Cr$_2$O$_3$ in corundum: Ultrahigh contents under reducing conditions

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Abstract

Xenocrysts and xenoliths in Upper Cretaceous pyroclastics on Mount Carmel (northern Israel) represent a series of similar magma-fluid systems at different stages of their evolution, recording a continuous decrease in oxygen fugacity ($f_{O_2}$) as crystallization proceeded.

Corundum coexisting with Fe-Mg-Cr-Al spinels, other Fe-Mg-Al-Na oxides, and Fe-Ni alloys in apparent cumulates crystallized at $f_{O_2}$ values near the iron-wüstite (IW) buffer ($f_{O_2} = $ IW±1) and is zoned from high-Cr cores to lower-Cr rims, consistent with fractional crystallization trends. The reconstructed parental melts of the cumulates are Al-Cr-Fe-Mg oxides with ca. 2 wt% SiO$_2$. Corundum in other possible cumulates that contain Cr-Fe (Fe 45 wt%) alloys has low-Cr cores and still lower-Cr rims. Corundum coexisting with Cr$^2+$ ($f_{O_2} = $ IW-5) in some possible cumulates has low-Cr cores, but high-Cr rims (to >30% Cr$_2$O$_3$). These changes in zoning patterns reflect the strong decrease in the melting point of Cr$_2$O$_3$, relative to Al$_2$O$_3$, with decreasing $f_{O_2}$. The electron energy loss spectroscopy (EELS) analyses show that all Cr in corundum that coexists with Cr$^2+$ is present as Cr$^{3+}$. This suggests that late in the evolution of these reduced melts, Cr$^{3+}$ has disproportionated via the reaction 3Cr$^{3+}$(melts) → 2Cr$^{2+}$(Crn) + Cr$^6+$.

The most Cr-rich corundum crystallized together with β-alumina phases including NaAl$_2$O$_7$ (diaoyudaole) and KAl$_4$O$_7$ (kahlenbergite) and β”-alumina phases; residual melts crystallized a range of (K,Mg)$_2$(Al,Cr)$_{10}$O$_{17}$ phases with the kahlenbergite structure. The parental melts of these assemblages appear to have been Al-Cr-K-Na-Mg oxides, which may be related to the Al-Cr-Fe-Mg oxide melts mentioned above, through fractional crystallization or liquid immiscibility.

These samples are less reduced ($f_{O_2}$ from IW to IW-5) than the assemblages of the trapped silicate melts in the more abundant xenoliths of corundum aggregates ($f_{O_2} = $ IW-6 to IW-10). They could be considered to represent an earlier stage in the $f_{O_2}$ evolution of an “ideal” Mt. Carmel magmatic system, in which mafic or syenitic magmas were fluxed by mantle-derived CH$_4$+H$_2$ fluids. This is a newly recognized step in the evolution of the Mt. Carmel assemblages and helps to understand element partitioning under highly reducing conditions.

Keywords: High-Cr ruby, ultra-reducing conditions, Mt. Carmel, mantle-derived methane, mantle-derived hydrogen

Introduction

Cr is a common multivalent element, and its oxidation state in minerals potentially carries information on the oxygen fugacity ($f_{O_2}$) of their crystallization environment (Schreiber and Haskin 1976). However, this feature is not generally useful in mantle petrology because the redox reactions that define steps in the valence state of Cr occur at relatively low $f_{O_2}$ compared to most igneous and metamorphic environments, so that Cr$^{3+}$ is the most common form. The Cr$^{3+}$-Cr$^{2+}$ transition (as defined by the CrO-Cr$_2$O$_3$ buffer reaction) lies at $f_{O_2}$ just above the iron-wüstite (IW) buffer (IW+0.5) (Fig. 1a), and is potentially observable in the most reduced parts of the deep subcontinental lithospheric mantle (SCLM) (e.g., Yaxley et al. 2012). At high temperatures, the reduction of Cr$^{3+}$ to Cr$^{2+}$ occurs at $f_{O_2}$ of ~IW-5 (Fig. 1a), conditions that are not common on Earth but must (as will be shown here) occur locally. To illustrate the behavior of Cr under highly reducing conditions, we describe zoning patterns in a series of corundum cumulates and report the occurrence of corundum (ruby) with >30 wt% Cr$_2$O$_3$ and inclusions of Cr$^6+$ and Cr$_2$N; this assemblage requires $f_{O_2}$ near IW-5. We also attempt to define the petrological setting of this assemblage within the evolution of a series of magmatic systems, some of which...