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Chromium in Corundum: Ultra-high Contents Under Reducing Conditions

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An exploration project run by Shefa Yamim (A. T. M.) Ltd has recovered a variety of gemstone minerals from Cretaceous pyroclastic vents and associated alluvial deposits at Mt Carmel, Israel [1]. Among these are several types of corundum (Al_2O_3), including rubies with <2 wt% Cr_2O_3 and sapphires in a variety of colours from yellows through to greens, blues and purples, with a range of chemical impurities e.g. Ti, Fe, V, Ga. The most scientifically interesting type of corundum is the inclusion-rich 'Carmel Sapphire™', which contains a variety of mineral phases; some of these have only been seen in meteorites previously, e.g. tistarite (Ti_2O_3) [2], and others have not previously been described, e.g. carmeltazite ($ZrAl_2Ti_4O_{11}$) [3]. These minerals indicate very low oxygen fugacities, at least 7 log units below the Iron-Wustite buffer (ΔIW-7), and are interpreted as reflecting the presence of CH_4+H_2-rich fluids [1,4]. These discoveries have led to a new understanding of fluid transfer and redox conditions in the crust and mantle.

Here we describe another variety of Cr-rich corundum (Fig. 1) with Cr concentrations up to 32 wt.% Cr_2O_3, representing a composition in the solid solution series between corundum and eskolaite (Cr_2O_3), and considerably more Cr-rich than previously known examples. These crystals are a deep purple (Fig. 1), but while purple in corundum usually is due to a combination of Ti and Cr, in this case the crystals are Ti-free and contain much higher concentrations of Cr. The cores of the crystals have relatively low Cr concentrations (1-2 wt.% Cr_2O_3) and the Cr concentration increases towards the rim. In the highest-Cr areas, the material consists of sub-grains with small but distinct variations in Cr content (Fig. 1a, 2). On the surface of the illustrated crystal there are abundant balls (<10μm to 100's of μm) of native Cr; Transmission Electron Microscopy (TEM) studies show that these are associated with chromium nitride CrN (carlsbergite; Fig. 2), otherwise known only from iron meteorites.

Electron Energy Loss Spectroscopy (EELS) analyses show that the valence of the Cr changes from Cr^{3+} in the corundum (both low-Cr and high-Cr types) to Cr^{2+} in the carlsbergite and finally Cr^0 in the chromium metal. The coexistence of all three valence states suggests that the oxygen fugacity was constrained by the CrO/Cr buffer, and that Cr was undergoing a crystallographically-controlled disproportionation, $Cr^{2+} \rightarrow Cr^{3+} + Cr^0$. The oxygen fugacity implied by this reaction lies at ca ΔIW-5, less reducing than the conditions inferred from the Ti^{3+}-bearing, but Cr-free, assemblages in the Carmel Sapphire. These unusual high-Cr rubies thus appear to represent an earlier stage in the crystallization of the Mt Carmel magmas.

References:

[1] WL Griffin et al., Mineralogy and Petrology **112** (2018), p. 101.
[2] WL Griffin et al., Geology **44** (2016), p. 815.
[3] WL Griffin et al., Minerals **8** (2018), p. 601.
[4] SEM Gain et al., elsewhere in these proceedings.

