Immiscible metallic melts in the upper mantle beneath Mount Carmel, Israel: Silicides, phosphides and carbides

William L. Griffin¹, Sarah E.M. Gain¹², Martin J. Saunders², Jin-Xiang Huang¹, Olivier Alard¹, Vered Toledo³ and Suzanne Y. O’Reilly¹

¹ARC Centre of Excellence for Core to Crust Fluid Systems (CCFS) and GEMOC, Earth and Environmental Sciences, Macquarie University, NSW 2109, Australia; bill.griffin@mq.edu.au
²Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, WA 6009, Australia
³Shefa Gems Ltd., Netanya 4210602, Israel

Abstract

Xenolithic corundum aggregates in Cretaceous mafic pyroclastics from Mount Carmel contain pockets of silicate melts with mineral assemblages (SiC (moissanite), TiC, Ti₂O₃ (tistarite), Fe-Ti-Zr silicides/phosphides) indicative of magmatic temperatures and oxygen fugacity (fO₂) at least 6 log units below the Iron-Wüstite buffer (ΔIW≤-6). Microstructural evidence indicates that immiscible, carbon-rich metallic (Fe-Ti-Zr-Si-P) melts separated during the crystallization of the silicate melts. The further evolution of these metallic melts was driven by the crystallization of two main ternary phases (FeTiSi and FeTiSi₂) and several near-binary phases, as well as the separation of more evolved immiscible melts.

Reconstructed melt compositions fall close to cotectic curves in the Fe-Ti-Si system, consistent with trapping as metallic liquids. Temperatures estimated from comparisons with experimental work range from ≥1500 °C to ca 1150 °C; these probably are maximum values, due to the solution of C, H, P and Zr. With decreasing temperature (T), the Si, Fe and P contents of the Fe-Ti-Si melts increased, while contents of Ti and C decreased. The increase in Si with declining T implies a corresponding decrease in fO₂, probably to ca ΔIW-9. The solubility of P in the metallic melts declined with T and fO₂, leading to immiscibility between Fe-Ti-Si melts and (Ti,Zr)-(P,Si) melts. Decreasing T and fO₂ also reduced the solubility of C in the liquid metal, driving the continuous crystallization of TiC and SiC during cooling. The lower-T metallic melts are richer in Cr, and to some extent V, as predicted by experimental studies showing that Cr and V become more siderophile with decreasing fO₂.

These observations emphasise the importance of melt-melt immiscibility for the evolution of magmas under reducing conditions. The low fO₂ and the abundance of carbon...
in the Mt Carmel system are consistent with a model in which differentiating melts were
fluxed by fluids that were dominated by CH$_4$+H$_2$, probably derived from a metal-saturated
sublithospheric mantle. A compilation of other occurrences suggests that these phenomena
may commonly accompany several types of explosive volcanism.

Keywords: Mt Carmel, oxygen fugacity, metallic melts, immiscibility, mantle methane

Introduction

The oxygen fugacity ($f_{O2}$) of Earth’s lithospheric mantle typically lies within the range
defined by the QFM (quartz-fayalite-magnetite) and IW (iron-wüstite) buffer reactions, and
broadly decreases relative to these buffers with depth (Frost and McCammon, 2008; Yaxley
et al., 2012). There are indications that the sublithospheric upper mantle, and the lower
mantle, are saturated in Fe metal or Fe-Ni-S melts, constraining $f_{O2}$ to near the IW buffer
(Frost and McCammon, 2008; Zhang et al., 2016). However, there also is evidence that some
volumes of the upper mantle have experienced much more reducing conditions, defined by
minerals such as moissanite (SiC), which commonly occurs in kimberlites (Huang et al., 2020;
Shiryaev et al., 2011) and requires $f_{O2}$ at least 6 log units below the IW buffer ($\Delta f_{IW}$-6) at
lithospheric pressure ($P$) and temperature ($T$) (Ulmer et al., 1998). Another example is the
super-reduced mineral association (native elements, carbides, silicides) described from
chromitites and peridotites in the ophiolites of the Yarlung-Zangbo suture of southern Tibet,
and similar bodies in the Polar Urals (Griffin et al., 2016b; Yang et al., 2015). Others include
unusual basalt-borne xenoliths (Liu et al., 2015) and a possibly kimberlitic beach pebble (Di
Pierro et al., 2003) whose origins are unclear.

These occurrences raise the question of how such reduced conditions could be
imposed, at least locally, on the more oxidized upper mantle, and how the resulting mineral
assemblages could be preserved from oxidation through reaction with the surrounding
mantle (Schmidt et al., 2014). Unfortunately, most of the ophiolitic and kimberlitic
occurrences are known from mineral separates, which provide little context for
understanding processes (Pujol-Solà et al., 2018; Zhang et al., 2016). However, similar
mineral associations have been recognized in melt pockets trapped in xenolithic corundum
aggregates in Cretaceous mafic pyroclastic deposits from the Mount Carmel area of
northern Israel (Fig. SD1; Griffin et al., 2018d; Xiong et al., 2017). This remarkable
occurrence provides new insights into the localized development of super-reducing conditions within the upper mantle or lower crust, with implications for the nature of mantle-derived C-O-H fluids and their significance in magmatic processes.

Over the last decade, the Shefa Yamim Ltd (now Shefa Gems Ltd) exploration project, focused on placer gem deposits, has recovered abundant xenocrysts of corundum as single crystals (sapphire, ruby) and as aggregates of skeletal and hopper-shaped crystals of corundum (trademarked as “Carmel Sapphire”) as well as moissanite (SiC) from pyroclastic vents and tuffs on Mt Carmel (primarily the Rakefet Magmatic Complex; Fig. SD1), and related alluvial deposits (Griffin et al., 2018d; Toledo et al., 2015; Xiong et al., 2017). Crystals of moissanite can be over 4 mm long; sapphire crystals are up to 2 cm (5.7 carats), while ruby crystals are typically smaller, but may contain up to >35 wt% Cr$_2$O$_3$ (Griffin et al., 2021). Pieces of “Carmel Sapphire” up to 12.2 carats in weight (ca 18 x 10 mm) have been available for this study, and stones of >33 cts have been recovered.

The mineral parageneses of the melts trapped in the corundum aggregates are complex; over 130 phases have been identified, of which ca 50% are previously unreported; others are until now known only from meteorites (Bindi et al., 2019; Griffin et al., 2019a; Griffin et al., 2020a; Griffin et al., 2020b; Griffin et al., 2018c; Griffin et al., 2018d; Huang et al., 2020). This paper discusses another important aspect of the Mount Carmel corundum-moissanite association: the separation and evolution of immiscible, carbon-rich Fe-Ti-Zr-Si-P melts during the crystallization of the silicate melts. Our aim is to document these parageneses, and to compare the phase relationships among the melts and their crystallization products with data from experimental metallurgy, to constrain the conditions prevailing within the magmatic system prior to eruption.

Geological setting

The material described here is derived from Cretaceous volcanic centers and related alluvial deposits in the Mt Carmel-Kishon River area of northern Israel (southern Galilee; Fig. SD1). This region experienced mafic volcanism during and following the Permo-Triassic rifting related to the opening of the Neo-Tethys ocean (Segev and Rybakov, 2011). Geophysical anomalies and the distribution of zircon xenocrysts in the Cretaceous pyroclastic deposits suggest the existence of a large volume of mafic rocks buried beneath
Mt Carmel, perhaps near the crust-mantle boundary (Ben-Avraham and Hall, 1977; Griffin et al., 2018c; Gvirtzman et al., 1990).

The relatively sparse Early Cretaceous continental magmatism in Israel (137-139 Ma; Segev, 2005, and references therein) comprises subalkaline to alkaline basalts, nephelinites, basanites, picrites and microgabbros with hotspot/mantle plume geochemical and isotopic signatures (Garfunkel, 1989; Laws and Wilson, 1997; Stein and Hofmann, 1992; Stein and Hofmann, 1994).

The Late Cretaceous (94-98 Ma, Turonian-Cenomanian) volcanic activity in northern Israel took place across a heavily faulted area of ca 150 km² in the Mount Carmel-Umm El Fahm area (Fig. SD-1b), and produced pyroclastic deposits of mafic to ultramafic composition in vents and layered deposits (Sass, 1980). The explosive volcanism took place in a shallow marine environment, during the deposition of marine carbonates and other sediments. In addition to the corundum aggregates discussed here, the pyroclastic deposits carry mantle-derived xenoliths (spinel peridotites, garnet ± spinel pyroxenites, garnet websterites), lower-crustal xenoliths (garnet-ilmenite granulites), megacrystic Mg-ilmenite, amphibole, and clinopyroxene, and a suite of xenocrysts (olivine, orthopyroxene, Cr-diopside, pyrope garnet) derived from mantle peridotites and pyroxenites in a subcontinental lithospheric mantle ca 100 km thick (Apter, 2014; Esperança and Garfunkel, 1986; Kaminchik et al., 2014; our unpublished observations; Mittlefehldt, 1986).

