | | | | 51.6 | | | | | | | | | | |
| F | | | | | | | | | | | | | | | |
| B | 69.9 | | | | | 58.4 | 65.24 | | | | 70.3 | | | | 66.1 |
| N | | | | | | | | 31.45 | | | | | | 37.7 | |
| C | | | | | | | | 6.15 | | | | | | | |
| O | | 60.23 | | | | | | 15.83 | | | | | | 15.5 | |
| sum | 100.03 | 99.90 | 100.00 | 100.15 | 100.00 | 100.1 | 100.0 | 99.8 | 100.0 | 100.0 | 100.00 | 100.03 | 99.99 | 100.1 | 99.95 |

* T*, tistarite; CTAZ, carmeltazite

-SY

| $TiB_2$ EMP n=2 | Ti(N,O) EMP n=2 | silicide 1 $(Ti,Fe)_2(Si,P)$ | silicide 2 $Ti_3(Si,P)$ | $TiB_2$ | silicide FeTiSi | Ti oxide 1 $Ti_4AlO_5$ | Ti oxide 2 $Ti_5Al_2O_8$ | $TiB_2$ | silicide Fe3Si | $TiB_2$ n=4 | Ti(N,O,C) EMP n=3 | silicide $(Fe,Cr,Ti)_2Si$ | silicate | sulfide TiS | $TiB_2$ core | $TiB_2$ rim | sulfide TiS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 15.2 | 14.6 | | 20.1 | | | 2.1 | 13.4 | 1.7 | 0.24 | 20.5 | 9.8 | | | | |
| | | | | | | | | | | | | | 7.3 | | | | |
| 69.42 | 79.8 | 64.5 | 84.4 | 70.1 | 35.9 | 66.3 | 54.9 | 27 | 0.3 | 55.3 | 75.2 | 7.2 | 17.8 | 49.7 | 31.2 | 31.1 | 53.8 |
| 0.06 | | | | | | 8.7 | 13.2 | | | 0.75 | 0.06 | 0.92 | 20.4 | | | | |
| | | 2.3 | | 0.7 | 2.3 | | | 4.0 | 5.1 | 2.8 | | 12.8 | | | 2.1 | 0.12 | |
| 0.22 | | 1.5 | | 2.2 | 1.2 | | | 13.5 | 1.8 | 12.5 | 0.48 | 5.0 | | | 3.5 | | |
| | | 9.4 | 0.78 | | 0.41 | | | 4.1 | | | | 0.61 | | | | | |
| | | 6.6 | | 0.30 | 36.6 | | | 13.4 | 79.0 | 4.3 | 0.05 | 51.7 | | 0.53 | 0.46 | 0.26 | |
| | | 0.61 | | | 0.81 | | | | | | | 1.4 | | 0.74 | | | 0.2 |
| | | | | | | | | | | | | | 8.2 | | | | |
| | | | | | | | | | | | | | | 33.3 | | | 45.2 |
| 29.87 | | | | 26.1 | | | | 35.5 | | 22.5 | | | | | 37.4 | 32.8 | |
| | 9.5 | | | | | | | | | | 10.7 | | | | | | |
| | | | | | | | | | | | 4.0 | | | | | | |
| | 10.4 | | | | | 24.9 | 31.8 | | | | 8.5 | | 36.2 | 11.0 | | | |
| 99.6 | 99.7 | 100.1 | 99.8 | 99.4 | 97.3 | 99.9 | 99.9 | 99.6 | 99.6 | 99.8 | 99.2 | 100.1 | 99.7 | 95.3 | 74.7 | 64.3 | 99.2 |
| | | | | Ti* | | | | CTAZ | | | | | | | | | |
| | | | | 0.30 | | | | 0.78 | | 0.22 | | | | | 0.51 | | |
| | | | | 1.8 | | | | 7.5 | | 2.50 | | | | | 1.40 | | |
| | | 19.11 | 22.5 | | 32.28 | | | 1.61 | 23.6 | 1.64 | | 32.72 | 8.39 | | | | |
| | | | | | | | | | | | | | 1.93 | | | | |
| 34.4 | 55.7 | 58.79 | 76.33 | 37.6 | 33.83 | 42.44 | 31.65 | 12.16 | | 31.2 | 48.9 | 6.74 | 8.95 | 49.45 | 15.3 | 18.4 | 44.4 |
| 0.05 | | | | | | 9.88 | 13.5 | | | 0.75 | 0.07 | 1.53 | 18.19 | | 0.4 | | |
| | | 1.93 | | 0.34 | 2 | | | 1.66 | 4.8 | 1.45 | | 11.03 | | | 0.95 | 0.07 | |
| 0.1 | | 1.28 | | 1.1 | 1.06 | | | 5.72 | 1.7 | 6.6 | 0.3 | 4.4 | | | 1.65 | | |
| | | 13.24 | 1.09 | | 0.6 | | | 2.85 | | | | 0.94 | | | | | |
| | | 5.16 | | 0.14 | 29.56 | | | 5.17 | 69.9 | 2.08 | | 41.5 | | 0.64 | 0.19 | 0.13 | |
| | | 0.48 | | | 0.67 | | | | | | | 1.14 | | 0.45 | | | |
| | | | | | | | | | | | | | 8.12 | | | | |
| | | | | | | | | | | | | | | 49.46 | | | 55.6 |
| 65.48 | | | | 61.3 | | | | 70.8 | | 56.23 | | | | | 81.5 | 81.5 | |
| | 22.6 | | | | | | | | | | 23.79 | | | | | | |
| | | | | | | | | | | | 10.37 | | | | | | |
| | 21.7 | | | | | 47.68 | 54.85 | | | | | 16.55 | 54.43 | | | | |
| 100.00 | 100.04 | 99.99 | 99.92 | 100.48 | 100.00 | 100.00 | 100.00 | 99.97 | 100.00 | 100.00 | 100.00 | 100.00 | 100.01 | 100.00 | 100.0 | 100.1 | 100.0 |

