CH₄ interaction with basalt magma: super-reducing conditions beneath Mt Carmel, Israel

W.L GRIFFIN¹, S.E.M. GAIN¹, J-X. HUANG¹, V. TOLEDO² AND SUZANNE Y. O'REILLY¹

¹ARC Centre of Excellence for Core to Crust Fluid Systems, (CCFS) and GEMOC, Macquarie University, Sydney, NSW 2109, Australia (*bill.griffin@mq.edu.au) ²Shefa Yamim (A.T.M.) Ltd., Akko, Israel

Aggregates of hopper-formed corundum crystals, and crystals (>4mm long) of moissanite (SiC), are common in the pyroclastic ejecta of Cretaceous volcanoes exposed on Mt Carmel, and in associated alluvials. Melt pockets within the corundum aggregates contain anhydrous assemblages (SiC, TiC, Fe-Ti-Zr silicides/phosphides, native V) requiring high T (1600-1200 °C) and low fO_2 (Δ IW -8 to -11). The melt pockets show the peritectic reaction cor+melt \rightarrow An, and late crystallization of hibonite +grossite+spinel, implying T of 1550-1250 °C and depths just below the crust-mantle boundary.

Paragenetic studies suggest that the low fO_2 reflects interaction of basaltic magmas with CH_4 at high fluid/melt ratios, generating H_2 and leading to progressive reduction of the magma. At fO_2 $\Delta IW=$ -7, crystallization of SiC began and rapidly desilicated the magma, leading to supersaturation in Al_2O_3 , the rapid growth of skeletal to hopper-formed corundum, and the immiscible separation of Fe-Ti-Si-P-C melts. At the point of maximum desilication the assemblage hibonite+grossite+spinel+CaF2 is accompanied by droplets of native V ($\Delta IW=$ -11), confirming that progressive reduction continued throughout the desilication process and the crystallization of corundum. The final stage in the evolution of the system was the deposition of abundant amorphous carbon (with sulfides and Na-K-Al fluorides) as the matrix in breccia veins, probably related to the explosive eruptions.

The abundance of SiC, TiC and amorphous C emphasizes the importance of C-rich fluids in the evolution of the magmatic system. There is no evidence of Cretaceous subduction in this region that might supply slab-related fluids. We suggest that the hot-spot magmas were accompanied in their ascent by large fluxes of CH_4 , equilibrated in the deep mantle where $fO_2 = IW$. Reports of similar mineral assemblages in other regions of explosive volcanism (e.g. Kamchatka), and in ophiolites in Tibet and the Polar Urals, suggest this type of process may be more widespread than previously suspected, especially in plate-boundary settings.

This process may also operate beneath cratons, as reflected in the abundance of SiC in kimberlites and its occurrence as inclusions in diamonds. If so, this represents a previously unrecognized piece of the global carbon cycle.

References: Griffin et al. 2016a. *Journal of Petrology* 57, 655-684. Griffin et al., 2016b. *Geology* 44, 815-818.