Assertions that the highly reduced assemblages from Mt Carmel area are of anthropogenic origin (Litasov et al., 2019a; Litasov et al., 2019b) are untenable on the basis of detailed geological evidence (Griffin et al., 2020c; Griffin et al., 2019b). In brief: (1) all of the mineral assemblages described in this and previous papers are found in situ in the Cretaceous pyroclastic rocks; (2) the associated alluvial deposits do not come from the bed of the modern Kishon River, but from paleoplacers resting on bedrock at the base of Pliocene-Pleistocene terraces well above the current drainage, and overlain by 4-10 meters of undisturbed sediments; (3) much of the heavy-mineral assemblage, including abundant moissanite, also is found in lithified Miocene beach placers, deposited during a marine incursion that spread surface materials across the Yizra’el valley. All of these deposits predate human occupation. Contrary to statements by Litasov et al., the area is pastoral, rather than industrial, and the main primary sources (the volcanoes) lie on Mt Carmel, well above the Kishon valley, and in an extensive nature reserve. The same geological facts make
it unlikely that the super-reduced phases have formed by lightning strikes (Griffin et al., 2018a).

Background: The Mount Carmel magmatic system

Most Carmel Sapphire comprises aggregates of skeletal to hopper-formed corundum crystals; this morphology indicates rapid crystallization from Al₂O₃-supersaturated melts or fluids (Figures 1, SD2; Griffin et al., 2016a). Melt pockets trapped within and between the corundum crystals contain mineral assemblages (tistarite (Ti₂O₃), SiC (moissanite), TiC, Fe-Ti-Zr silicides/phosphides) indicative of high T and low fO₂ (down to ΔIW ≤ -6). Even lower fO₂ (ΔIW-9 to -10) is required by the precipitation of a coarse-grained hibonite-grossite-vanadium assemblage (Griffin et al., 2019a; Griffin et al., 2020b), also found in the volcanic debris.

The major questions relate to (1) the genesis of melts that could rapidly precipitate large volumes of corundum; (2) the processes that ultimately could produce fO₂ comparable to that of the early solar nebula. There is much yet to learn about this magmatic system, but basic paragenetic studies (Griffin et al., 2016a; Griffin et al., 2019a; Griffin et al., 2020a; Griffin et al., 2018b; Griffin et al., 2020b; Griffin et al., 2020c; Griffin et al., 2018d) and the abundance of carbon in the xenoliths (see below) suggest that the low fO₂ reflects the interaction of evolved magmas with mantle-derived (CH₄+H₂) at high fluid/melt ratios. An overview of the different parageneses in the melt pockets (Griffin et al., 2016a; Griffin et al., 2018d; Xiong et al., 2017) recognises four general types: silicate glasses that crystallize oxides and silicates (Type S); Ti-oxynitrides and Ti-borides (Type N; Griffin et al., 2020a); desilicated, fluoride-rich assemblages (Type DF; hibonite-grossite; Griffin et al., 2019a); Fe-Ti-Zr silicides and phosphides, associated with TiC and SiC (Type A, this work).

The ejected material probably represents snapshots of individual melt-fluid subsystems, sampled by the eruptions at different stages of their evolution. However, if all of the material is treated as samples of a single system defined by declining fO₂, we can identify several stages of a proposed idealized process.

1. Precipitation of vesicular, Mn-rich wüstite, found in large (mm-to cm) fragments, which may reflect fO₂ near the magnetite - wüstite (MW) buffer.
2. Precipitation of Mg-rich calcite (large zoned crystals with resorbed Sr-rich cores, 
\[ {^{87}Sr/^{86}Sr = 0.70334 \pm 0.00013; \text{our unpublished in situ analyses}} \] probably occurred near the EMOD buffer (\( \Delta IW + 1.5 \)), taking up CO\(_2\) released by the partial oxidation of introduced CH\(_4\).

3. Separation of immiscible melts of Fe metal (Fe\(_0\)), Fe-oxides and Ti-oxides, with minor silicate components; these occur as abundant, commonly vesicular spherules up to a few mm across (Xiong et al., 2017). Their mineralogy suggests \( fO_2 \) equivalent to the iron-wüstite (IW) buffer. The low Ni contents (<1 wt%) of the Fe\(_0\) melts suggest a mafic, rather than an ultramafic, parental melt.

4. Separation of immiscible, carbon-rich Fe-Ti-silicide melts, from which TiC and SiC crystallized (Huang et al., 2020; this work). This would lead to rapid desilication of the magma, producing Al\(_2\)O\(_3\)-supersaturation in the residual magma.

5. Rapid growth of skeletal/hopper corundum crystals, trapping pockets of Ca-Al-Si oxide melt (Oliveira et al., 2020). Continued crystal fractionation and reduction in \( fO_2 \) led to further immiscibility, producing many of the alloy assemblages described here.

6. Precipitation of coarse hibonite+grossite+spinel aggregates, and immiscible separation of vanadium (V\(^0\)) melts, from late low-Si oxide melts that are not clearly related to the corundum aggregates (Griffin et al., 2020b).

The important role of CH\(_4\) in the evolution of this system is reflected in the precipitation of abundant SiC and TiC, the obvious presence of abundant volatiles (stages 1, 3) and the abundance of amorphous carbon in networks of breccia veins through the corundum aggregates, injected during or shortly before explosive eruption (Fig. SD4). The occurrence of native vanadium (V\(^0\)) and vanadium dihydride (VH\(_2\); Bindi et al., 2019) implies a coexisting fluid phase dominated by H\(_2\), at least at late stages (Griffin et al., 2019a).

Quench-textured dmisteinbergite (a polymorph of anorthite) in the melt pockets reflects the peritectic reaction Liq + Crn \( \rightarrow \) An, equivalent to the incongruent melting of anorthite (An \( \rightarrow \) Liq + Crn). This well-studied reaction is experimentally constrained to pressures (\( P \)) >0.9 GPa and temperatures (\( T \)) of ca 1450 °C (Goldsmith, 1980).

Thermodynamic modelling in the CaO-Al\(_2\)O\(_3\)-SiO\(_2\) system (Ottonello et al., 2013) suggests that grossite is not stable at \( P >1 \) GPa. The same modelling shows that the trapped silicate melts would not be in equilibrium with corundum at \( P <1 \) GPa. These \( P-T \) estimates place the proposed site of fluid-melt interaction in the uppermost mantle; the crust-mantle boundary in the area has been geophysically defined at ca 25 km depth (Segev and Rybakov,
Numerical modelling of zoning patterns in the corundum aggregates indicates that corundum initially grew in open systems that closed as crystallization proceeded, and that this happened on geologically short timescales (days to years; Oliveira et al., 2020).

**Sampling and Methods**

The field sampling and laboratory processing procedures, designed to exclude contamination, have been described in detail by Griffin et al. (2021).

The corundum aggregates and the included phases have been characterized using optical microscopy, scanning electron microscopy (SEM, FE-SEM) and energy-dispersive X-ray spectroscopy (SEM-EDS), electron microprobe analysis (EMP-WDS), cathodoluminescence (CL), 3D-CT scanning, LA-ICP-MS analysis (trace elements), FIB-TEM (imaging, crystallography, TEM–EDS, EELS) and Raman spectroscopy. The details of methods are given in the Supplementary Data.

Table 1 includes both SEM-EDS and EMP-WDS analyses, because in some cases phases large enough to be analyzed by SEM were too small to analyze with the available conventional EMP. Where the two types of data can be compared, the results show good correspondence, even though the averaged data for each phase are not necessarily from the same grains (see Table 1). TEM-EDS analyses are given in Table 2.

**Results**

**Petrography**

*Corundum and melt pockets*

Most fragments of the Carmel Sapphire are yellow-orange to dark brown in colour. Nearly all are irregular in shape, but some are rectangular prisms with depressed faces consistent with hopper growth (Fig. SD2a). Transparent fragments (Fig. SD2b) reveal intricate 3-dimensional networks of darker or brighter material. These represent pockets of silicate melts (darker in Fig. SD2c) and metallic melts (brighter) trapped between and within crystals. Strong CL correlates negatively with Ti contents (high Ti = darker CL) and outlines growth zoning and skeletal growth (Fig. 1); Ti contents typically rise toward melt pockets (Oliveira et al., 2020). Many larger specimens are cut by veins consisting mainly of carbon, and one of the largest specimens is a breccia of corundum fragments and minor SiC in a
carbon matrix. Raman spectroscopy, EBSD spectra and TEM analysis all indicate that the carbon is amorphous.

The corundum aggregates represent a complex, rapidly evolving mesh of growing crystals, melts and fluids, in which the sizes and shapes of trapped melt volumes were continuously changing (Oliveira et al., 2020). An important part of this evolution, as discussed below, was the multistage immiscibility between silicate melts, silicide melts and a fluid phase that was dominated by CH$_4$ and H$_2$ (Griffin et al., 2019a; Huang et al., 2020).

High-resolution 3D-µCT images (Figure SD2) show that a single "melt" volume may contain silicate melts (glasses) in one branch, silicide melts ("alloys") in another, and fluids (seen as "voids" in these images) in a third one. This can make it difficult to identify coexisting phases in 2D images. However, most aggregates contain many trapped melt pockets, and an overview of these can identify the coexistence of certain phases and help to recognize immiscibility relationships, even when these features may not be directly observable in a given pocket.

