

Synchrotron-Based Micro-XRF Spectroscopy Investigation of Zoned Aquamarine and Emerald Crystals

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Beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, is one of the main mineral hosts of the “critical mineral” Be, but also forms several highly-priced gem-quality varieties, including emerald (green) and aquamarine (blue). These colored beryl varieties originate due to the occurrence of elemental impurities, but questions remain about the origin of the color, including the relative abundance of substituting chromophore elements, particularly Fe, Cr, V, and Mn. Synchrotron radiation X-ray fluorescence (XRF) spectroscopy is a powerful, non-destructive, *in-situ* technique that enables acquisition of high-resolution elemental distribution maps within materials. Knowing the distribution of elements within beryl can help explain a variety of properties and processes, including: the origin of color and color treatment, identify impurities that can affect Be extraction and purification, understand the evolution of mineralizing fluids, and advance applications in nanotechnologies and nano-materials.

We present the first detailed, high-resolution synchrotron micro-XRF elemental maps of Fe, Cr, V, and Mn of a green-zoned emerald crystal from Chivor, Colombia, and a blue color-zoned aquamarine crystal from Minas Gerais, Brazil. Intra-crystal zonation in elemental abundance is visible in bands down to 50 micrometers thick perpendicular to the c axis of the crystals that match color variations. Higher Fe contents in the darker green compared to the very light green zone of the emerald crystal and Fe-Cr co-variation demonstrate that Fe darkens the green color generated by chromophore Cr and in less degree, V. Marked chemical contrast between the two color zones reflects decreasing Fe and Cr content of the hydrothermal fluid during crystallization. In the zoned aquamarine crystal, zoning in Fe contents match visible color changes from colorless to pale blue, medium blue, and darker blue, not seen for Cr, Mn, and V, confirming that Fe is the main chromophore. Overall, increasing Fe contents correlate with green and blue color variations and are attributed to darkening both colors. The new results demonstrate the usefulness of high-resolution synchrotron-based micro-XRF spectroscopy mapping to elucidate intra-crystal elemental variations in individual crystals to explain the cause of color differences as well as changing conditions of the mineralizing fluids and melts during crystal growth.