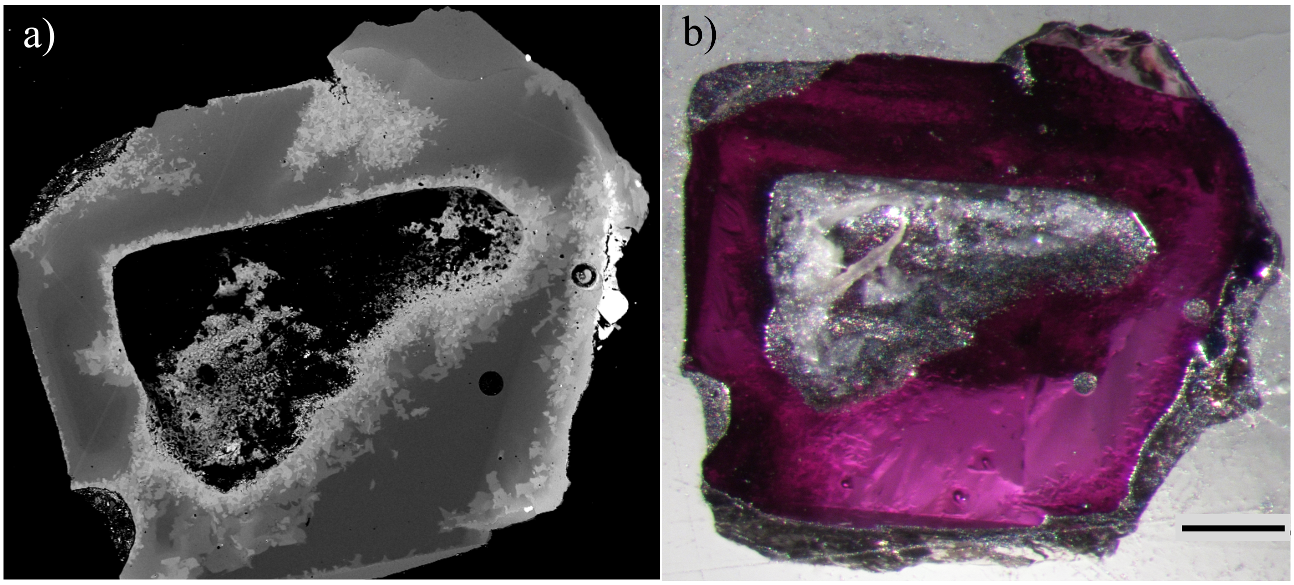

Figure 1. Chromium rich corundum; a) backscattered electron - scanning electron microscope (BSE-SEM) image, b) light microscope image; scale bar 200µm.

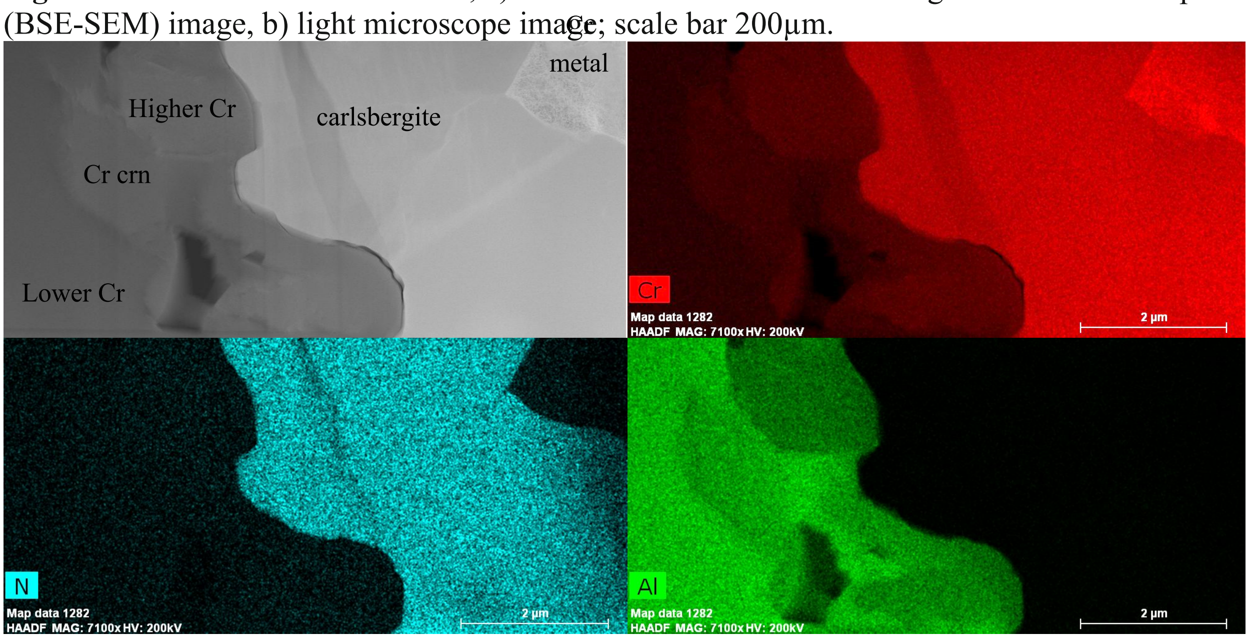

Figure 2. High angle annular dark field (HAADF) Scanning TEM (STEM) image and associated EDS element maps of a Focused Ion Beam (FIB-SEM) prepared TEM sample, showing the carlsbergite in the boundary between the chromium-rich corundum (crn) and the chromium metal, and varying Cr concentrations in the corundum.

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