A combined LA-ICP-MS, EPMA, and nanoSIMS approach to measure Be and high-field strength elements in sapphire-hosted TiO_2 clouds

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Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) was adopted by many gem labs in the early 2000's to detect Be-diffused gem corundum (Al_2O_3). Such stones have been heat-treated in the presence of Be which diffuses into the lattice and acts as a strong chromophore, often producing an attractive pink-orange color. Nonetheless, LA-ICP-MS analyses of corundum that was known to be unheated showed the presence of so-called "natural Be" which is usually found in "milky"or "cloudy" areas and is almost always correlated with Ti concentrations in addition to other high field strength elements (HFSE) such as Zr, Nb, Ta, W, and Th. Focussed Ion Beam Transmission Electron Microprobe analyses by Shen and Wirth (2012) [1] demonstrated that these clouds were composed of exsolved nanoscale TiO_2 particles taking the α-PbO_2 structure.

We present here the results of LA-ICP-MS analyses characterizing the trace element contents of natural-Be containing metamorphic blue sapphires from well-known gem producing regions in Myanmar, Sri Lanka, Indian Kashmir, Tanzania, and Madagascar as well as lesser-known specimen localities such as Afghanistan. In some stones these "cloudy" areas contain micron-sized TiO_2 needles allowing quantitative concentrations of the HFSE to be measured by Electron Probe MicroAnalysis (EPMA). These HFSE are always found to be contained within TiO_2. In some cases, Ti is replaced by up to 9 at.% Ta. Beryllium is too light to be measured by EPMA, so nanoSIMS (Secondary Ion Mass Spectrometry) is required to positively identify its host phase. In some cases the Be was seen to be highly concentrated in the TiO_2 phase while in others Be could not be detected, likely indicating that it is spread throughout the corundum host at low concentrations. Initial results suggest that when concentrations of HFSE such as Ta are high, Be is hosted in TiO_2. It is likely that in these cases Be^{2+} is incorporated into this phase during TiO_2 exsolution in order to help charge compensate the substitution of HFSE such as Ta^{5+} or W^{6+} for Ti^{4+}.

[1] Shen, A.H. and Wirth, R. (2012) *Gems & Gemology*, **48**, 150-151.