| | | | | Fig. 8 WLG1124B 1124B/15 | | | | | Fig. 9a SY-01 1129 | | | Fig. 10 SY-01 1129 | | Fig. 11 WLG1124E 1124E/8 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| silicide 9 (Ti,Fe)$_3$Si$_2$ | silicide 7 (Fe,Ti,Cr)Si | silicide 6 FeTiSi | incl in TiB2 FeTiSi | TiB$_2$ | TiB$_2$ EMP n=4 | spinel | Ti(N,O,C) EMP n=4 | glass | TiB$_2$ | ZrP | glass | MgAl$_8$O$_{13}$ | hibonite | TiB$_2$ EMP n=4 | Ti$_2$(N,O)$_3$ EMP n=3 |
| 27.3 | 33.3 | 23.0 | 23.5 | | 0.05 | | | 21.6 | | 0.32 | 19.6 | 0.12 | | 0.01 | 0.31 |
| | | | | | | | | | | 69.4 | | | | 0.04 | |
| 37.0 | 17.5 | 27.6 | 28.2 | 71.0 | 68.35 | 3.9 | 74.55 | 0.51 | 69.1 | 4.5 | 0.3 | 55.1 | 53.3 | 66.6 | 67.24 |
| | | | | | 0.05 | 37.8 | 0.09 | 20.8 | | 0.2 | 24.8 | | | 0.02 | 0.13 |
| 9.1 | 15.5 | 4.1 | 4.1 | | 0.12 | | | | | | | | | 0.25 | 0.02 |
| 3.7 | 3.3 | 2.5 | 2.5 | | 1.03 | | 0.08 | | | | | | | 1.0 | 0 |
| | | | | | | | | | | 24.2 | | | | | |
| 21.1 | 27.8 | 40.6 | 39.3 | | | | | | | | | | | 0.01 | 0 |
| 1.2 | 2.1 | 1.6 | 1.5 | | | | | | | | | | 0.12 | 0.00 | 0 |
| | | | | | | 11.4 | | | | | 0.84 | 6.4 | 0.45 | | |
| | | | | | | | | 14.65 | | | 17.4 | | 5.96 | | |
| | | | | | | | | | | | 1.5 | | | | |
| | | | | | | | | | | | 0.88 | | | | |
| | | | | | | | | 0.23 | | | 3.1 | | | | |
| | | | | | | | | 0.23 | | | 0.37 | | | | |
| | | | | | | | | | | | 0.39 | | | | |
| | | | | 29.0 | 31.2 | | | | 27.6 | | | | | 31.0 | 0 |
| | | | | | | | 14.50 | | | | | | | | 22 |
| | | | | | | | 2.00 | | 3.0 | | | | | n/a | n/a |
| | | | | | | 39.5 | 9.00 | 38.5 | | | 30.3 | 38.4 | 38.0 | n/a | 9.5 |
| 99.4 | 99.5 | 99.4 | 99.1 | 100.0 | 100.84 | 92.6 | 100.2 | 96.5 | 99.7 | 98.7 | 99.5 | 100.0 | 97.8 | 98.9 | 99.2 |
| | | | | Ti*, CTAZ | | | | | | | | | | | |
| 40.6 | 48.4 | 36.5 | 36.6 | | 0.04 | | | 17.73 | | 0.68 | 16.84 | 0.1 | | 0.01 | 0.31 |
| | | | | | | | | | | 45.86 | | | | 0.01 | |
| 32.3 | 14.9 | 25.1 | 25.8 | 35.6 | 32.9 | 1.84 | 46.82 | 0.25 | 34.00 | 5.69 | 0.16 | 43.3 | 43.7 | 32.48 | 39.18 |
| | | | | | 0.04 | 31.69 | 0.1 | 17.77 | | 0.44 | 22.02 | | | 0.02 | 0.13 |
| 7.3 | 12.2 | 3.4 | 3.5 | | 0.05 | | | | | | | | | 0.14 | |
| 3.0 | 2.6 | 2.1 | 2.2 | | 0.47 | | 0.05 | | | | | | | 0.5 | |
| | | | | | | | | | | 46.99 | | | | | |
| 15.8 | 20.3 | 31.7 | 30.8 | | | | | | | | | | | | |
| 0.9 | 1.6 | 1.2 | 1.2 | | | | | | | | | | 0.05 | | |
| | | | | | | 10.61 | | | | | 0.83 | 5.56 | 0.41 | | |
| | | | | | | | | 8.43 | | | 10.46 | | 3.29 | | |
| | | | | | | | | | | | 0.26 | | | | |
| | | | | | | | | | | | 0.92 | | | | |
| | | | | | | | | 0.14 | | | 1.88 | | | | |
| | | | | | | | | 0.17 | | | 0.28 | | | | |
| | | | | | | | | | | | 0.49 | | | | |
| | | | | 64.4 | 66.5 | | | | 60.12 | | | | | 66.93 | |
| | | | | | | | 31.12 | | | | | | | | 43.61 |
| | | | | | | | 5.01 | | 5.88 | | | | | n/a | |
| | | | | | | 55.85 | 16.91 | 55.48 | | | 45.52 | 51.0 | 52.55 | n/a | 16.56 |
| 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 99.7 | 99.7 | 100.0 | 100.0 | 100.1 | 99.8 |