The mineral associations recognized in the petrographic study are summarized below.

Native Iron (Fe$^0$)

Spheres of native iron (Fe$^0$) occur as isolated inclusions in corundum, and more rarely in pockets of Ca-Al-Si oxide glass (Fig. 2). The slightly irregular borders and apparent intergrowth with the phenocryst phases (TiAl$_2$O$_5$, tistarite and spinel in this example) suggest that the Fe$^0$ melt was in equilibrium with the oxide melt.

Silicides and phosphides

Many of the silicide and phosphide phases occur in rounded balls of Fe-Ti-silicides enclosed in the silicate glasses and intergrown with oxide and silicate phases, or isolated in corundum. Some of these relationships are shown in Figure 3, where balls and irregular masses of FeTiSi are enclosed in an unknown Mg-Ti-Al oxide together with tistarite (Ti$_2$O$_3$), Carmelitazite (ZrAl$_2$Ti$_4$O$_8$) and Ca-Al-Si oxide glass. The FeTiSi contains many small euhedral grains of TiB$_2$. On closer inspection by TEM (Fig. 3c), the FeTiSi appears to be breaking down into three distinct silicides, enriched in Fe, Ti and Cr, respectively. The irregular boundaries among these phases suggest that this unmixing occurred in the molten state. Figure 3c also shows that euhedral TiB$_2$ crystallized from the silicide, probably before the unmixing (Griffin
et al., 2020a), and the silicide is associated with TiS. The hexagonal structure (P6_3mc) of this sulfide, as measured by TEM-ED, distinguishes it from wassonite (rhombohedral, R3m), found in the Yamato 691 enstatite chondrite (Nakamura-Messenger et al., 2012).

The Fe-Ti silicides contain euhedral crystals of TiC (khamrabaevite) that indicates crystallization of TiC directly from the silicide melts. The microstructures (Fig. 4) suggest that growing corundum crystals trapped and overgrew early TiC crystals, while expelling the host Fe$_3$Si melt into progressively smaller interstitial pockets. TEM imaging shows a narrow zone of (Zr,Ti)$_2$P along the contact between the two phases; this may have formed as Zr and P were expelled from one or both phases on cooling. Similarly, isolated grains of Fe$_3$Si commonly are rimmed by grains of TiC, TiB$_2$ and/or Ti(N,O) (Fig. 5). Silicide melts within glass pockets, apparently coexisting with tistarite and/or carmeltazite, may show similar concentrations of TiC, but in these cases it is not clear how much of the TiC has crystallized from the metallic melt, or from the oxide melt (Fig. 6).

The coexistence of immiscible silicide and oxide melts implies that similar major phases should be found in both types of melts, though at different abundances and with small differences in composition. The first phase to crystallize from many oxide melts is a Mg-Al spinel, and similar spinels are found in some silicide melts (Fig. 7), intergrown with a Ca-Al-Ti oxide phase ([Ca,Mg]$_2$(Al,Ti,Zr)$_{10}$O$_{17}$) and TiC. The same Ca-Al-Ti oxide occurs intergrown with carmeltazite in a nearby pocket of Ca-Al-Si oxide glass. The irregular outlines of the spinel grains in the silicides suggest that they crystallized against the melt phase, but after TiC. In this case a phosphide phase ([Fe,Ti]$_2$(Si,P)) with straight edges also appears to have crystallized from the original silicide melt, leaving an FeTiSi phase in the liquid state. This occurrence of Fe-Ti-Si-P phases is relatively common (Fig. 8). However, in many of the Fe-Ti silicide melts that show breakdown to ≥2 phases, as in Figure 3, the microstructures suggest the separation of immiscible melts. The most common minor, apparently exsolved, melts are richer in Ti and/or P than the original bulk silicide (Fig. 9).

A spectacular example of melt immiscibility is shown in Figure 10; spheres consisting of intergrown Zr-Ti-U phosphides and Ti-Zr-Fe silicides are embedded in a Ca-Al-Si oxide glass that also has crystallized Mg-Al spinel and hibonite (CaAl$_{12}$O$_{19}$). More commonly, the Zr-Ti silicides and phosphides are found as isolated inclusions in the corundum, many associated with TiC (Fig. 11). The fluidal contacts revealed in TEM images suggest that the silicides and phosphides in Figure 11 separated as melts, while the Zr-Ti-U phosphate...
crystallized from the silicide melt (cf. Fig 10). Other examples of these phases and their relationships to TiB₂ and TiC are shown in Griffin et al. (2020a).

Relationship to SiC

Moissanite (SiC) is a rare phenocryst in the Ca-Al-Si oxide melt pockets; most of the abundant moissanite recovered from the ejecta and alluvial deposits occurs as single grains. A study of the inclusion assemblages in such grains (Huang et al., 2020) shows that the SiC crystallized from a silicon-rich melt with minor contents of Fe, Al and Ca; some of the inclusion phases are identical to those found in the Fe-Ti silicide assemblages in the corundum aggregates. One sample (Fig. 12) illustrates some of these relationships. In an inclusion in corundum, a large TiC crystal has crystallized from a Ti-Fe silicide melt, along with a crystal of the undescribed phase Ti₃SiC₂ (a natural “MAX phase”). The latter crystal is separated from the silicide matrix by a zone of TiSi, from which abundant SiC has crystallized. These relationships are consistent with immiscibility between the oxide and silicide melts in the corundum, and the metallic melts that crystallized the bulk of the SiC in the overall magmatic system.

Mineral chemistry

Fe-Ti Silicides

Most of the phases described here show a range of solid solution. Where individual analyses are plotted in the Fe-Ti-Si ternary (Fig. 13a), clusters of data can be identified (Fig. 13b). Average analyses for each cluster are given in Table 1, and Table 2 gives TEM-EDS analyses of some individual phases found in FIB foils. Analyses plotted in Figure 13 may contain up to 6 wt% Zr and/or 5 wt% P, as well as small amounts of Mn, Ni, Cr, Al and V (Table 1); these minor elements have been grouped with the major elements (Mn and Ni with Fe; Cr, Al and Zr with Ti; P with Si). The presence of such minor elements may distort the apparent relationship between the plotted compositions and the phase boundaries as defined in the simple ternary system. However, at these low levels the distortions are not expected to affect the conclusions drawn here.

Cluster 1. The mean composition is near Fe₂Si₅ (Table 1, #1); all are drop-shaped blebs, or occasionally euhedral crystals, within inclusions of metallic Si (Si⁰) in crystals of SiC, some
enclosed in corundum aggregates. A series of other analyses, also from inclusions in SiC (Huang et al., 2020), extends toward the composition of cluster 3.

Cluster 2. All analyses are from a single melt pocket enclosed in corundum; a crystal of Ti$_3$SiC$_2$ (Table 1, # 16) is separated from a matrix of zangboite (FeTiSi$_2$) by a reaction zone of Ti$_{1-x}$Si$_2$+x and SiC (Fig. 12; Table 2, #8). This phase, with a mean composition of (Ti,Fe)Si$_2$ (Table 1, #2), also occurs as irregular dark areas within the zangboite matrix. However, TEM-EDS analyses of inclusions in the matrix (Table 2, #6, 7) have less Fe and compositions closer to Ti$_2$Si$_3$.

Cluster 3. The mean composition corresponds to zangboite (FeTiSi$_2$; Table 1, #3), which includes the main phase in the melt inclusion shown in Figure 12 (Table 2, #5). It is found as isolated 5-10 µm inclusions in both corundum and moissanite (Huang et al., 2020) and in one case coexists with (Fe,Ti)$_3$Si$_2$ (cluster 4). Zangboite is also found in heavy-mineral separates from chromitites in the Luobusa ophiolite of southern Tibet (Xiong et al., 2017; Xu et al., 2015). It corresponds to the liquidus phase $\tau_1$ in the synthetic Fe-Ti-Si system (Weitzer et al., 2008); Fig. 13a).

Cluster 4. The mean composition is close to (Fe,Ti)$_3$Si$_2$ (Table 1, #4). The analyses represent small rounded inclusions in corundum; one surrounds a rectangular grain of zangboite. This phase has been found in spinel-peridotite xenoliths from the Avacha volcano on Kamchatka (Ishimaru et al., 2009), but has no formal name.

Cluster 5. Ten analyses have a mean composition corresponding approximately to the mineral xifengite (Fe$_5$Si$_3$; Table 1, #5). One is enclosed in a Ca-Al-Si glass together with carmeltazite (ZrAl$_2$Ti$_3$O$_{11}$), Ti(N,O) and TiC (Fig. 6). Others form the cores of inclusions in corundum, with irregular, apparently exsolved blebs of (Fe,Ti)$_2$(Si,P) and/or (Fe,Ti)$_{11}$Si$_5$ (Fig. 9a). Xifengite has been found in placers in the Yan mountains of Hebei Province, China, and in the Is River in the Middle Urals region of Russia (Yu, 1984).

