

Quantification of Bastnaesite and Hydroxylbastnaesite Using Electron Probe Microanalysis and Cathodoluminescence

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The Mountain Pass mine, California, hosts a world-class rare earth element (REE) deposit where most of the REEs are contained in the mineral bastnaesite (REECO_3F). The current attention surrounding REEs prompted a reflectance spectroscopy flight path over the deposit to examine the extent of mineralization and to better understand ore formation. Spectral mapping of data collected by the NASA/JPL AVIRIS-NG imaging spectrometer in 2014 at 5300 m altitude with 4 m pixel resolution was able to demonstrate that most REEs reside in the bastnaesite form. In addition, a second, less abundant REE phase was spectrally detected and attributed to [hydroxylbastnaesite](#) (REECO_3OH). These spectral mineral maps were used to locate areas of putative hydroxylbastnaesite and several field samples were collected and submitted for [hydroxylbastnaesite](#) electron probe microanalysis (EPMA) to confirm its presence. EPMA of bastnaesite and hydroxylbastnaesite presents many challenges due to the nature of the material: several light elements occur in a heavy element dominant matrix with unmeasurable elements present, such as hydrogen. The use of higher accelerating voltages is preferred so that the REE $L\alpha$ x-ray lines can be measured with enough overvoltage. However, to prevent absorption of the light elements, it is best to use a lower accelerating voltage which would require use of the REE $M\alpha$ x-ray lines whose physical constants are not well known. Table 1 summarizes the $F(c) \mu$ values at various accelerating voltages, where $F(x)u$ is the fraction of generated x-rays that are emitted from a material. At 7 kV, $F(c) \mu$ for C $K\alpha$ is over 0.5 but the overvoltage for analysis of the Sm $L\alpha$ x-ray line is close to one and not sufficient to excite the x-ray. One solution to this predicament is to combine REE concentrations acquired at high accelerating voltage with the light element concentrations acquired at low accelerating voltages.

The REE and Ca analyses were collected at 15 kV accelerating voltage, 20 nA beam current, and 5 μm beam diameter on a JEOL 8530F Plus. The light elements, C, O, and F, were analyzed at 7 kV, 20 nA beam current, and 5 μm beam diameter. Time dependent intensity corrections were turned on due to the beam sensitive nature of the material. The primary standards (BaF_2 , CePO_4 , LaPO_4 , PrPO_4 , SmPO_4 , NdPO_4 , and CaCO_3) and samples were coated with ~ 5 nm iridium at the same time in a Leica ACE600. Corrections for REE peak interferences were used. The results of the analysis show an intergrowth of compositions that fall between endmember bastnaesite and $\text{REE}(\text{CO}_3)(\text{F}_{0.5}\text{OH}_{0.5})$. Minor amounts of Ca, up to 0.4 wt.%, are also present. To date, endmember hydroxylbastnaesite has not been observed.

Another method of observation to determine the distribution of bastnaesite-hydroxylbastnaesite is to acquire simultaneous fluorine x-ray intensity maps and a hyperspectral cathodoluminescence dataset. These analyses were collected with the xCLent system the JEOL 8530F Plus operated at 7kV, 30 nA, and 30 msec dwell. Fluorine was acquired on three spectrometers and Ca was acquired on two spectrometers and later added together. Peak fitting of the sum CL spectra from the bastnaesite areas was conducted followed by generation of peak intensity maps. Figure 1 reveals the fluorine concentration is correlated to the intensity of the 1.3955 eV peak. The detail in the CL peak intensity map is superior to that shown in the fluorine map. Work is under way to create a regression line for this correlation as well as investigate possible peak shifts related composition.

Table 1. Bastnaesite F(c) μ values at various accelerating voltages. Operating conditions should be optimized to increase F(c) μ for light elements. The Sm L α overvoltage (E_o/E_c) is given at each accelerating voltage using an edge energy of 6.716 keV.

Element	15kV	10kV	7kV
Ce K α F(c) μ	0.9470	0.9770	0.9915
F K α F(c) μ	0.2711	0.4645	0.6362
O K α F(c) μ	0.3206	0.5198	0.6825
C K α F(c) μ	0.2230	0.4033	0.5783
Sm L α (E _o /E _c)	2.23	1.489	1.042

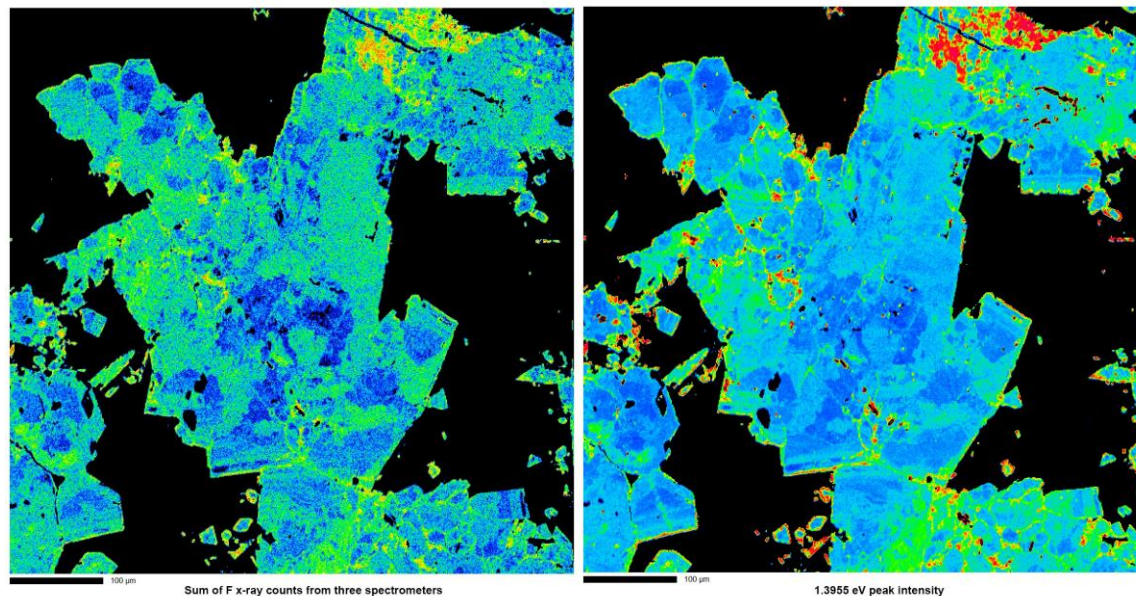


Figure 1. The fluorine x-ray intensity map (left) and 1.3955 eV peak intensity map (right) are correlated with the CL map showing more detail than the x-ray intensity map. Greens are higher relative intensity than blue areas.

References

Macrae, C., Wilson, N. & Torpy, A. (2013). Hyperspectral cathodoluminescence. *Mineralogy and Petrology* 107(3), 429-440.