**BSE**

Crn

Ti-rich

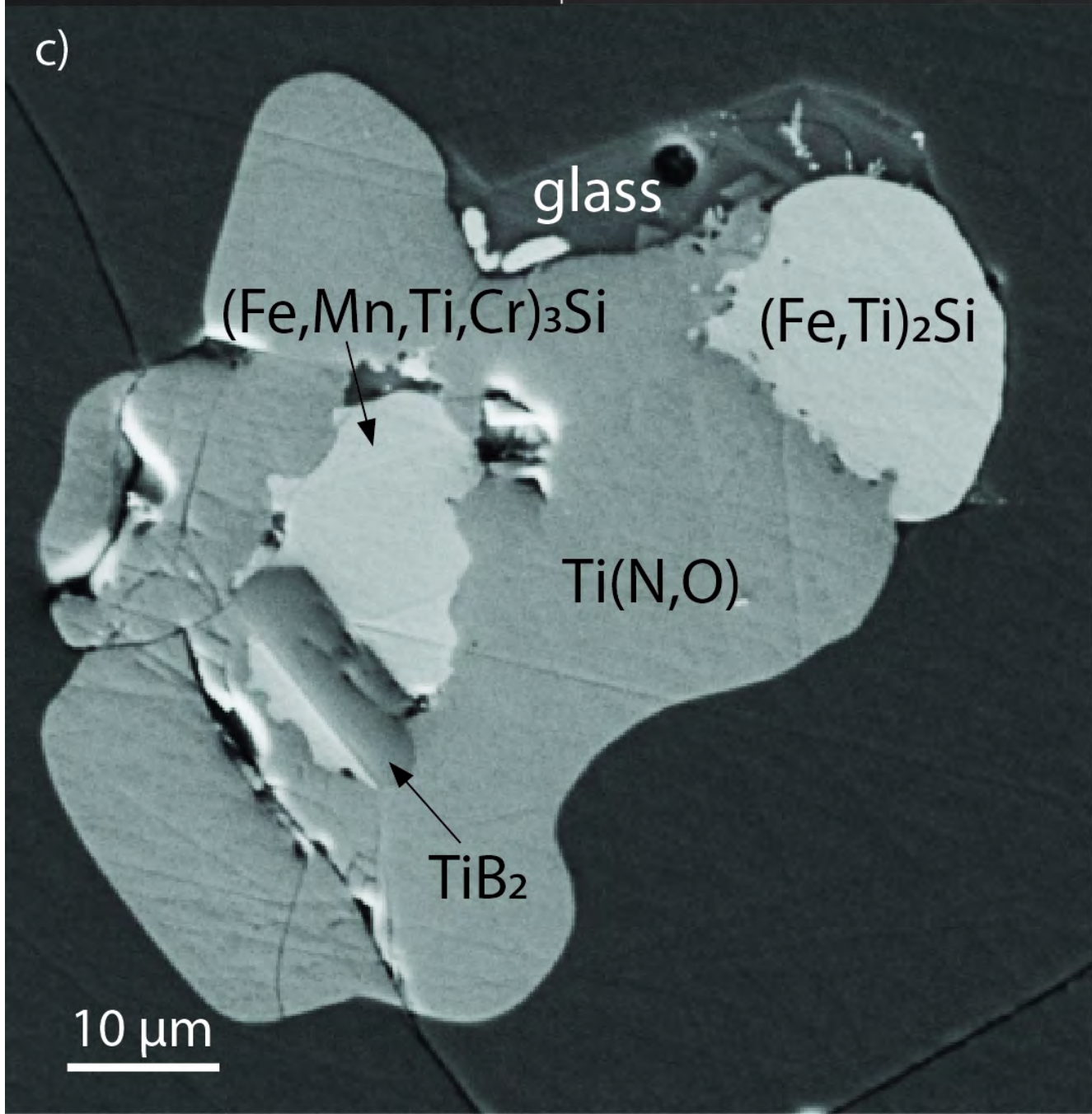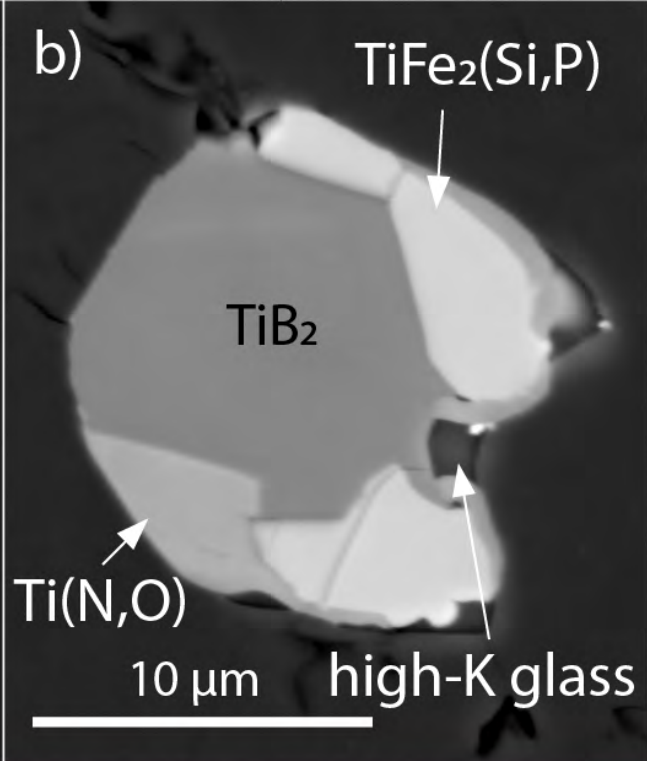