Cluster 6. This large cluster can be divided into three more homogeneous subgroups, with mean compositions corresponding to gupeiite (Fe$_3$Si), Fe$_3$Si$_2$ and (Fe,Cr)$_3$(Si,P) (Table 1, # 6-8). The first typically occurs as irregular masses interstitial to corundum crystals, associated with abundant TiC (Figs 4a, 4b,5). A FIB section across the contact between a TiC crystal and gupeiite (Fig. 4c) shows they are separated by a zone of (Zr,Ti)$_2$P (Table 2, # 9). The second type (Fe$_3$Si$_2$) also occurs as large irregular pockets, typically associated with crystals or irregular blebs of Fe-Ti-Si-P phases (Table 1, #6, 9). A TEM image shows a sharp
contact between the two phases (Fig. 8), with zoned inclusions of (Fe,Ti)$_3$(Si,P) (cf. Table 1, #10). The third, more Cr-rich type ((Fe, Cr)$_3$(Si, P)); Table 1, #8) typically occurs as small grains/droplets, associated with carmeltazite, Ti(N,O) and TiB$_2$, either enclosed in corundum, or in melt pockets with Ca-Al-Si oxide glass. Gupeiite is found in alluvial deposits in the Yan Mountains (China) together with xifengite (Yu, 1984). It also occurs with xifengite, FeSi, FeSi$_2$, SiC and TiC in soils of the Alpine foreland (Hiltl et al., 2011).

**Cluster 9.** This small group of analyses (Table 1, #9) has a mean composition near (Fe,Ti)$_{11}$Si$_5$; they all represent small, apparently exsolved volumes in Fe$_5$Si$_3$.

**Cluster 10.** Three SEM analyses represent small isolated inclusions in corundum. Two TEM-EDS analyses represent inclusions in (Fe,Ti)$_2$Si (Fig. 8); one is zoned toward a rim enriched in Fe and depleted in Ti. The compositions range from (Ti, Fe)$_3$Si to (Fe,Ti)$_7$(Si,P)$_3$ (Table 1, #10; Table 2, #14,15).

**Cluster 11.** Most of these analyses make up the cores of complex zoned inclusions in corundum, surrounded by the grains gathered in cluster 12 (see below), and by shells consisting of the unknown phase MgTi$_2$Al$_4$(Si,Zr)O$_{10}$ and several other phases (Fig. 3a). The mean composition of the cores (Table 1, #11) is FeTiSi, which corresponds to the τ$_2$ phase of Weitzer et al. (2008), with some Cr in solid solution. The spread of the analyses corresponds to the known range of solid solution in FeTiSi at T ≥1100 °C (Weitzer et al., 2008). However, TEM imagery (Fig. 3b, 3c) shows that the FeTiSi in at least one case now comprises three distinct Ti-Fe-Cr silicides, which appear to have unmixed on cooling. One is dominated by Ti, another by Fe, and the third by Cr; this unmixing on the micron scale probably accounts for the high standard deviation on the mean SEM-EDS analyses (Table 1, #11).

**Cluster 12.** This is a sub-horizontal array of points with a mean composition near FeTi$_5$Si$_2$ (Table 1, #12) but with a wide range in Ti/Fe, and significant but variable levels of Cr, V and Mn. Some of these analyzed grains occur with FeTiSi in zoned inclusions in corundum, but show straight edges suggestive of crystal forms. Others occur as rectangular crystals in a matrix of Ca-Al-Si-O glass inclusions in corundum. The mean composition corresponds to the τ$_6$ phase of Weitzer et al. (2008) but it may not represent a single phase.

**Cluster 13.** Nine analyses all represent small isolated inclusions in corundum (one with TiSi$_3$); the mean composition is Ti$_5$Si$_4$ with ca 5 at.% Fe in solution (Table 1, #13).
Cluster 14. Three analyses with a mean composition near \((\text{Ti, Fe})_3\text{Si}\) (Table 1, #14) represent small blebs grouped around TiC crystals in 10-µm inclusions, or coexisting with \(\text{Fe}_3\text{Si}, (\text{Fe, Ti})_2\text{Si}, \text{Ti}(\text{N,O})\) and \(\text{TiB}_2\) (Fig. 5). The mean composition is also close to that of the subsolidus phase \(\text{Ti}_5\text{Si}_3\) (Fig. 13b).

Cluster 15. A small group of analyses corresponding to \(\text{Ti}_3\text{Si}\) (Table 1, #15) represents lamellae in complex inclusions with TiC, TiSi and other phases, and in balls of silicide-phosphide phases (Table 2, #3). C is not visible in the EDS spectra. \(\text{Ti}_3\text{Si}\) is a subsolidus phase that appears below ca 1170 °C (Fig. 13b).

Miscellaneous individual analyses

A number of analyses, mostly of small isolated inclusions in corundum, fall outside the obvious clusters in Figure 13b; most have compositions that cannot be expressed as rational formulae. Many of these lie on or near cotectic lines in Figure 13a, suggesting that they represent trapped melts rather than distinct phases. However, one analysis represents a high-Ti alloy \((\text{Ti}_{84}\text{V}_{1.5}\text{Cr}_{1.5}\text{Fe}_6\text{Si}_{2.5})\), which occurs as a small rectangular crystal in \(\text{Fe}_3\text{Si}\). A series of analyses extending from the \((\text{Fe}+\text{Mn}+\text{Ni})\) corner lies along the edge of the field of Fe solid solution in Figure 13b; all of these are individual inclusions in corundum.

Fe-Ti Phosphides, Silicide/Phosphides

Analysis 17. A single 10-µm sphere of \((\text{Cr,Ti,Fe})_\text{P}\) (Table 1, #17) occurs in a pocket of Ca-Al-Si glass, together with early-crystallizing tistarite and carmeltazite.

Cluster 18. Four irregular grains associated with \(\text{Ti}(\text{N,O})\) and \(\text{TiB}_2\) have a mean composition of \((\text{Fe, Ti})_3\text{P}\) (Table 1, #18). There is only minor solid solution toward \((\text{Fe, Ti})_2\text{Si}\).

Cluster 19. A relatively common phase, with mean composition \((\text{Fe, Ti})_2(\text{Si,P})\) (Table 1, #19). All occurrences are enclosed within balls or irregular masses of \(\text{Fe}_3\text{Si}\), either as triangular to rhomb-shaped areas suggestive of crystals, or as irregular blebs suggesting liquid immiscibility (Fig. 14). There is significant solid solution; Si/P (at.%) ranges from 1.0 to 4.2.

Zr-Ti Phosphides, Silicides (Figure 15)
Cluster 20. (Zr,Ti)P (Table 1, # 20) is found as a 5-µm triangular crystal coexisting with Mg-Al spinel and hibonite interstitial to corundum, and in the irregular cores of silicide balls. It also occurs as a rim between TiC and Fe$_3$Si in Figure 4c.

Cluster 21. Four grains of relatively uniform composition, with a mean of (Zr,Ti)(P,Si) (Table 1, #21) These are closely associated with TiC, TiSi$_2$ and other Zr-Ti silicides (Fig. 11); some appear to have crystal forms.

Analysis # 22. Zr$_3$Ti$_7$(Si,P)$_8$ is found as subhedral grains intergrown with (Zr,Ti)Si$_2$ and (Zr,Ti)$_2$P in a 30µm ovoid inclusion in corundum that also contains a large crystal of TiC and a grain of a U-rich Zr-Ti-P-Si phase (Fig. 11d; Table 2, #9-12).

Clusters 23-25. These phases occur in spherical aggregates embedded in Ca-Al-Si glass within a melt pocket in corundum (Fig. 10a). TEM imaging reveals an equilibrated equigranular microstructure with open voids (Fig. 10b). One of the phases identified by SEM-EDS is (Ti,Zr,Fe)(Si,P)$_2$ (Table 1, # 23). Analysis #24 (Table 1) is the mean of 13 analyses with relatively constant Si, but a range in Ti/Zr (at.%) from 0.6 to 1.5. The mean composition can be expressed as (Ti, Zr)Si$_2$ (see also Table 2, #11). This phase also occurs as inclusions in TiC, and coexisting with TiC and/or FeTiSi$_2$ in isolated inclusions; these grains tend to have the highest Ti/Zr. The third component of the spherical crystalline aggregates has a mean composition of (Ti,Zr)Si$_7$ (Table 1, # 25); a TEM-EDS analysis (Table 2, # 1) has the composition (TiZr)$_3$Si$_7$, within the range of variation in the SEM analyses.

TEM analysis also identified a uranium-rich phase (18-23 wt% U; Fig. 10c). The mean of two grains in two different samples fits an approximate empirical formula of (Zr,Ti,U)$_5$(P,Si)$_3$ (Table 2, #2 and #12).

