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

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ABSTRACT

Hibonite (CaAl2O4) is a constituent of some refractory calcium-aluminum inclusions (CAIs) in carbonaceous meteorites, commonly accompanied by grossite (CaAl2O4) 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 (fO2)] 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 fO2 extending from 7 log units below the iron-wustite buffer (ΔIW = –7; SiC, TiO2, Fe-Ti silicide melts) to ΔIW ≤ –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 → (low-REE) hibonite → grossite + spinel ± krotite → CaAl2O4 + fluorite. V appears as spheroidal droplets, with balls up to millimeter size and spectacular dendritic intergrowths, included in hibonite, grossite, and spinel. Texturally late V averages 12 wt% Al and 2 wt% Mn. Spinels contain 10–16 wt% V in V-free samples, and <0.5 wt% V in samples with abundant V. Ongoing paragenetic studies suggest that the fO2 evolution of the Mt Carmel magmatic system reflects the interaction between OIB-type mafic magmas and mantle-derived CH4+H2 fluids near the crust-mantle boundary. Temperatures estimated with 1 atm phase-equilibrium studies range from ca. 1500 °C down to 1200–1150 °C. When fO2 reached ca. ΔIW = –7, the immiscible segregation of Fe(Ti)-silicide melts and the crystallization of SiC and TiC effectively desilicated the magma, leading to supersaturation in Al2O3 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 (CaAl2O4), 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

INTRODUCTION

Hibonite (CaAl2O4) was described as a new mineral in 1956 (Curien et al. 1956) and is named after Paul Hibon, who found centimeter-sized black crystals in a placer deposit in Madagascar in 1953. It is a constituent of some refractory calcium-aluminum inclusions (CAIs) in carbonaceous chondrites, commonly associated with grossite (CaAl2O4) and corundum (Grossman et al. 1988; Beckett et al. 2006). Hibonite also occurs as microscopic grains in meteorites, and it is one of the oldest minerals in the solar system.

The type locality of hibonite is the Esiva alluvial deposits, in Tulear Province, Madagascar. The material was probably derived from nearby deposits of thorianite-bearing skarns, which are widespread in the Pan-African (565–515 Ma) granulate belts of Madagascar and Tanzania (Rakotondrazafy et al. 1996). In these rocks, early corundum + spinel + scapolite assemblages