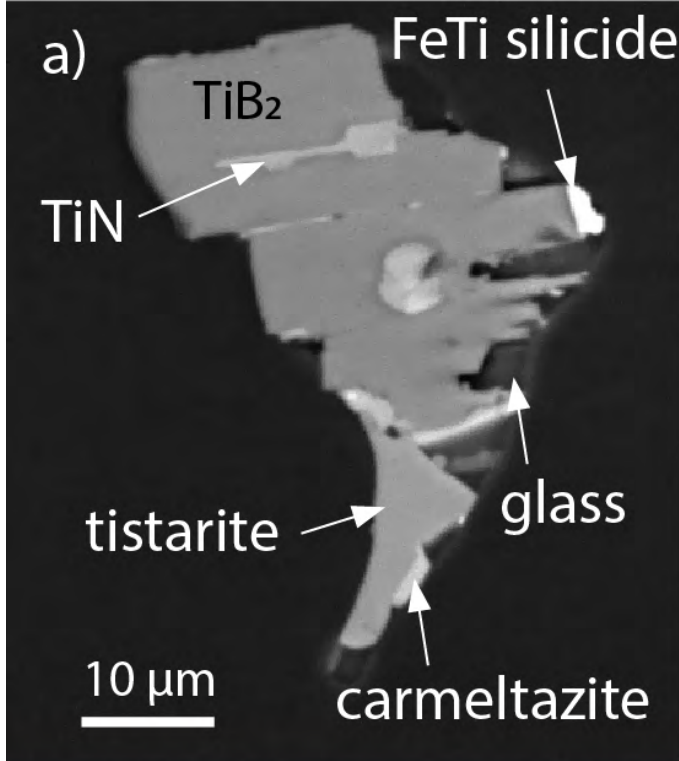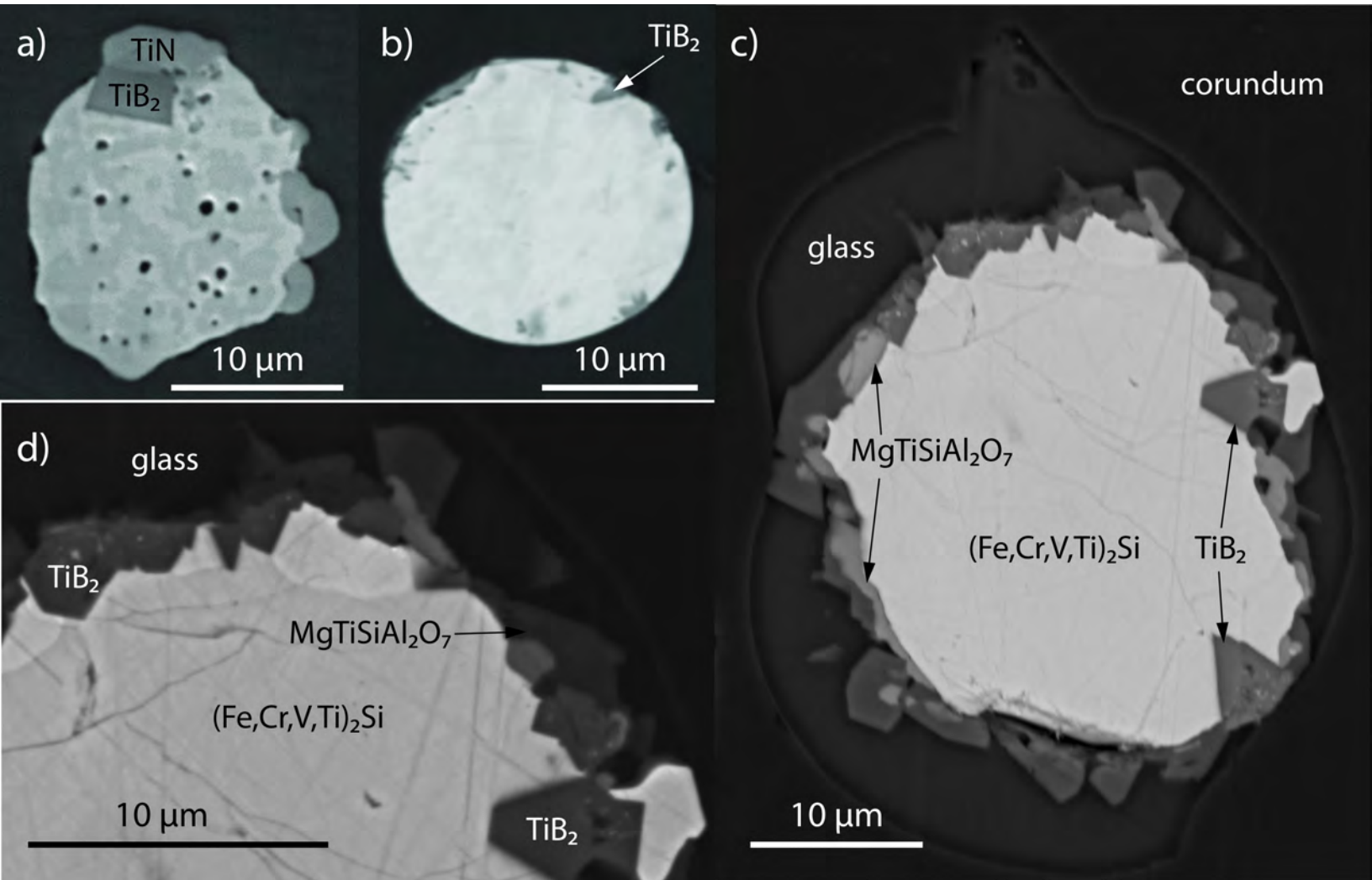Fe-Ti silicide