DISCUSSION

Comparison of observations with experimental studies

Fe-Ti silicides

Nearly all experimental work relevant to the phases described here has been done at one atm pressure, in the course of metallurgical research. However, given the relatively shallow conditions (near 1 GPa) estimated for the crystallization of the corundum-SiC system at Mt Carmel (Griffin et al., 2016a; Griffin et al., 2018d), the determined phase relationships are likely to be relevant, while the temperatures of crystallization may be slightly underestimated. The melting curve of Fe provides a possible reference point.
(Sinmyo et al., 2019); at 1 GPa the melting point is only 100 °C higher than at 1 atm. On the other hand, the presence of minor elements (Mn, Ni, Cr, Al, V) and the presence of H$_2$ in the fluid phase (see below) may lower liquidus temperatures by at least this much, relative to the simple system.

The liquidus phases along the Fe-Si join (Fig. 13a) are (1) the $\beta_2$ phase, which represents solid solution of Si in Fe, and crystallizes as Fe$_3$Si from 1215 °C to a eutectic with (2) Fe$_2$Si, with a narrow field of crystallization just above 1200 °C, leading to a eutectic with (3) FeSi which crystallizes from 1412 °C to 1215 °C, ending in a eutectic with (4) Fe$_2$Si$_5$, which crystallizes over a narrow $T$ range near 1215 °C, to a eutectic with Si. With the addition of Ti, there is a small field in which Fe$_5$Si$_3$ is on the liquidus from ca 1175 to 1150 °C.

On the Ti-Si join, Ti$_5$Si$_3$ is the dominant phase, crystallizing on the Ti-rich side from ca 1920 °C to a eutectic with Ti at 1330 °C, and on the Si-rich side through a series of peritectics that crystallize Ti$_5$Si$_4$ from 1920 to 1570 °C, then TiSi from 1570 to 1487 °C, a eutectic with TiSi$_2$. TiSi$_2$ also crystallizes down to a eutectic with Si at ca 1330 °C.

The Fe-Ti join is relatively simple. Fe$_2$Ti is on the liquidus from ca 1400 °C to eutectics with Fe at ca 1300 °C and FeTi at ca 1320 °C; FeTi is on the liquidus down to a eutectic with Ti at ca 1050 °C (Fig. 13c).

The center of the Fe-Ti-Si liquidus diagram (Fig. 13a) is controlled by two ternary phases: FeTiSi$_2$ and FeTiSi ($\tau_1$ and $\tau_2$ of Weitzer et al., 2008). These two phases melt congruently above 1500 °C and 1700 °C respectively, and crystallize from ternary melts along a complex series of cotectics and peritectic points that fall from temperatures of ca 1660 to 1263 °C on the Ti-rich side of the phase diagram, and from ca 1530 to 1150 °C on the Fe-rich side.

The subsolidus phase relationships at 900 °C (Fig. 13b) have been constructed by Weitzer et al. (2008); they note that these relationships are also valid at 1000 °C. A reconstruction by Stein et al. (2005) at 1150 °C (Fig. 16) shows the transition between the liquidus and the high-$T$ subsolidus situation, while a section at 800 °C (not shown) extends the subsolidus to lower $T$. The most important differences between the liquidus situation and the isothermal section at 900 °C are: the disappearance of Fe$_2$Si and its replacement by Fe$_5$Si$_3$ with solid solution toward Ti$_5$Si$_3$; the extensive solid-solution fields of “Fe$_3$Si” toward Fe, and of Fe$_2$Ti (the Laves phase) toward Si; the appearance of Ti$_5$Si coexisting with Ti and...
Ti$_5$Si$_3$; and the appearance in the 900 °C section of several ternary phases, none of which have been found in this study.

These relationships allow some evaluation of the origin of some of the clusters of data shown in Figure 13b. It should be kept in mind that these melts were evolving in individual, separated pockets of trapped melt. The ongoing growth of corundum was continually changing the size, shape, and connectivity of these pockets (Oliveira et al., 2020), and this would influence the evolution of single volumes of melt, for example by overgrowing and isolating crystals and melt droplets (Fig. 4). It is also probable that individual ejecta, especially from different vents, may represent samples of similar, but not identical, systems at different stages of their cooling histories.

Figure 17 shows tie lines between apparently coexisting phases, as based on petrographic relationships. Green tie lines connect Fe$_3$Si-type phases (clusters 6-8) with compositions near FeTiSi; these tie lines are consistent with subsolidus equilibration, as is the zoning of the inclusion shown in Fig. 8. However, most of the tie lines (red in Fig. 17) have negative slopes and cross-cut the subsolidus tie lines in this part of the phase diagram, and the pairs of phases joined by these tie lines cannot be in equilibrium at subsolidus conditions. Most of these analyses lie on or near cotectic curves; this and the microstructures (e.g. Figs 7,9,14) suggest that these represent mutually immiscible melts. Unfortunately we have found no experimental data on immiscibility in the Fe-Ti-Si system with which to test this interpretation.

On the basis of this type of analysis and petrographic observations, it is possible to assign the analysed grains to liquidus phases (crystallizing from the melt), trapped melts modified to various degrees by fractional crystallization, or subsolidus phases representing recrystallization of earlier-crystallized phases, or of solidified melts (Table 1). The phases identified as crystallizing directly from melts have moderately high concentrations of Cr and V (Table 1), and these two elements show a broad positive correlation, suggesting that most liquidus phases concentrated Cr and V relative to the residual liquids. In contrast, xifengite (a subsolidus phase?) has high V but low Cr. Cluster 8 represents a Cr-rich version of Fe$_3$Si, and on that basis also may represent a liquidus phase.

Within the limitations noted above, these phase assemblages give a basis for estimating the temperatures under which the corundum-SiC system was crystallizing. The crystallizing phases and melts on the Ti-Si side of Fig. 13c imply temperatures in the range
1660-1280 °C. The temperatures of first crystallization for the three important phases Ti$_5$Si$_3$ (>2100 °C), FeTiSi (ca 1700 °C) and (Fe,Ti)Si$_2$ (ca 1500 °C) are much higher, but each can crystallize down to 1300-1400 °C along the cotectics that surround their fields of primary crystallization. The assemblages on the Fe-Si side of Fig. 13c imply lower crystallization temperatures ranging down to 1175-1150 °C.

These $T$ estimates probably are maximum values. Such melts may take up significant amounts of hydrogen from the ambient fluids, lowering liquidus temperatures by hundreds of degrees (Fukai, 2006); the addition of carbon to the Fe-Si system also strongly depresses the liquidus of Fe-Si alloys (Vander Kaaden et al., 2017). However, it is significant that few of the trapped melts have crystallized into the various 2- and 3-phase assemblages illustrated in the isothermal sections at 1150 and 1000-900 °C. This suggests that the temperatures in the corundum-SiC system had not dropped much below 1150 °C by the time crystallization was interrupted by the explosive eruption of the host magma.

**Fe-Ti phosphide-silicides**

We have not been able to access experimental data on the liquidus configuration of the Fe-Ti-P(Si) system. An isothermal section of the Fe-Ti-P system at 800 °C (not shown) is dominated by the ternary phase FeTiP, which has not been identified in this study. Binary diagrams show that FeTiP is a liquidus phase from $T>$1500 °C, so its absence is unexpected. (Fe,Ti)$_2$P (cluster #18) shows a significant solid solution toward FeTiP. Analysis #18 (Table 1) and cluster #19 may represent mixtures of two or more phases.

**Zr-Ti silicides, phosphides**

The analyses of Ti phosphides define two clusters, one between Ti$_3$P and Ti, the other between Ti$_3$P and Ti$_2$P. The latter would correspond to mixtures of Ti$_2$P and liquids crystallizing that phase from ca 1920-1760 °C in the experimental system, while the former could represent Ti$_3$P and coexisting liquids from ca 1760-1495 °C (Ohtani et al., 2006). These temperatures would be lowered by solid solution with both Si and hydrogen. The points around the mean composition (Zr,Ti)P (cluster 21) do not represent obvious subsolidus phases, and are tentatively interpreted as trapped melts. However, several of the individual analyses taken from FIB-TEM foils (Table 2) lie close to recognized subsolidus phases, which is consistent with their microstructural appearance.
The Ti-Zr-Si plot (Fig. 15a) shows a nearly continuous series of analyses on the Ti-Si join; some of these contain several at.% P as well (Table 1). The spread of analyses corresponds to a sequence of peritectic reactions on the binary liquidus from ≥2000-1550 °C, and may represent crystals, reaction products and trapped melts. These temperatures also probably represent maximum estimates, and would be lowered by solid solution of Si, Fe and H. The spread of points in clusters 23 and 24 represents extensive solid solution approximately along the TiSi₂-ZrSi₂ join. An isothermal section of this ternary at 500 °C (Zhan et al., 2009) shows ca 10% solid solution along this join from each end member; the present data suggest higher temperatures, but with no real constraints. The phase represented by analysis #25 in Table 1 is consistent with a eutectic melt (T ca 1300 °C) which would be crystallizing both Si (observed as inclusions in SiC) and a (Ti, Zr)Si₂ phase. Cluster 21 (Fig. 15b) lies in a 3-phase field at 1200°C, and may represent mixtures, or a liquidus melt composition inherited from higher T.

