Super-reducing conditions in ancient and modern volcanic systems: implications for the carbon budget of the deep lithosphere

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Introduction

Estimates of the oxygen fugacity (fO_2) of the cratonic subcontinental lithospheric mantle (SCLM) range from above the quartz-fayalite-magnetite (QFM) buffer to just above the iron-wustite (IW) buffer, and generally decrease with depth. While several lines of evidence suggest that the sublithospheric mantle may be constrained by the IW buffer (the presence of metallic Fe), there also is evidence that at least localized volumes of siginficantly lower fO_2 must exist within the SCLM, and perhaps within the deeper mantle. In this contribution, we describe a remarkable example of super-reducing conditions in an off-craton volcanic setting (Griffin et al., 2016a), and discuss its implications for other tectonic settings, and for the transfer of carbon and hydrogen from the deeper mantle.

Super-reducing conditions in a Cretaceous volcanic system, Mt Carmel, Israel

Aggregates of hopper-formed crystals of Ti-rich corundum are abundant in Upper Cretaceous basaltic pyroclastic rocks (vent breccias, tuffs) exposed on Mt Carmel near Haifa, Israel. Melt pockets trapped within and between corundum crystals contain mineral assemblages (SiC (moissanite), TiC, Fe-Ti-Zr silicides/phosphides and native V) that require P $\geq$ 1 GPa, T = 1500-1100 °C and extremely low fO_2 (ΔIW -10 to-12) (Griffin et al., 2016a). Mineral parageneses suggest that the corundum and the low-fO_2 assemblages developed through interaction of basaltic magmas with mantle-derived (CH_4+H_2) at high fluid/melt ratios, leading to progressive lowering of fO_2.

A schematic illustration of the process is shown in Figure 1; this model envisions a magma chamber being flushed by a steady supply of $CH_4 \pm H_2$, but other configurations are possible. The material described here comes from at least 8 different volcanoes, with eruptions spread over ca 10 Ma, providing snapshots of similar magmatic systems erupted at different stages of their evolution, and has been used to reconstruct the evolution of a single synthetic system. The early oxidation of CH_4 may have led to the precipitation of abundant, commonly vesicular, wustite found as ejecta in the pyroclastics; this suggests fO_2 at or below the QFM buffer. The CO_2 released by this reaction may in turn have driven the precipitation of abundant high-Mg calcite, also found in the ejecta; this could continue to fO_2 as low as the EMOD/G buffer. The progressive lowering of fO_2 to the IW buffer is marked by the appearance of a suite of mutually immiscible melts: native Fe, Fe-oxide/silicate melt and Ti-oxide/silicate melt. This reaction appears to have removed most of the FeO from the system; none of the silicate phases in the trapped melts (see below) have significant contents of Fe. The removal of the Fe-FeO buffer would allow fO_2 to decline (rapidly?) to the levels (ΔIW = -6 to -8) where SiC could precipitate. This would desilicate the melt (now dominated by $CaO-Al_2O_3-MgO$), driving it into the field where corundum is on the liquidus. The hopper form of the corundum aggregates implies Al_2O_3-supersaturation, causing the rapid growth of corundum, and the trapping of melt pockets, some of which contain silicide melts that precipitated abundant TiC. The desilication process apparently continued to near-completion, leading, in some cases, to a coarse-grained assemblage of hibonite ($CaAl_{12}O_{19}$) + grossite ($CaAl_6O_{10}$) + MgAl spinel + fluorite + native V, at $fO_2 \leq \Delta IW$ -11. Many of the larger corundum aggregates are cut by breccia veins of amorphous (commonly vesicular) carbon, and this material also

occurs in parallel-sided veinlets down to the sub-micron (TEM) scale, emphasising the important role of carbon in the evolution of these systems.

Not a unique occurrence

Similar mineral assemblages (+ diamond) occur in the "ophiolitic" peridotites of the Yarlong-Zangbo and Bangong-Nujuang suture zones (southern Tibet; Xu et al., 2009; Zhang et al., 2016; Griffin et al., 2016b; F. Xiong et al., 2017) and the Polar Urals (Yang et al. 2016). In each of these cases, as in the Mt Carmel example, most of the more highly reduced phases, including nitrides, silicides and
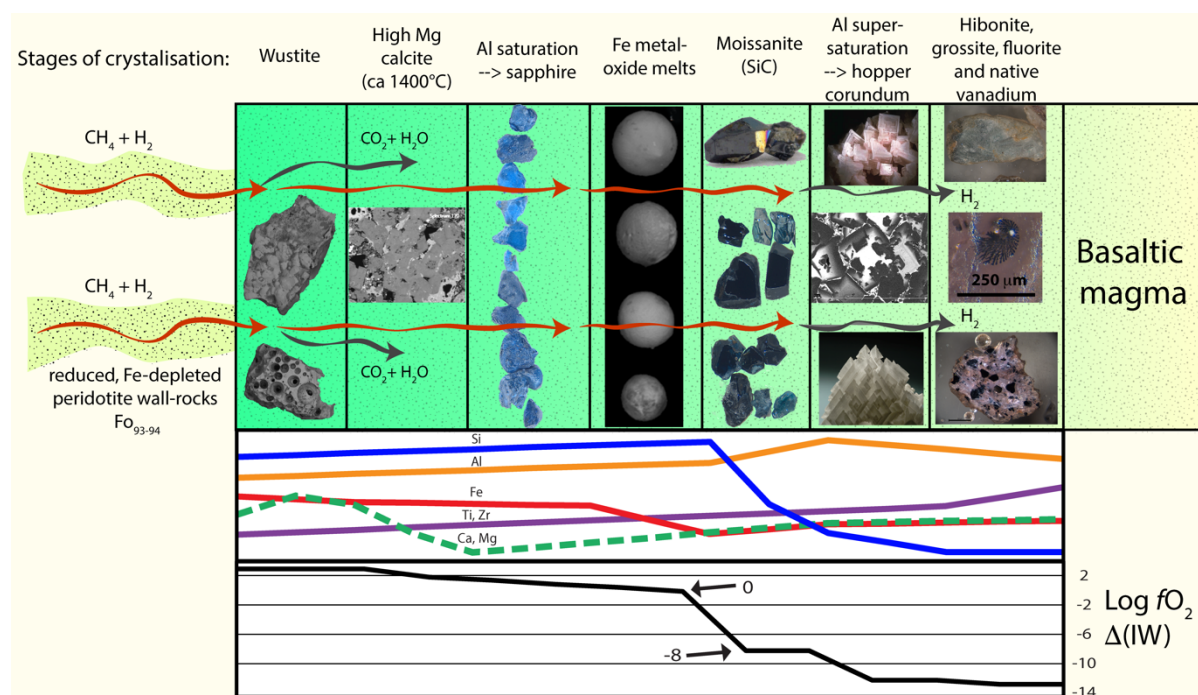