Ti-poor

20 μm

**BSE**

Crn

Ti-rich

Fe-Ti silicide

Ti-poor
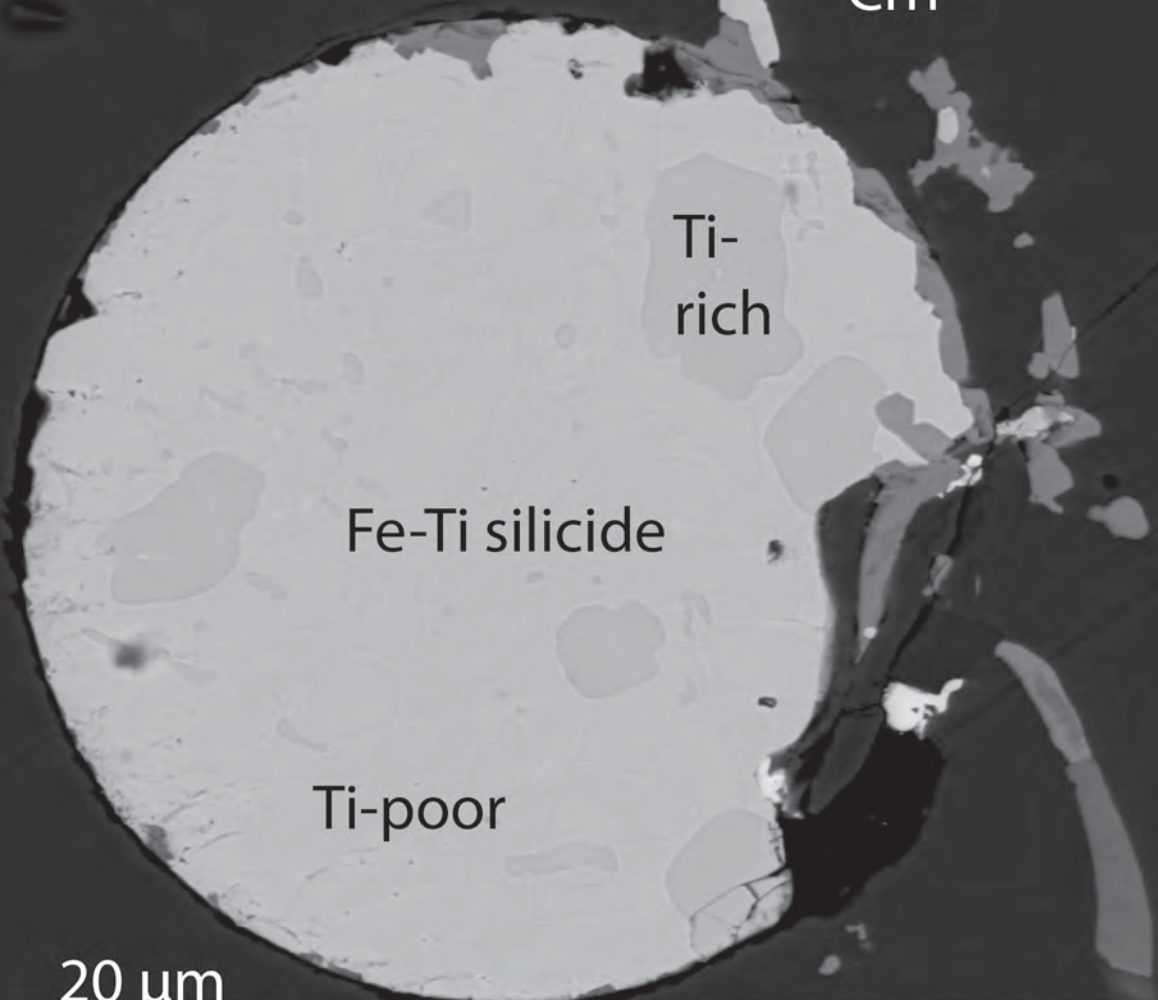