Micro-XRF Mapping of Chemically Zoned Beryl: Fast, Non-Destructive, and Precise

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Beryl ($Be_3Al_2Si_6O_{18}$) is a chemically complex gem-forming mineral with highly variable composition found in geologic settings worldwide. It is an important mineral for understanding fractionation in magma bodies with economic concentrations of critical metals such as lithium, beryllium, cesium, and tantalum. Trace element distribution in single crystals can be critical to unravel crystallization history and degree of magmatic fractionation. In pegmatites, beryl may form euhedral megacrystals that are commonly too large to examine in detail through conventional microanalytical techniques. These techniques can include LA-ICP-MS, electron microprobe, FTIR, and X-Ray diffraction. Collecting this information with these techniques can be time- and sample preparation-intensive and may not be suitable for large samples.

In this study, one beryl crystal, ~8 cm wide and 6 cm tall, from Brunswick pegmatite field, Sagadahoc County, ME is investigated for 2D elemental distribution and standardless quantification [1]. Measurement is done with a Bruker M4 TORNADO micro-XRF benchtop instrument. It is equipped with a Rh X-ray tube and polycapillary lens with 20 μm spot. Mapping parameters are detailed in Table 1. The M4 TORNADO combines high spatial resolution with rapid data processing and a high-speed motorized xyz-stage for sample positioning. The method is non-destructive and requires no special sample preparation. Sample preparation for this beryl involved cutting the crystal perpendicular to the c-axis, cleaning it in distilled-deionized water, and placing the sample (> 3 cm thick) on the stage for measurement. Sample selection was based on preliminary qualitative portable-XRF (pXRF) results collected along traverses of points at 5 mm intervals and a dwell time of 60 seconds, using a Bruker Tracer 5i unit [2].

Figure 1 displays Zn (top) and Cs (bottom) X-ray distribution maps at three different measurement parameters. Smaller pixel sizes produce crisp, visually stunning maps of the outer, middle, and core zones. Although map resolution declines as pixel size increases, > 2 mm tick compositional zones remain evident in all maps. At the highest resolution (50 μm pixel sizes) beautifully detailed maps are produced over 16 hours and 25 minutes. However, these data show that less than an hour is sufficient to visualize the elemental distribution patterns and even to quantify the zones at mm-scale. In contrast, sub-mm features such as Cs-rich, Zn-poor alteration along fractures and patches are largely lost at 300 μm pixel resolution.

With Bruker's position tagged spectroscopy ("HyperMap"), a full spectrum of each measured pixel is saved. This is critical to analyze multiple compositional zones in the beryl post-acquisition. Sections from each zone are investigated separately using the software's Object Area function (Figure 2 red rectangles). Data from pixels in each selected area are integrated to produce an average spectrum for each zone (outer, mid, core). All Zn peaks from the three zones and three maps are overlaid in Fig. 2 for

comparison. Note that each zone's Zn peaks overlap very well. This is reflected in the quantification from each zone in Table 2 where the relative standard deviation of each zone is quite low.

Quantification is performed utilizing a standardless fundamental parameters (FP) method. The FP quantifies using the theoretical relationship between measured X-ray intensities and concentrations of elements in the sample. The M4 TORNADO quantification algorithm integrates the derivation of net peak intensities and calculation of sample composition into one step. This approach incorporates multiple physical effects such as self-absorption and secondary excitation. There are several advantages to the FP method. For instance, strong peak overlaps and pronounced absorption effects are treated to the best of knowledge, providing more robust results for quantification as it can use a larger set of fluorescence lines for calculation. Based only on these physical parameters and the measured spectra, concentrations in the specimen can be obtained accurately. This is in spite of the fact that XRF spectra are heavily affected by matrix effects such as absorption and enhancement. While micro-XRF is often a technique used for structured and inhomogeneous samples, bulk-FP algorithms require a homogeneous sample of infinite thickness. Thus, the sample itself typically limits the attainable quantification accuracy. Here, we show the quality of the standardless FP quantification with M4 TORNADO. Table 2 details FP quantification of the data pulled from each zone in the crystal for 50 μm, 150 μm, and 300 μm pixel size maps. Relative standard deviation between the spectra from each zone is extremely small, demonstrating that fast map data can be used with confidence to quantify major and trace elements in place of long maps. Accuracy of results can even be improved by a one-point calibration, i.e., type calibration, making it a standard-supported FP quantification.

