The origin of needle-like rutile inclusions in natural gem corundum: A combined EPMA, LA-ICP-MS, and nanoSIMS investigation

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ABSTRACT

Trace-element chemistry and microscopic observations of included gem corundum (α-Al2O3) suggest a new model of syngeneic growth of oriented rutile inclusions rather than the usual interpretation of their growth through exsolution. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is now a robust method for measuring trace elements in gem-quality corundum (ruby and sapphire). Nonetheless, the corundum structure is relatively unforgiving for substitutional components and typically only a small handful of minor to trace elements are measured by LA-ICP-MS (Mg, Ti, V, Cr, Fe, Ga). Less commonly, trace elements such as Be, Zr, Nb, Sn, La, Ce, Ta, and W are found in natural corundum. Their concentrations are typically correlated with high contents of Ti and silky or cloudy zones in the corundum that contain a high concentration of needle-like rutile or other oxide inclusions. Three metamorphic-type sapphires from Sri Lanka, Madagascar, and Tanzania were studied here using LA-ICP-MS, electronprobe microanalysis (EPMA), and nanoSIMS to document correlations between the various trace elements and their distribution between the corundum and included, oriented rutile TiO2 needles. NanoSIMS and EPMA measurements show concentration of Be, Mg, Fe, V, Zr, Nb, Ce, Ta, and W in the rutile needles. The relative atomic concentrations of Mg and Ti from LA-ICP-MS measurements suggest the corundum-rutile intergrowth grew as a mechanical mixture of the two phases as opposed to rutile formation through exsolution from the corundum host. This scenario is also suggested for the three magmatic-type sapphires studied here based on the presence of glassy melt inclusions in close association with included, oriented oxide needles. The preservation of a glassy melt inclusion requires fast cooling, whereas exsolution of the oxide inclusions would require slow cooling and annealing at a temperature lower than sapphire formation. The studied sapphires suggest the likely origin of the oriented, needle-like rutile inclusions to be syngenetic epitaxial coprecipitation of both rutile and corundum. The interpretation of such oriented oxide inclusions has important implications for understanding the geological formation conditions based on trace element data or using such data to separate sapphires and rubies based on their geographic origin.

Keywords: Corundum, sapphire, exsolution, immiscibility, gemology, trace element chemistry, melt inclusions, nanoSIMS, LA-ICP-MS, EPMA, rutile inclusions

INTRODUCTION

Oriented, needle-shaped oxides are among the most common inclusions in gem-quality corundum, Al2O3 (ruby and sapphire). Frequently encountered oriented oxide inclusions include rutile (TiO2), hematite (Fe2O3), and ilmenite (FeTiO3) and more rarely pseudobrookite, an Fe,Ti oxide (Hughes 1997; Izokh et al. 2010). Oriented rutile needles are generally aligned in the basal plane (perpendicular to the c-axis) and parallel to the crystallographic directions of the second-order hexagonal prism and hematite and ilmenite reportedly form in the basal plane of the first-order prism with oriented needles in both cases intersecting themselves at an angle of 60°/120° (Hughes 1997). Except for star rubies and sapphires, such inclusions, in general, are considered to detract from the gem’s value. However, the advent of heat treatment of sapphires to extreme temperatures (often around 1500 °C or more) starting in the 1960s relied on the dissolution of TiO2 needles to enhance the blue coloration of otherwise worthless, milky “geuda” corundum (Emmett et al. 2003). The underlying mechanism in this case is the dissolution of rutile needles and the incorporation of Ti4+ into the corundum lattice to pair with Fe2+ causing blue color through absorption of visible light by an Fe2+-Ti4+ intervalence-charge transfer (e.g., Emmett and Douthit 1993).

Phenomenal star sapphires and rubies rely on the presence of such oriented needle-like inclusions to produce asterism. In fact, synthetic star sapphires and rubies have been produced for many decades by dissolving Ti into synthetic corundum at very high temperatures (~1800 °C, Schmetzer et al. 2015) and subsequently annealing at a lower temperature to exsolve TiO2 needles. At first glance, the ability to both dissolve and precipitate rutile needles at high temperature seems to support the hypothesis that such