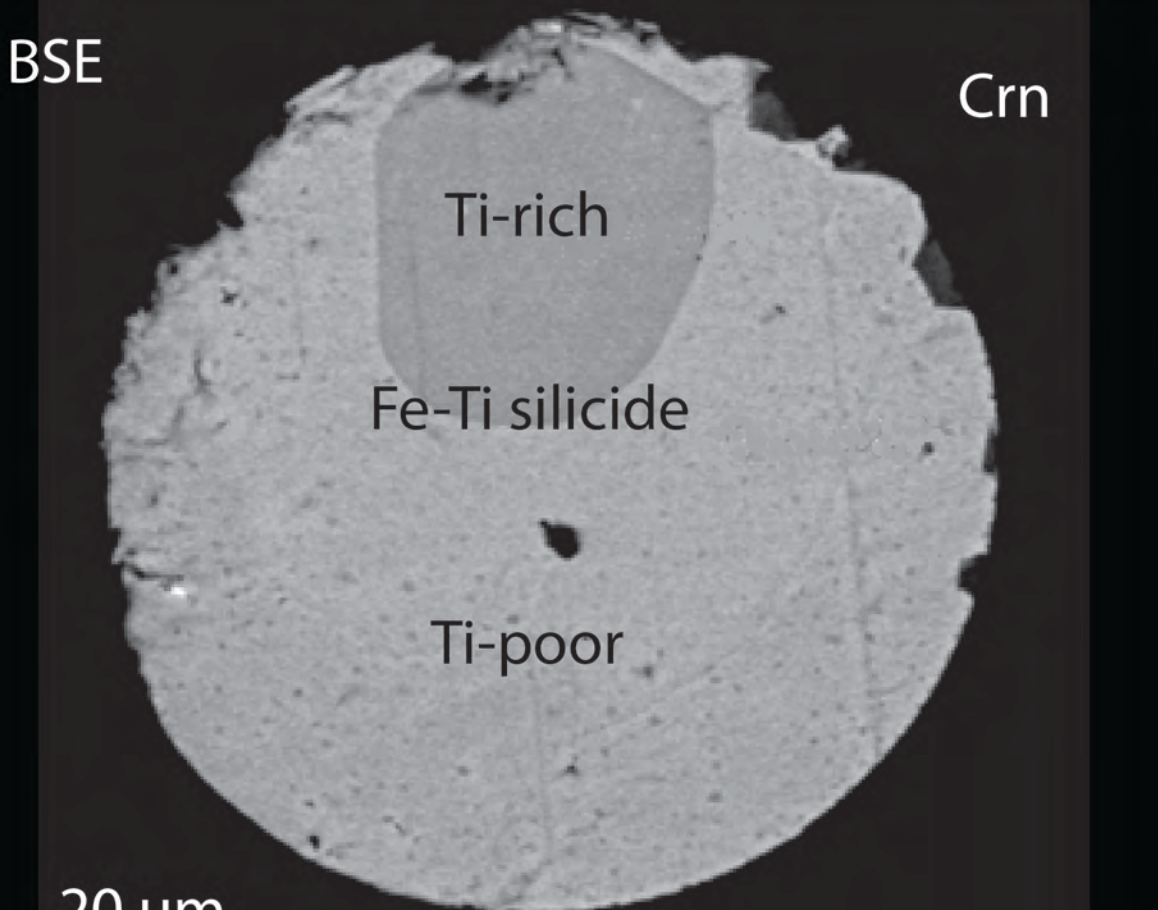
20 μm
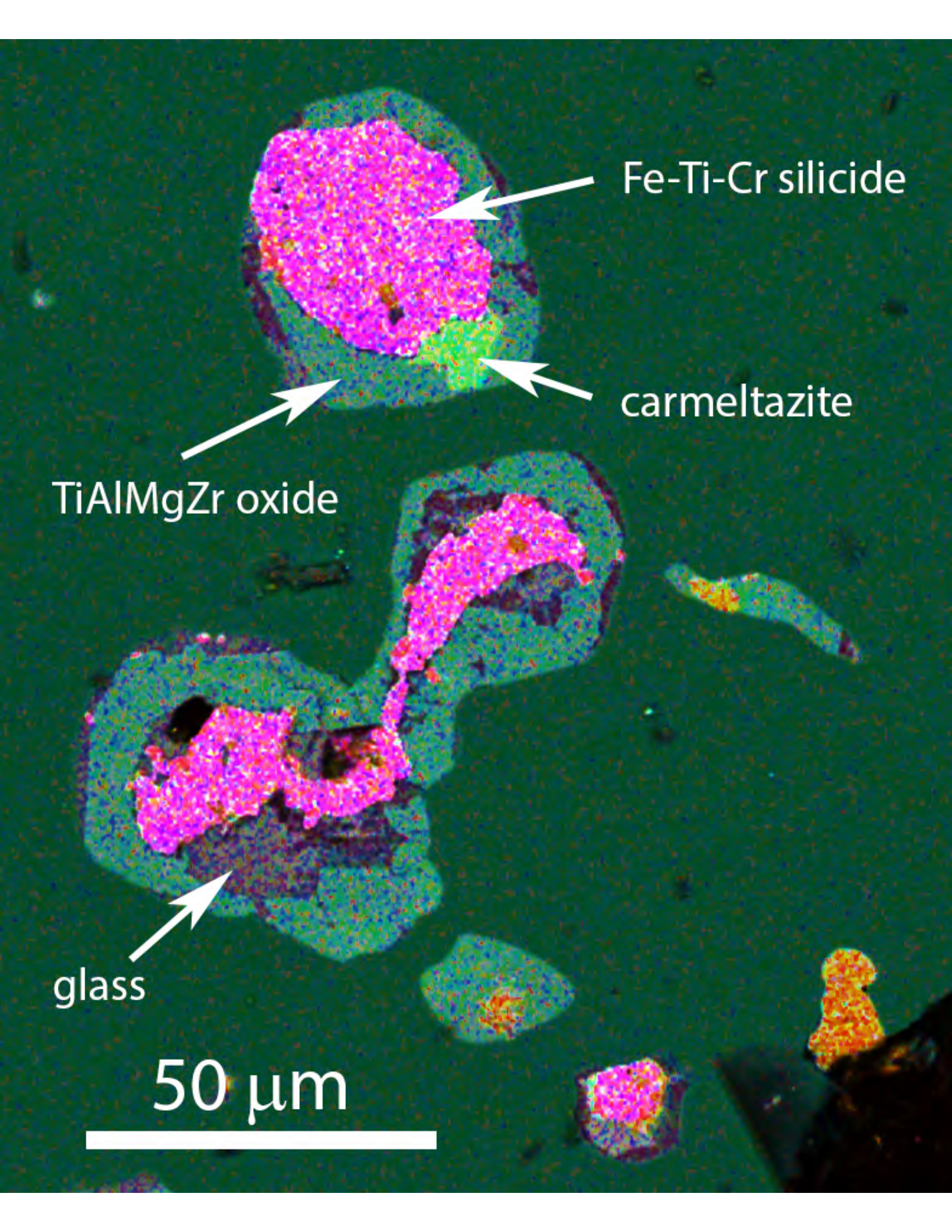
Fe-Ti-Cr silicide