There is excellent agreement between the micro-XRF compositional mapping and pXRF qualitative point traverses, confirming that the coarse-grained beryl crystallized from an evolving, highly fractionated pegmatite magma. However, the spatial resolution, the duration of analysis, and the ease of data processing are far superior for the benchtop compared to the portable instrument. This micro-XRF study proves that precise compositional mapping and quantitative trace-element geochemistry of geologic samples, such as the samples in this study, can be achieved non-destructively with little to no sample preparation, and in short analytical runs. Future quantitative analysis independently calibrated through LA-ICP-MS is needed to confirm the accuracy of the trace element results.

|	Map 1	Map 2	Map 3
Mapping area/ mm	87.9 x 62.8	87.9 x 62.8	87.9 x 62.8
Number of pixels	2208048	245534	61237
Pixel size/ μm	50	150	300
Time per pixel/ ms	20	30	30
Total time/ hr:min	16:25	2:20	0:38
Tube high voltage/ kV	35	35	35
Tube current/ μA	800	800	800
Chamber pressure/ mbar	2	2	2

Table 1. X-ray mapping parameters for three different pixel sizes/maps.

Spectrum	O	Na	Al	Si	Ca	Mn	Fe	Zn	Ga	Rb	Cs
Core 50um	54.86	0.57	10.30	33.16	0.01	0.01	0.67	0.18	0.03	0.02	0.19
Core 150um	54.96	0.55	10.28	33.11	0.01	0.01	0.67	0.18	0.03	0.02	0.19
Core 300 um	54.97	0.52	10.25	33.15	0.01	0.00	0.68	0.18	0.03	0.02	0.20
Mean value:	54.93	0.55	10.28	33.14	0.01	0.01	0.68	0.18	0.03	0.02	0.19
Rel Std Dev [%]:	0.11	5.05	0.22	0.08	0.73	8.81	0.43	0.35	1.24	3.84	1.17
Spectrum	O	Na	Al	Si	Ca	Mn	Fe	Zn	Ga	Rb	Cs
Mid zone 50um	55.11	0.48	10.16	33.01	0.02	0.01	0.83	0.13	0.03	0.02	0.19
Mid zone 150um	55.11	0.47	10.18	33.03	0.01	0.01	0.81	0.14	0.03	0.02	0.18
Mid zone 300 um	55.31	0.47	10.14	32.88	0.01	0.01	0.82	0.13	0.03	0.02	0.18
Mean value:	55.18	0.47	10.16	32.97	0.01	0.01	0.82	0.13	0.03	0.02	0.19
Rel Std Dev [%]:	0.21	1.59	0.23	0.24	3.81	7.18	1.21	1.45	2.21	3.75	3.92
Spectrum	O	Na	Al	Si	Ca	Mn	Fe	Zn	Ga	Rb	Cs
Outer zone 50um	55.16	0.47	10.00	32.84	0.01	0.01	1.08	0.12	0.03	0.03	0.24
Outer zone 150um	55.29	0.45	9.99	32.74	0.01	0.01	1.09	0.12	0.03	0.03	0.24
Outer zone 300 um	54.81	0.46	10.06	33.11	0.01	0.01	1.11	0.12	0.03	0.02	0.25
Mean value:	55.09	0.46	10.02	32.90	0.01	0.01	1.09	0.12	0.03	0.03	0.24
Rel Std Dev [%]:	0.45	2.64	0.37	0.58	3.06	0.96	1.30	1.02	0.22	3.45	2.21

