

A terrestrial magmatic hibonite-grossite-vanadium assemblage: Desilication and extreme reduction in a volcanic plumbing system, Mount Carmel, Israel

**WILLIAM L. GRIFFIN^{1,*}†, SARAH E.M. GAIN¹, JIN-XIANG HUANG¹, MARTIN SAUNDERS²,
JEREMY SHAW², VERED TOLEDO³, AND SUZANNE Y. O'REILLY¹**

¹ARC Centre of Excellence for Core to Crust Fluid Systems (CCFS) and GEMOC, Earth and Planetary Sciences, Macquarie University, New South Wales 2109, Australia ORCID 0000-0002-0980-2566

²Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, Western Australia 6009, Australia

³Shefa Yamim (A.T.M.) Ltd., Netanya 4210602, Israel

ABSTRACT

Hibonite (CaAl_2O_9) is a constituent of some refractory calcium-aluminum inclusions (CAIs) in carbonaceous meteorites, commonly accompanied by grossite (CaAl_4O_7) and spinel. These phases are usually interpreted as having condensed, or crystallized from silicate melts, early in the evolution of the solar nebula. Both Ca-Al oxides are commonly found on Earth, but as products of high-temperature metamorphism of pelitic carbonate rocks. We report here a unique occurrence of magmatic hibonite-grossite-spinel assemblages, crystallized from Ca-Al-rich silicate melts under conditions [high-temperature, very low oxygen fugacity (f_{O_2})] comparable to those of their meteoritic counterparts. Ejecta from Cretaceous pyroclastic deposits on Mt Carmel, N. Israel, include aggregates of hopper/skeletal Ti-rich corundum, which have trapped melts that crystallized at f_{O_2} extending from 7 log units below the iron-wustite buffer ($\Delta\text{IW} = -7$; SiC, Ti_2O_3 , Fe-Ti silicide melts) to $\Delta\text{IW} \leq -9$ (native V, TiC, and TiN). The assemblage hibonite + grossite + spinel + TiN first crystallized late in the evolution of the melt pockets; this hibonite contains percentage levels of Zr, Ti, and REE that reflect the concentration of incompatible elements in the residual melts as corundum continued to crystallize. A still later stage appears to be represented by coarse-grained (centimeter-size crystals) ejecta that show the crystallization sequence: corundum + Liq \rightarrow (low-REE) hibonite \rightarrow grossite + spinel \pm krotite \rightarrow $\text{Ca}_4\text{Al}_6\text{F}_2\text{O}_{12}$ + fluorite. V^0 appears as spheroidal droplets, with balls up to millimeter size and spectacular dendritic intergrowths, included in hibonite, grossite, and spinel. Texturally late V^0 averages 12 wt% Al and 2 wt% Mn. Spinel contains 10–16 wt% V in V^0 -free samples, and <0.5 wt% V in samples with abundant V^0 . Ongoing paragenetic studies suggest that the f_{O_2} evolution of the Mt Carmel magmatic system reflects the interaction between OIB-type mafic magmas and mantle-derived CH_4+H_2 fluids near the crust-mantle boundary. Temperatures estimated by comparison with 1 atm phase-equilibrium studies range from ca. 1500 °C down to 1200–1150 °C. When f_{O_2} reached ca. $\Delta\text{IW} = -7$, the immiscible segregation of Fe,Ti-silicide melts and the crystallization of SiC and TiC effectively desilicated the magma, leading to supersaturation in Al_2O_3 and the rapid crystallization of corundum, preceding the development of the hibonite-bearing assemblages. Reports of Ti-rich corundum and SiC from other areas of explosive volcanism suggest that these phenomena may be more widespread than presently realized, and the hibonite-grossite assemblage may serve as another indicator to track such activity.

This is the first reported terrestrial occurrence of krotite (CaAl_2O_4), and of at least two unknown Zr-Ti oxides.

Keywords: Hibonite, native vanadium, grossite, krotite, super-reduced conditions, mantle methane, Mt Carmel; Volatile Elements in Differentiated Planetary Interiors