carmeltazite

TiAlMgZr oxide

glass
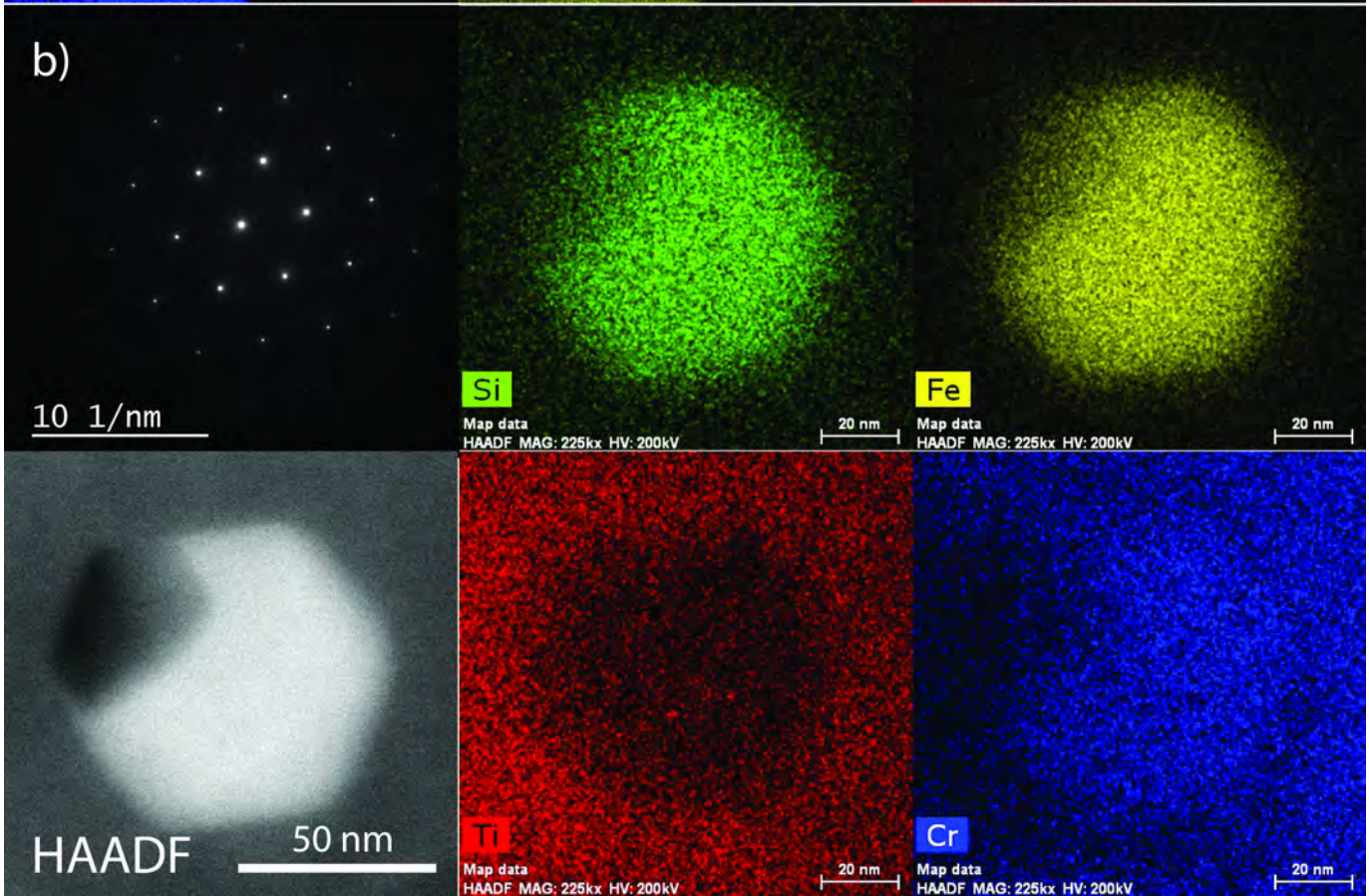
50 μm

a) TiB₂, TiN, FeTi silicide, tistarite, glass, carmeltazite, 10 μm
b) TiFe₂(Si,P), TiB₂, Ti(N,O), high-K glass, 10 μm
c) glass, (Fe,Mn,Ti,Cr)₃Si, (Fe,Ti)₂Si, Ti(N,O), TiB₂, 10 μm

a) TiN, TiB$_2$ — 10 μm

b) TiB$_2$ — 10 μm

c) corundum, glass, MgTiSiAl$_2$O$_7$, (Fe,Cr,V,Ti)$_2$Si, TiB$_2$ — 10 μm

d) glass, TiB$_2$, MgTiSiAl$_2$O$_7$, (Fe,Cr,V,Ti)$_2$Si, TiB$_2$ — 10 μm

a) carbon vein
AlMgTiZrO
3 silicide phases
TiS
Ca phase
amorphous
TiB$_2$
SiO
amorphous

b)
Ti
Map data
HAADF MAG: 7100x HV: 200kV
1 µm

Si
Map data
HAADF MAG: 7100x HV: 200kV
1 µm

Fe
Map data
HAADF MAG: 7100x HV: 200kV
1 µm

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

a)

HAADF
