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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-Al_2O_3) suggests a new model of syngenetic 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 TiO_2 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