SiC relations

SiC is on the liquidus in Si-rich melts from ca 2720 to 1520 °C (Kawanishi et al., 2009). At 1500-1450 °C (Fig. 18), SiC can coexist with a range of Fe-Si melts, but if the system is carbon-saturated, SiC coexists with carbon and a melt of Fe₃Si composition, which can dissolve several percent C. At 1300-1250 °C, this assemblage is still stable, but the content of C in the Fe₃Si is lower. The reconstructed melt inclusions in the SiC can coexist with SiC at 1450°C, but not at temperatures as low as 1250 °C (Fig. 18b;) (Huang et al., 2020). In more Si-rich melts SiC can coexist with Fe₃Si + FeSi, or FeSi +Si; FeSi has not been observed in the samples studied by Huang et al. (2020). Takahashi et al. (2013) have shown that as fO₂ decreases (to < ΔIW-4.8), the solubility of carbon in Fe-rich melts decreases, and the solubility of Si increases. The low contents of carbon in the Fe₃Si samples analysed here (Table 1) thus are consistent with both carbon saturation and very low fO₂. However, the carbon content of the Fe₃Si will also be affected by the crystallization of TiC (Fig. 4) and there are not enough data to use the reconstructed C content of the alloy phase to estimate temperatures.

At subsolidus temperatures (1200 °C, 0.24 GPa) the phase relations are consistent with the petrographic relationships. SiC coexists with Ti₅SiC₂ and Ti₅Si₂ (Fig. 12b), and Ti₅Si can coexist with TiC.
Composition and evolution of Fe-Ti-Si-P-C melts

To follow the evolution of the metallic melts the bulk compositions of six large, complex Fe-Ti-Si-P-C inclusions (e.g. Figs 4, 8, 9 and others) have been reconstituted, based on point-counting of phase abundances in BSE images and EDS maps (Table 3). This procedure is subject to the uncertainties inherent in using 2D images to estimate phase distributions in 3D objects, but in this case the results appear to carry useful information.

The reconstructed melt compositions fall close to cotectic curves in the Fe-Ti-Si ternary liquidus diagram (Fig. 19), suggesting they were trapped as metallic melts. Apparent temperatures range from ca 1600 °C (Table 3, #41) to ca 1150 °C; these probably represent maximum values, as noted above. During cooling, the Si and Fe contents of the Fe-Si melts increase, while Ti and C decrease. The textural relationships (Fig. 4) indicate large-scale crystallization of TiC early in the evolution of the melts, while TiC is less abundant in the more Fe-rich melts. The distribution of the reconstructed melts on Figure 19 indicates that they cannot all represent sequential stages in the evolution of a single parental melt.

Instead, it seems probable that several different sub-systems have been sampled, with different parental melt compositions and consequently different melt-evolution paths.

The solubility of Si, Ti and C in Fe-rich melts is strongly dependent on $fO_2$ (Corgné et al., 2008; Gessmann et al., 2001; Putter et al., 2017). In the case of the earliest melts, we can assume $fO_2$ was around ΔIW-7, since Ti$_2$O$_3$ (tistarite) is an early-crystallizing phase in the silicate melts coexisting with the metallic melts (Griffin et al., 2016a). The Si content (8 wt%) in the highest-$T$ melt (#41 in Table 3) is broadly consistent with the experimental data of Gessman et al. (2001) at projected conditions of ΔIW-7, 1 GPa and 1600 °C; lower $P$ or $T$ would decrease the level of Si expected in the melt, but the available experiments do not account for the potential solubility of H$_2$ in Fe melts and its effects on melting points (Fukai, 2006).

The lower-$T$ reconstructed melts have Si contents up to >20 wt%; this is not consistent with the decrease in Si expected with declining $T$ (Fig. 20). An isobaric increase in Si content (with decreasing $T$) thus requires a large decrease in $fO_2$. This is consistent with other evidence that the $fO_2$ of the idealized system dropped during the evolution of the melts, first to ΔIW-6 (appearance of SiC), then to ΔIW-7 (stability of Ti$_2$O$_3$) and then to ΔIW-9 (appearance of V$^5$) (Griffin et al., 2019a; Griffin et al., 2020b); the presence of TiB$_2$ (Griffin et
may indicate even lower $f_{O_2}$. A decrease in both $T$ and $f_{O_2}$ also will reduce the
solubility of C in the metal liquid (Takahashi et al., 2013) (Fig. 20), driving the more or less
continuous crystallization of TiC (and possibly SiC) during the evolution of the melt. The
depletion of C from the metallic melts relatively early in their evolution may explain the
apparent absence of Fe$_3$C (cohenite) in the melt pockets.

The lower-$T$ metallic melts are richer in Cr, and to some extent V (Table 3); this is
predicted by experimental studies showing that these elements become more siderophile
with decreasing $f_{O_2}$ (Corgne et al., 2008; Putter et al., 2017). The maximum Cr content (3.5
wt%) is reached in inclusion #9b (estimated $T = 1300^\circ$C) and drops again in the two lower-$T$
inclusions. This may indicate that all Cr has been sequestered in the metallic melt by this
stage; alternatively, it could reflect a change in $D_{Cr}^{metal/silicate}$ at very low $f_{O_2}$ (Putter et al.,
2017). However, a 2D sampling effect cannot be excluded.

With the exception of melt 9a (Table 3), the content of P increases with declining $T$.
Experimental data (Gu et al., 2019; Putter et al., 2017; Steenstra et al., 2017) predict that P
becomes more siderophile with declining $T$ and decreasing $f_{O_2}$, which is consistent with the
pattern shown in Figure 19, but is less siderophile in high-Si melts. The exsolution of
phosphide-rich melts from some Fe-Si melts (Figs 8, 9) therefore may reflect the increasing
levels of Si in the lower-$T$ melts (Table 3), leading to immiscibility despite the higher
solubility of P in metallic melts at low $T$ and low $f_{O_2}$.

A generalized picture of the evolution of the metallic melts in the corundum
aggregates, emphasizing the observed role of successive episodes of liquid immiscibility
with decreasing $f_{O_2}$, is shown in Fig. 21. The early stages of the reduction process, prior to
the crystallization of corundum, are assumed to be responsible for the immiscible
separation of abundant spheroids of native Fe (Fe$^0$), some of which are surrounded by shells
of stoichiometric wüstite (FeO) (Xiong et al., 2017). These are accompanied by, and often
attached to, spheres of Fe-oxide melts and Ti-oxide melts, both with minor Si and Ca. The
separation of these metal and metal-oxide melts from the silicate melt is interpreted to
have occurred near $f_{O_2} = IW$.

The next stage of immiscibility ((2) in Fig. 21a) produced the separation of C-rich
silicide melts, from which SiC crystallized. These melts may have in turn exsolved into
complementary fractions with higher and lower Si/(Fe+Ti). The microstructures in the melt
inclusions in SiC suggest that the more Fe,Ti-rich fraction crystallized FeTiSi$_2$ ($\tau_1$ in Fig. 13) as
liquidus phase, and then FeTiSi$_2$ + SiC from cotectic melts (Huang et al., 2020). These melts included in SiC may in turn provide a link to the metallic melts in the corundum aggregates (Fig. 20; Table 4). The maximum Si contents of the reconstructed Fe-Ti-Si melts in the corundum aggregates are ca 25 wt%, while the minimum values of the Fe-Ti-Si melts included in SiC are ca 52 wt%; Fe/Ti (wt%) is 2.7 and 1.9 in the respective melts. We suggest that the most Fe,Ti-rich melts in the SiC and the most Si-rich metallic melts in the corundum aggregates may be conjugate immiscible melts; both would be C-saturated and both have crystallized SiC and FeTiSi$_2$, but in different proportions, consistent with equilibrium between immiscible melts.

The continued separation of such silicide melts ((3) in Fig. 21b) would desilicate the coexisting silicate melts, inducing supersaturation in Al$_2$O$_3$ and the rapid crystallization of the hopper/skeletal corundum at fO$_2$ ca ΔIW-7 to -9, and leaving a complex, Si-depleted oxide melt (Fig. 21b). The separation of the Fe-Ti silicide melts appears to have removed essentially all remaining Fe from the coexisting silicate melts; none of the oxide or silicate phases crystallized from the trapped silicate melts contain Fe. Crystallization of abundant TiC (Fig. 4) suggests that the metallic melts also were saturated in C; subtraction of TiC decreased melt volume and concentrated minor components, until Zr,Ti-rich phosphide/silicide melts became immiscible in the dominant Fe-Ti-Si melts, and Fe-Ti-Zr phosphide/silicide phases crystallized (Tables 1, 2), some with SiC and other carbides (Fig. 12; (4) in Fig. 21b). The end point of this idealized process might be the low-Si oxide melts that crystallized the coarse-grained hibonite-grossite assemblages, coexisting with vanadium- and vanadium-alloy melts (Griffin et al., 2019a, 2020b; Fig. 21a). The phase relationships discussed above suggest that this evolution spanned a range of temperature from ca 1500-1150 °C, before being terminated by explosive eruption. This lower- T limit is consistent with the presence of the phase Ca$_4$Al$_6$F$_2$O$_{12}$ in the hibonite-grossite-spinel aggregates (Kim, 2011; Griffin et al., 2018a). As noted above, the higher temperatures probably are maximum values, due to the solution of carbon, hydrogen and other elements.

