Beryllium in Pink and Yellow Sapphires

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Pure corundum consists only of aluminum oxide (Al_2O_3), but in nature this mineral always contains minor to trace amounts of other elements as impurities. For example, natural untreated blue sapphires may contain roughly a few hundred to tens of thousands ppm of iron and titanium, depending on the type of deposit in which they formed. Until recently, however, beryllium (Be) had not been documented in untreated corundum. Therefore, it was assumed that the presence of *any* Be in corundum was indicative of beryllium treatment.

In 2006, we did a comprehensive analysis of 500 sapphires (Shen et al., 2007) and found 17 blue sapphires with Be concentrations that were highly variable from one area of the stone to the next. This was not consistent with the results obtained on known beryllium-treated stones. One of these anomalies was a 2.6 ct round brilliant-cut blue sapphire that showed clear evidence of heat treatment. Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) analyses of a few spots on the girdle showed up to 13.3 ppmw (parts per million by weight is used throughout this article) Be associated with an angular milky cloud within the stone, with essentially no Be found elsewhere. The cloud also showed consistently elevated concentrations of niobium (Nb) and tantalum (Ta), which had never been seen in any Be-diffused samples. We concluded that the source of the Be must be the cloud and that the uneven distribution of Be and its association with Nb and Ta could be used to identify naturally occurring Be.

Since then, we have detected beryllium in other colors of sapphires, some of which we can identify as occurring naturally—either by their association with clouds or because of their Be-Nb-Ta association. In this contribution, we describe a pink sapphire with natural Be and a yellow sapphire with an indeterminate Be source.

For the heated purplish pink sapphire (6.3 ct) in figure 1, we recorded the following gemological observations: discoid fractures with lacy rims, pink color zones showing hexagonal growth, a blue zone surrounded by clouds near the culet in which the cloud appeared to be yellowish, and a few faint clouds on or near the girdle. LA-ICP-MS analysis showed a Be range from 0 ppmw (below detection limit) to 5.6 ppmw around the whole girdle. The highest Be concentrations were associated with the cloud. When the chemical data was plotted, clear Be-Nb-Ta-Ti correlations were observed (figure 2). This was consistent with Be of natural origin.

This Be-Nb-Ta correlation worked beautifully in blue and pink sapphires, but it might not apply to other colors. The heated yellow sapphire seen in figure 3, weighing ~12 ct, showed numerous planes of particulate clouds throughout the stone. Straight and angular growth and associated yellow and blue color zones were seen by immersing the stone in methylene iodide. Twelve spots around the girdle of the stone were analyzed by LA-ICP-MS. Be was present in 10 of these; the two that showed none were adjacent to each other and were in turn adjacent to the spot that showed by far the lowest concentration of Be (0.47 ppmw). All the other spots showed Be concentrations of 1.78 ppmw or higher. Nb and Ta were also present in low concentrations (0–0.04 and 0–0.12 ppmw, respectively), but their correlation to Be was the exact opposite of what we expected. The highest concentrations of these elements were found in the spots with the lowest amounts of Be, including the two spots that showed none. Curiously, though, there was a direct correlation with zirconium (Zr) (0–3.2 ppmw) and hafnium (Hf) (0.05–0.4 ppmw)—the same type of correlation we found for Be-Ta and Be-Nb in blue sapphire (figure 4). In addition, some spots showed ~0.08 ppmw tungsten (W).

This yellow stone is puzzling because we do not have a clear understanding of the relationship of these elements (Be-Zr-Hf-W), especially when the Be-Nb-Ta correlation does not exist in this stone at all. The fact that two of the analysis spots detected no beryllium at all would argue against the stone being Be–diffused, since no surface-conformal color zoning was present. It seems likely that this is another natural occurrence of Be, but it is unlike any examples we have seen in blue sapphire.

Additional research and chemical fingerprinting for elements such as Be-Zr-Hf-W are being conducted in the GIA Laboratory, particularly on yellow to orange sapphires.

Reference

Shen A., McClure S., Breeding C. M., Scarratt K., Wang W., Smith C., Shigley J. (2007) "Beryllium in Corundum: The Consequences for Blue Sapphire." *GIA Insider*, Vol. 9, Issue 2 (January 26, 2007)

Figure 1. This 6.3 ct purplish pink sapphire is the first of this color in which our laboratory detected natural Be with Ta and Nb.