Figure 1. Model for the evolution of the Mt Carmel corundum-SiC system(s), as a progressive interaction between mantle-derived volatiles (CH4±H2) and a basaltic magma. The evolution of the melt composition and the fO_2 of the system is illustrated schematically in the lower panels; the curves for elemental abundance are not to scale. The most important aspects are the drop in Fe (especially FeO) at the IW buffer, the rapid desilication of the melt following the onset of SiC crystallization, and the extremely low fO_2 required by the presence of abundant native V in the hibonite-grossite assemblage. The incongruent melting of anorthite suggests P ≥9kb, while phase relationships in immiscible silicide melts indicate T = 1500-1200 °C.

carbides, are found as inclusions in grains of Ti-rich corundum. The main difference between the "ophiolitic" and the Mt Carmel occurrences is that some carbon in the former occurs as diamond (in breccias of amorphous carbon; Yang et al. 2014; Zhang et al. 2016). Q. Xiong et al. (2017) therefore have suggested that the "ophiolitic" occurrences reflect crystallization in late-magmatic systems related to the rapid emplacement of the host peridotites to shallow depths (McGowan et al., 2015; Griffin 2016b). Similar processes probably are occurring today beneath the Kamchatka volcanic arc, where mafic pyroclastic volcanic rocks carry diamond, SiC and Ti-rich corundum (Gordeev et al., 2014).

The streaming of low-fO_2 fluids from the deep upper mantle thus may accompany many types of deep-seated volcanism, especially in tectonic situations (continental collision zones, deep subduction zones, major transform faults) that allow the rapid ascent and focussing of deep-seated magmas. If the fO_2 of the deep upper mantle is controlled by the IW buffer, then C-O-H fluids will be dominated by CH4+H2, like those trapped in metal-bearing Type II diamonds (Smith et al., 2016). The rapid transport of such fluids to shallower depths as components of deep-seated magmas (including kimberlites) is thus inferred to produce local, perhaps transient, volumes of low-fO_2 assemblages.

SiC is a key indicator for these processes; it is widespread in Siberian kimberlites, and the small number of reports from S. African kimberlites could simply reflect different approaches to the study and processing of kimberlites. However, in both cratons, SiC occurs as inclusions in diamond, and we have separated SiC from Roberts Victor eclogites, apparently associated with the metasomatism that generated diamonds in these rocks. The most common inclusion in SiC from all of these localities is silicon metal, with morphologies suggesting trapping as a liquid, which subsequently commonly exsolved $FeSi_2$ and related phases; these are high-temperature phases (1400-1500 °C) and thus are not related to late serpentinization. The extremely low fO_2 required for the formation of SiC strongly suggests the presence of H_2, which could be generated by the partial oxidation of CH_4 and the deposition of diamond (i.e. $SiO_2 + 3CH_4 \rightarrow SiC + C + 3H_2 + CO_2$). The isotopically light carbon ($\delta^{13}C$ = -25 to -33) of the SiC in the Mt Carmel samples (and kimberlitic SiC worldwide) is similar to that in the Tibetan diamonds and some Transition-Zone diamonds, and may reflect the composition of abiotic methane in the deep upper mantle.

Other implications

Redox melting in the presence of abundant $CH_4 \pm H_2$, rather than simply carbon, may be more efficient; it may also involve the desilication of wall rocks and their melts, and the production of Al-rich lithologies such as corundum eclogites with negative Eu anomalies. We suggest that all of these processes would accompany the arrival at the SCLM of kimberlites or other melts generated in the deep upper mantle or Transition Zone, and may have contributed significantly to the carbon budget of the lower lithosphere through time.

The recognition that $CH_4 \pm H_2$ may accompany melts rising from a deeper, metal-saturated mantle also suggests an explanation for the zones of high conductivity that mark the tracks of mantle-derived magmatic systems (from kimberlites to Bushvelds). The oxidation of CH_4 in rising fluids could propogate networks of microveinlets of amorphous carbon (even if later recrystallized to other forms), which might provide the fine-scale connectivity of conductive material in some mantle domains implied by the striking MT images now becoming more widely available.

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