Other Occurrences

The metallic melts described here are not unique; they have been observed worldwide in a variety of contexts. They are common in Kamchatka volcanoes and in mineral separates from ophiolitic chromitites in Tibet and the Polar Urals, where they may
be related to pre- or syn-emplacement magmatism (Griffin et al., 2018d; and references therin; Xiong et al., 2020; Xiong et al., 2017). Mantle-derived corundum from kimberlites of the East Azov area of the Ukrainian Shield, from the Karpinskaya pipe in the Arkhangelsk kimberlite province, and the Siberian Udachnya kimberlite, contains an inclusion assemblage similar to the Mt Carmel ones: tistarite, carmeltazite, TiN, native Fe, hibonite and a range of Fe-Ti silicides similar to those described here (Tatarintsev et al., 1987; Yatsenko et al., 2002; Yatsenko, 2016; Yatsenko et al., 2017; our unpublished data).

Yatsenko and coworkers have drawn attention to the wider distribution of mantle-derived corundum and defined an “explosive mantle-derived mineral association (EMMA)” The assemblage of corundum, carbides (TiC, SiC), Fe-Ti silicides and native elements (Fe, V) has also been documented in volcaniclastic layers (“visherites” or miaskitic lamproites) at several localities in the western Urals (Chaikovskii and Korotchenkova, 2012). Similar associations of metallic spherules requiring reducing conditions have been described in placers interpreted as related to the impact of a proposed "Yanshan meteorite" in the Yan mountains of Hebei Province, China, and in the Is River in the Middle Urals region of Russia (Yu, 1984). Nodules (mm- to cm-size) comprising Fe-Ti silicides, SiC and TiC have been found in soils of the Alpine foreland over an area of ca 3000 km$^2$; these nodules also have been interpreted as fragments of meteorites (Hiltl et al., 2011), despite the lack of Fe-Ni alloys in the deposits. Such occurrences may instead be related to explosive volcanism (the EMMA of Yatsenko et al., 2017). It seems probable that similar associations will be found in the ejecta of other explosive volcanoes, using detailed studies of fine-grained heavy minerals from pyroclastic deposits.

Implications

The silicides, carbides and phosphides described here represent a series of melts and their crystallization products, trapped within aggregates of skeletal- to hopper-shaped corundum crystals. Microstructures indicate that the Fe-Ti-Zr-Si-P melts were immiscible with the Ca-Al-Mg-silicate melts trapped in the same aggregates. Reconstructed metallic melts fall on or near cotectic curves in the Fe-Ti-Si system and were precipitating FeTiSi and FeTiSi$_2$ during cooling. The Si-C rich melts found as inclusions in SiC crystals from the same volcanic ejecta may represent a conjugate immiscible component. Ti-Si and Zr-Ti-(P-Si)
melts appear to have become immiscible with the Fe-Ti-Si melts as T and \( fO_2 \) declined from
ca \( \Delta IW-6 \) to \( \Delta IW-9 \) during the crystallization process.

All of these coexisting melts were carbon-saturated, leading to the continuous
precipitation of TiC and minor SiC during cooling. The saturation of the melts in carbon is
consistent with the observed abundance of amorphous carbon in the final eruption
products, and is a strong argument for the role of CH\(_4\) + H\(_2\) in the fluid phase that generated
the low \( fO_2 \). This in turn implies that the deeper mantle from which such fluids might
ascend is metal-saturated, with \( fO_2 \) buffered near IW; this implication needs to be factored
into partial-melting models used to explain the genesis of common magmas such as MORB.

These observations indicate that sequential liquid immiscibility plays an important role
in the evolution and diversification of melts at low \( fO_2 \) in the uppermost mantle; it leads
directly to the desilication of oxide melts, oversaturation in Al\(_2\)O\(_3\) and the crystallization of
abundant corundum. Similar processes probably occur in the deeper parts of cratonic roots,
as illustrated by the overall similarity of melt inclusions in SiC from kimberlites and from Mt
Carmel (Huang et al., 2020). They can also be recognized in the occurrence of similar silicide
alloys and inclusion-rich corundum in a range of explosive volcanic environments (Xiong et
al., 2017; Yatsenko et al., 2017), implying that reduced mantle-derived fluids may play a
little-recognized role in the genesis of such magmas.

Acknowledgements

WLG and SYO’R acknowledge the research funds for the TARDIS Project provided by
the ARC Centre of Excellence for Core to Crust Fluid Systems and geochemical laboratory
support through NCRIS AuScope and NSW Government Research Attraction and
Acceleration Program grants. This study used instrumentation funded by ARC LIEF and DEST
Systemic Infrastructure Grants, Macquarie University and industry. We especially thank
Manal Bebbington for her dedication to the preparation of difficult samples for in-situ
analysis, over many years, and Luca Bindi and Fernando Camara their encouragement and
incisive comments on earlier versions of the manuscript. The authors acknowledge the
scientific and technical assistance of Microscopy Australia at the Centre for Microscopy,
Characterization and Analysis, a facility funded by The University of Western Australia, and
State and Commonwealth Governments. This is contribution xxx from the ARC Centre of
Excellence for Core to Crust Fluid Systems (www.ccfs.mq.edu.au) and xxx from the GEMOC Key Centre (www.gemoc.mq.edu.au).

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Figure Captions

Figure 1. Cathodoluminescence (CL) images showing skeletal/hopper forms of corundum crystals in the NGC aggregates. The true colour in the lighter portions would be red to pink; darker tones correlate with higher Ti contents. (a) cross section of a hopper/skeletal corundum crystal; (b) section subparallel to growth direction showing aggregate structure and oriented growth; note zoning of crystals and skeletal structure in cores of grains.

Figure 2. FE-SEM image of sphere of native Fe⁰, rimmed by TiAl₂O₅, in a Ca-Al-Si oxide glass that has crystallized tistarite (Ti₂O₃). The tiny bright needles are a Ti-Zr oxide phase. The microstructures suggest that the Fe⁰ melt was immiscible in the Ca-Al-Si oxide melt, but in equilibrium with TiAl₂O₅ that was crystallizing from the oxide melt.

Figure 3. (a) Ball and irregular masses of FeTiSi, enclosed in corundum (Crn), surrounded by Ca-Al-Mg silicate glass and rimmed by an unknown oxide MgTi₂Al₄(Si,Zr)O₁₀ intergrown with carmeltazite (Ctz), TiS and Ti(N,O). (b) TEM-HAADF image of foil across boundary between
FeTiSi and MgTi₂Al₄(Si,Zr)O₁₀ along white line in (a). Note euhedral crystal of TiB₂ (zoned in Ti) in silicide, and TiS and an amorphous Ca phase along the boundary. (c) The FeTiSi (bulk composition) appears to be unmixing into three distinct phases.

Figure 4. Fe₃Si-TiC relationships. (a) BSE image of pool of Fe₃Si (white) trapped between euhedral crystals of corundum (Crn, dark). Grey areas are both TiC and Ti₃C (fcc, a = 0.25nm); note euhedral crystal outlines. The microstructures suggest that growing corundum crystals trapped and overgrew early TiC crystals, while expelling the more mobile Fe₃Si melt into smaller interstitial pockets. (b) Element maps of the area outlined in (a). (c) TEM-HAADF image across Fe₃Si-Ti₃C contact (red line in (a), showing an intermediate zone of (Zr, Ti)₂P. Dark curved line is a vein of vesicular amorphous carbon.

Figure 5. BSE image: Grain of Fe₃Si in corundum (Crn) with exsolved or included blebs of (Fe,Ti)₂Si and (Fe,Ti)₃Si, surrounded by grains of Ti(N,O) and TiB₂. Straight edges on parts of the Fe₃Si suggest crystal forms.

Figure 6. FE-SEM BSE image: Fe₅Si₃ enclosed in a pocket of CaO-Al₂O₃-SiO₂ glass in corundum, together with carmeltazite, TiN and TiC.

Figure 7. FE-SEM BSE images. (a) Composite inclusion of FeTiSi and (Fe,Ti)₂(Si,P) that appears to have crystallized Mg-Al spinel, TiC and an unknown phase (Ca,Mg,Fe)₂(Al,Ti)₁₀O₁₇. In an adjacent inclusion the assemblage is the unknown phase + carmeltazite + Ca-Al-Mg oxide glass. (b) Another inclusion in the same grain of corundum shows wavy contacts between spinel and FeTiSi and (Fe,Ti)₂(Si,P); the spinel has inclusions of TiC and FeTiSi.

Figure 8. Silicide-phosphide relationships. (a) Phase map and element maps showing rhombohedral crystals and irregular blebs of (Fe,Ti)₃(Si,P) in an interstitial grain of (Fe,Ti)₂Si. High-Ti rim on the silicide grain comprises crystals of TiC. (b) TEM-HAADF image and element maps of the zoned euhedral grain of (Fe,Ti)₃(Si,P) in the silicide grain shown in Figure 6a.
Figure 9. (a) BSE image of Fe$_5$Si$_3$ in the core of an alloy inclusion in corundum; exsolved blebs are (Fe,Ti)$_2$(Si,P) and (Fe,Ti)$_{11}$Si$_5$. (b) BSE image, phase map and element maps showing vermicular areas of (Fe,Ti)$_5$(Si,P)$_2$ in composite interstitial grain of (Fe,Ti)$_3$Si and (Fe,Ti)$_3$Si$_2$.

