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

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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 emphasize 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 CH4+H2, 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 (fO2) of Earth’s lithospheric mantle typically lies within the range defined by the quartz-fayalite-magnetite (QFM) and iron-wüstite (IW) 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 fO2 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 fO2 at least 6 log units below the IW buffer (ΔIW-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-Solé 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 (Online Materials1 Fig. OM1; 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.