Map data
HAADF MAG: 20.0kx HV: 200kV
400 nm

B
O
Map data
HAADF MAG: 20.0kx HV: 200kV
400 nm

Si
Map data
HAADF MAG: 20.0kx HV: 200kV
400 nm

Cr
Map data
HAADF MAG: 20.0kx HV: 200kV
400 nm

Fe
Map data
HAADF MAG: 20.0kx HV: 200kV
400 nm

Ti
Map data
HAADF MAG: 20.0kx HV: 200kV
400 nm

b)

10 1/nm

Si
Map data
HAADF MAG: 225kx HV: 200kV
20 nm

Fe
Map data
HAADF MAG: 225kx HV: 200kV
20 nm

HAADF
50 nm

Ti
Map data
HAADF MAG: 225kx HV: 200kV
20 nm

Cr
Map data
HAADF MAG: 225kx HV: 200kV
20 nm

a) tistarite, Crn, TiB₂, Spl, Carmeltazite, dmisteinbergite, Void, 100 μm

b) Ti-rich inclusions, Ti-rich needles

a) Crn, TiC, Ti$_2$Si, TiB$_2$, glass, ZrP, 10 μm

b) Crn, Ti(N,O), TiB$_2$, FeSi + TiSi, 10 μm

TiB$_2$

MgAl$_8$O$_{13}$

Ti hibonite

50 µm