Figure 10. Immiscible silicide-phosphide melt? (a) BSE image of bright porous (?) spheres of Fe-Ti-Zr silicides and phosphides in pocket of CaO-SiO$_2$-Al$_2$O$_3$ glass enclosed in hibonite; crystalline phases are Mg-Al-V spinel and hibonite (CaAl$_{12}$O$_{19}$). (b) enlargement showing crystalline structure, and apparent voids. Red line in (a) shows trace of FIB foil. (c) TEM-HAADF image and element maps of the ball, a granular intergrowth of (1),(Zr,Ti,U)$_5$(P,Si)$_3$; (2), (Ti,Zr,Fe)Si$_2$; (3), (Ti,Zr)$_3$Si$_7$.

Figure 11. (a) FE-SEM BSE images showing relationships among Zr-Ti phosphides and TiC. (b) 30-µm inclusion in corundum, with large crystal of SiC, and blobs of Zr-Ti-Si-P phases, in a matrix of (Ti,Zr)Si$_2$. Red line marks location of TEM FIB foil shown in (c) and (d). (c) TEM-HAADF image and (d) element maps across the silicide-phosphide boundary, showing a fluidal contact between Zr-Ti phosphide and Ti silicide. Note grain of (Zr,Ti,U)$_5$(P,Si)$_3$ among silicide crystals.

Figure 12. (a) BSE image of a melt inclusion in corundum, containing a large crystal of TiC and a lath-shaped crystal of Ti$_3$SiC$_2$ in a matrix of Fe-Ti silicides. Note rim on Ti$_3$SiC$_2$ crystal. (b) and (c), TEM-HAADF images of FIB foil taken along red line in (b). The rim on the Ti$_3$SiC$_2$ crystal is a mixture of euhedral SiC crystals (dark in Ti map below) and Ti$_{1-x}$Si$_{2+x}$. SiC crystals are smaller adjacent to corundum host; light spots in Ti$_{1-x}$Si$_{2+x}$ are Ti$_3$SiC$_2$. Lower panel: element maps of the area shown in (b). After Huang et al. (2020).

Figure 13. Fe-Ti-Si system at 1 atm pressure, after Weitzer et al. (2008). (a) Liquidus projection with analyses of individual alloy grains shown by points. Fields are labelled with the phase that crystallizes first from a melt in that field. For purposes of plotting, minor Mn and Ni are grouped with Fe; minor V, Cr and Al are grouped with Ti, and minor P is grouped with Si. Stars, inclusions in SiC, from Huang et al. (2020); b) Isothermal section at 900-1000 °C, plotted as described for (a). Tie lines represent coexisting phases; grey areas are fields of
solid solution. Enclosed numbered fields show clusters of points described in the text. (c) As in (a), with important points on the liquidus surface labelled with temperature in °C.

Figure 14. BSE images: Unmixing of Fe-Ti-Si-P melts. (a) Light phase is FeSi$_3$, dark phase is (Fe,Ti)$_2$(Si,P). See Table 1 for analytical data. (b) intergrowth of TiC, FeTi(Si,P) and two Fe-Ti-(Cr-V) silicides. Both grains are included in corundum.

Figure 15. Ternary plots showing compositions of Zr-Ti-Si-P phases. Subsolidus fields in (a) and (b) are from Oliynyk et al. (2012) at 800 °C and Colinet and Tedenac (2012) at 1050 °C, respectively. Numbered populations correspond to clusters in Table 1.

Figure 16. Analytical data and subsolidus phase relationships in the Fe-Ti-Si system at 1150 °C.

Figure 17. Tie lines between apparently coexisting phases in several melt pockets, plotted on the subsolidus phase diagram at 900-1000 °C and 1 atm. Green lines correspond to possible subsolidus equilibria. Red tie lines cross the tie-lines between subsolidus phases, and probably connect mutually immiscible liquids, or a liquid and a solid phase.

Figure 18. Phase relations in Fe-Si-Ti-C system. (a) Ti-Si-C at 1200 °C, 1 atm and >0.25 GPa, after Sambasivana and Petuskey (1992); (b) Fe-Si-C liquidus showing compositions of coexisting phases; 1450 °C compositions (red stars) after Huang et al. (2020). Red-shaded fields show observed three-phase assemblages.

Figure 19. Compositions of reconstituted melts, plotted on the Fe-Ti-Si liquidus diagram. Red circles in upper half of the plot are reconstructed melt inclusions in SiC crystals (Huang et al., 2020).

Figure 20. Experimental solubility of Si in Fe melts, as a function of P, T and $f$O$_2$ (after Gessmann et al., 2001). Star indicates maximum observed Si content in Mt Carmel Fe melts (8%) at its estimated T, showing the very low $f$O$_2$ required to stabilize this composition.
Figure 21. Schematic evolution of the melts by repeated immiscibility and fractional crystallization. The initial melt is shown as “syenitic” in origin; it is suggested that these melts had differentiated from basaltic precursors within the crust-mantle underplate, producing more felsic starting points for the proposed evolution. Circled numbers mark stages of immiscibility discussed in the text.

Supplementary Data

Figure SD1. Location maps. (a) structural framework of the Levant-Sinai region; red box marks area of (b) Geological framework of northern Israel, showing the location of Cretaceous magmatic centers in the Mt Carmel area.

Figure SD2. (a) 2-mm crystal of corundum showing depressed faces typical of hopper growth; (b) section of a grain of Carmel Sapphire, showing the 3D network of melt pockets around and within skeletal/hopper crystals. After Xiong et al., 2017; (c) 3D-µCT image of a fragment of Carmel Sapphire ca 2 mm across. Colours correspond to silicate melts (orange), metallic melts (white) and voids, presumably fluid-filled (green). Black areas are corundum.

Appendix: Sampling and Methods
Table 2. TEM-EDS analyses of phases in FIB foils

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Spherical silicide-phosphide aggregates in glass (Fig. 10)
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Additional Information:
- Single inclusion in corundum -- Ti3SiC2 lath in silicides with SiC, TiC
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good pattern
good pattern
unmixed in matrix
unmixed
### Table 2 (cont.) TEM-EDS analyses of phases in Fig. 12

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Silicide-Boride relationships (Fig. 3b)
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*estimated from Weitzer et al. (2008)
Figure 6

- TiC
- Fe$_5$Si$_3$
- Crn
- glass
- Ctz

Scale: 50 µm
Figure 10

a) BSE

b) BSE

glass

Crn

Hbn

Spl

20 μm

10 μm

c) HAADF

Map data 714
HAADF MAG: 28.5kx HV: 20
Figure 11

(a) \((\text{Zr}, \text{Ti})\text{Si}_2\) and TiC

(b) \((\text{Zr}, \text{Ti})\text{Si}_2\) and \((\text{Zr}, \text{Ti})(\text{P}, \text{Si})\)

(c) \((\text{Zr}, \text{Ti})_2\text{P}\)

(d) \((\text{Zr}, \text{Ti}, \text{U})_5(\text{P}, \text{Si})_3\)
Figure 13

(a) 

(b) 

(c)
Figure 16

Fe-Si-Ti
(1150°C)

Si+P

FeSi

Fe₅Si₃

Fe₄Si₃Ti

FeSiTi

Ti₅Si₄

Ti₅Si₃

Ti₃Si

α-Fe

Fe₂Si

Fe+Mn
+Ni

Fe₂Ti

FeTi

liquid

Ti+Al
+V+Cr
Fig. 18

(a) 1 atm 1200°C

(b) 1450°C

(c) 1250°C
Figure 20

- Log Si (wt%) in liquid metal vs. log $fO_2(\Delta IW)$
- Point marked with an asterisk: ~1600°C, ~1 GPa
- Various lines indicating different pressures and temperatures:
  - 9 GPa, 2000°C
  - 2.5 GPa, 1750°C
  - 18 GPa, 2200°C
- Shaded area indicating Mantle FeO and 7 wt% Si
- Arrow indicating increasing P-T
Figure 21

(a) "Syenitic" Melt

CH₄+H₂ → QFM → IW

Low-Fe Silicate melt

1. Fe, FeO, TiO₂

CH₄+H₂ → IW -6

Crn melts

CH₄+H₂ → IW -8

Si-C melts

SiC

Low Si oxide melt ~1200°C

Hib, Crs, Spn

S

V

(b) Fe-Ti-Si-C

P-Zr-Cr-V

1400-1500°C

carbon

Fe-Ti-Si-C

Fe-Si Ti-P-Cr-Zr-V

~1400-1300°C

Fe-Si-P Ti-P-Zr

4

SiC

Fe-Si Ti

~1200°C

Fe-Ti-P Si-Zr

SiC

Complex oxide melt

Ca-Al-Si-Mg-O melt

Crn