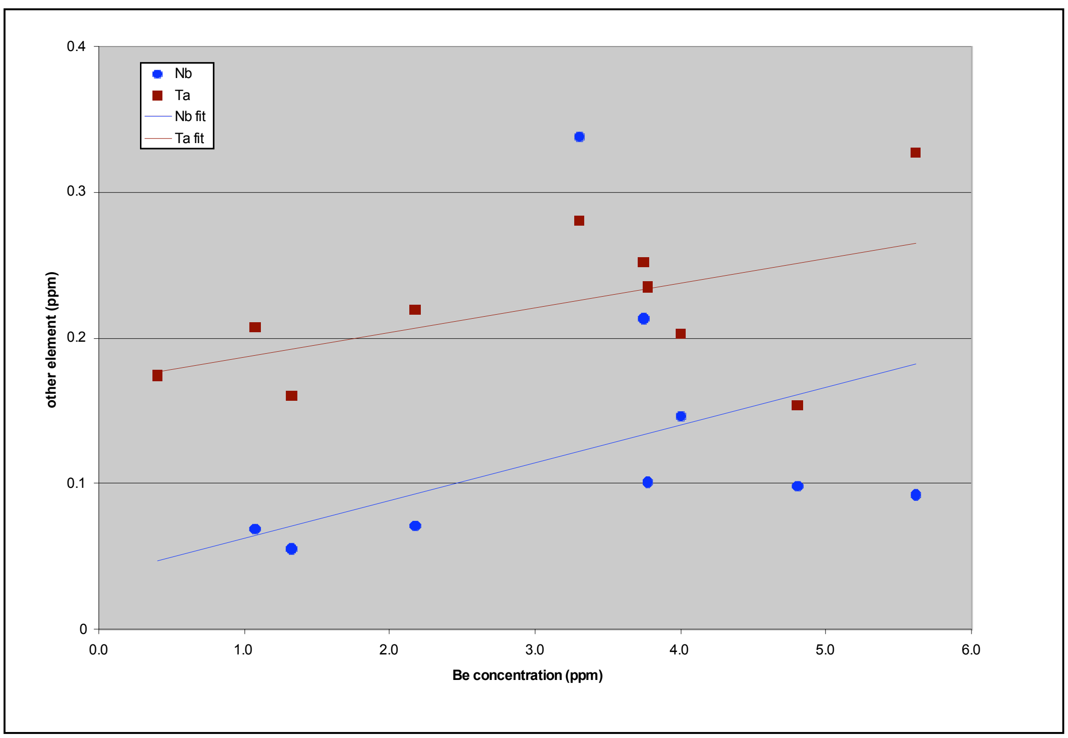

Figure 2. A plot of Nb vs. Be and Ta vs. Be. shows a clear Be-Nb-Ta correlation..

Figure 3. This 12 ct yellow sapphire has uneven Be distribution, but it does not have Be-Nb-Ta correlation as seen in blue sapphires and the pink sapphire in figure 1. However, its Be concentrations clearly correlated to Zr and Hf.

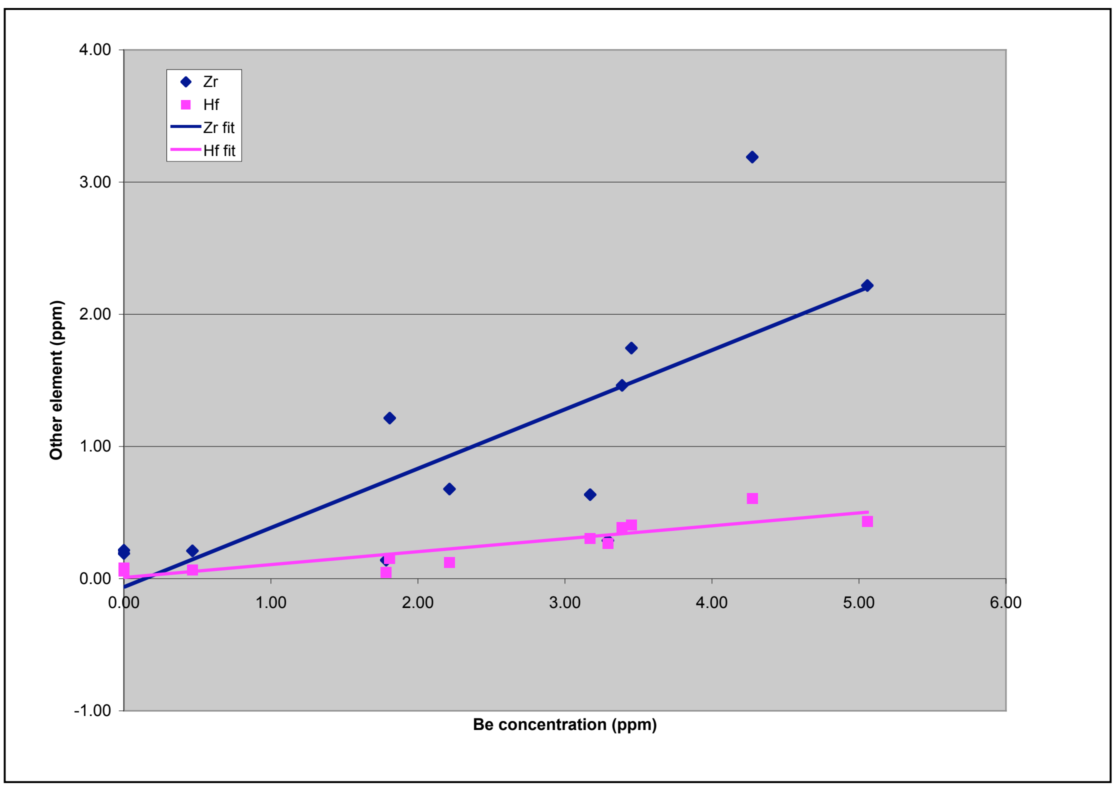

Figure 4. A plot of Zr vs. Be and Hf vs. Be. Clearly, Zr-Be and Hf-Be are correlated, but Nb-Be and Ta-Zr are not.