Table 2. Semi-quantification from each map's object areas. All values are reported as element wt. %. Beryllium (measured at 5.03%) is omitted as it is too light to be determined by XRF methods.
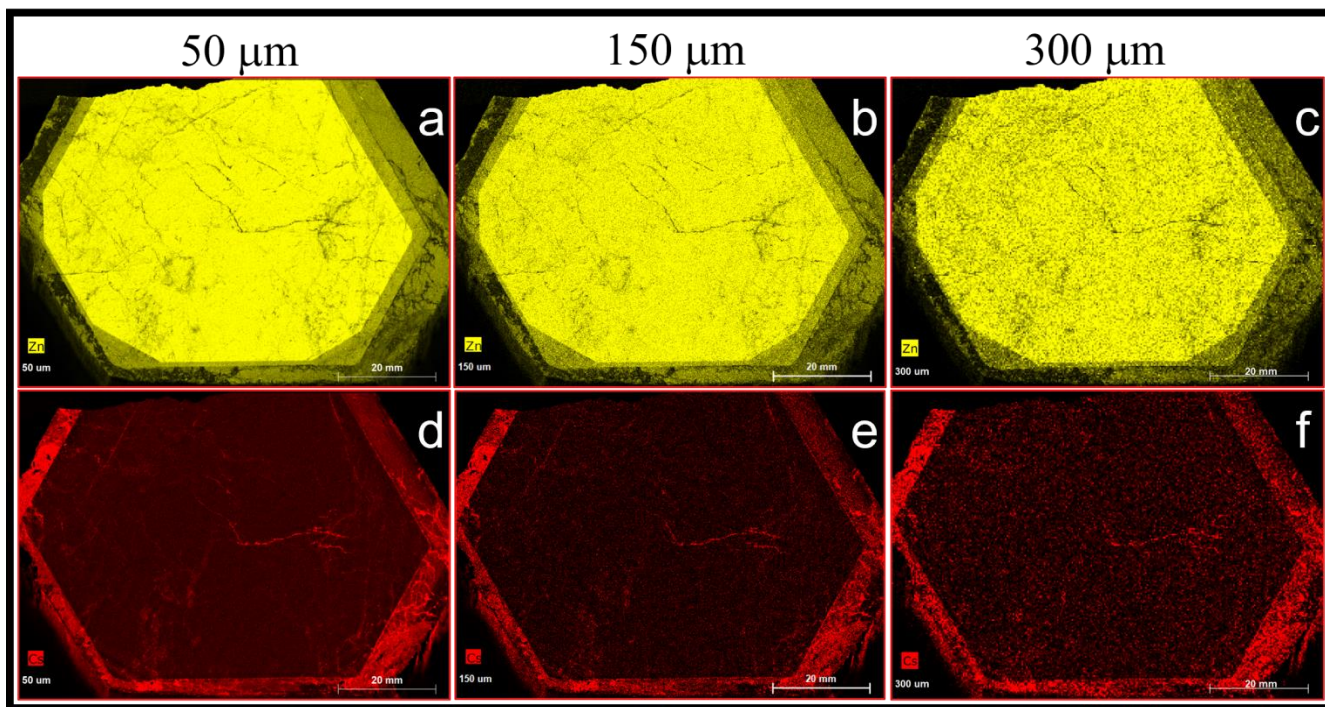
Figure 1. Zn (a, b, c) and Cs (d,e,f) X-ray distribution maps at all three measurement parameters. A and d are 50 μm, b and e are 150 μm, and c and f are 300 μm pixel size maps.
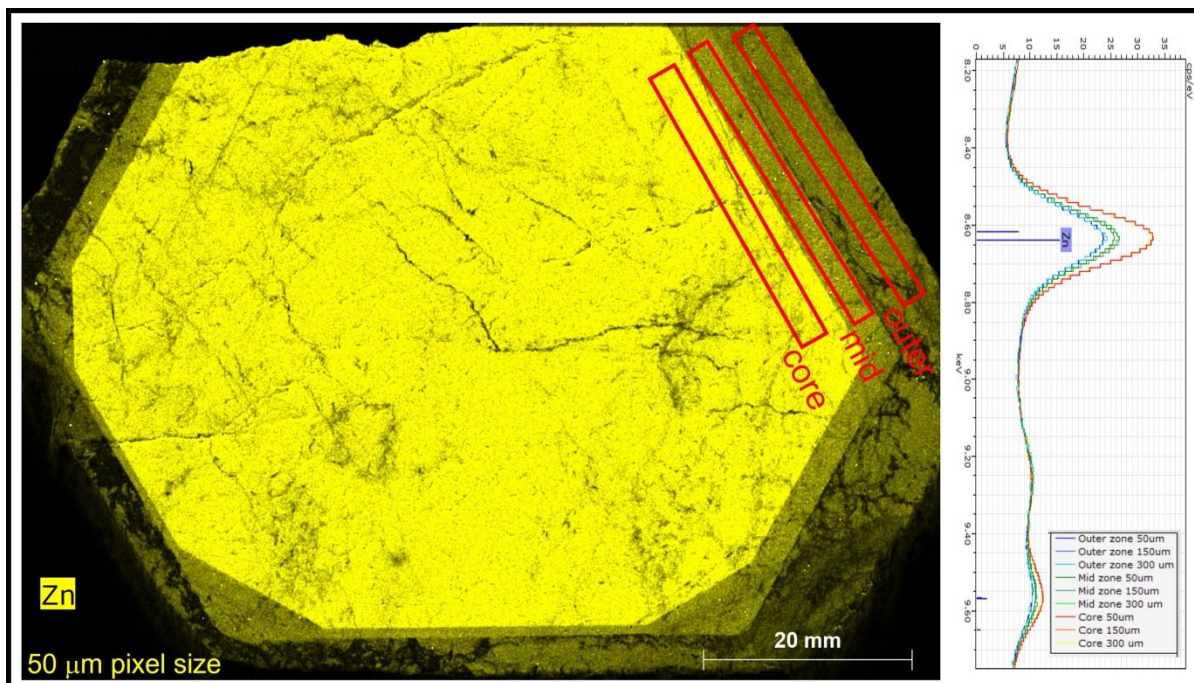
Figure 2. Red rectangles mark the location of outer, middle, and core object areas. Each rectangle produces its own bulk spectrum from only the pixels within the area. All Zn peaks from the three zones and three maps are overlaid at right for comparison. The three zones can be identified easily as the Zn peaks overlap very well for each zone.

References:

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[2] J Zieziul et al., Geological society of America Abstracts with Programs **54** (2022), doi: 10.1130/abs/2022NC-375617