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Cr_2O_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^0 (f_{O_2} = IW-5) in some possible cumulates has low-Cr cores, but high-Cr rims (to >30% Cr_2O_3). These changes in zoning patterns reflect the strong decrease in the melting point of Cr_2O_3, relative to Al_2O_3, with decreasing f_{O_2}. The electron energy loss spectroscopy (EELS) analyses show that all Cr in corundum that coexists with Cr^0 is present as Cr^{3+}. This suggests that late in the evolution of these reduced melts, Cr^{2+} has disproportionated via the reaction $3Cr^{2+}(\text{melt}) \rightarrow 2Cr^{3+}(\text{Crn}) + Cr^0$.

The most Cr-rich corundum crystallized together with β-alumina phases including $NaAl_{11}O_{17}$ (diaoyudaoite) and $KAl_{11}O_{17}$ (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