Approach for Quantifying Rare Earth Elements at Low keV

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The challenges of analyzing bastnaesite ($REECO_3F$) and hydroxylbastnaesite ($REECO_3OH$) include beam sensitivity, quantification of light elements in a heavy element matrix, the presence of elements that cannot be analyzed by electron probe microanalysis (H), and the use of x-ray lines whose physical constants are not well known. To overcome some of these challenges, Ca, La, Ce, Pr, Nd, and Sm were analyzed at 15 keV accelerating voltage and the light elements (C, O, F) were analyzed at 7 keV accelerating voltage [1]. This approach is ideal for samples that are homogeneous within the volume analyzed. However, for the bastnaesite of interest, this solution is unsatisfactory because backscattered electron imaging reveals chemical variations at scales of less than 1 µm (fig. 1). Monte Carlo simulations and wavescans of the rare earth element (REE) M family of x-rays were evaluated to determine the best analytical approach.

Monte Carlo simulations using Casino v2.42 [2] were run on a substrate of $CeCO_3F$ with a density of 5.00 g/cm3 at 15 keV and 7 keV accelerating voltage. Depth distribution curves, $\varphi(\rho z)$, reveal x-ray generation at 15 keV for the Ce L shell x-rays approaches 1.0 µm whereas the depth of Ce M shell x-ray generation at 7 keV is less than 0.4 µm (fig. 1). Similarly, the K shell x-ray generation depth for C, O, and F at 7 keV is also less than 0.4 µm (fig. 1). These simulations demonstrate an accelerating voltage of 7 keV or less and use of the REE M x-rays is necessary to acquire chemical information from the same volume of material for the light and heavy elements. Bastnaesite contains all REEs and therefore one must consider the energy of the highest x-ray line of interest, namely the Lu Mγ at 1.83 keV, to achieve an overvoltage (E_o/E_c) greater than 2. Bastnaesite is also an insulator and requires a conductive coating, therefore 7 keV was used to avoid contributions of the coating material to the analysis given the above constraints.

The USNM REE phosphate standards, Edinburgh REE glasses, CeO_2, LaB_6, and the metals of Sm, Dy, Gd, Er, and Yb were selected to evaluate the peak overlaps of the M family x-ray lines. The materials were coated with ~ 5nm iridium with a Leica ACE600 prior to analysis. Full spectrometer wavescans were collected at 7 keV accelerating voltage, 50 nA beam current, and 20 µm beam diameter on a JEOL 8530F Plus using TAP and TAPL crystals. The step size was 0.109 mm along the length of the spectrometer with a dwell of 3 seconds at each step. Mα and Mβ lines are broad and not individually resolved for the light REE but become more separated and sharper with increasing atomic number (fig. 2A). Mγ and Mζ lines for each REE are also present across the spectrometer range further complicating peak interference corrections (fig. 2A). The peak positions and overall shape for the Ce Mα and Mβ lines vary with the coordination of the element (fig. 2B). Significant shifts in position and shape were not observed when comparing the Ce Mγ peaks of CeO_2 and $CePO_4$ (fig. 2B). Similar results were seen when comparing the available REE metal to the phosphate (Sm, Dy, Gd, Er, Yb). These wavescans indicate the use of the Mζ or Mγ lines if matrix matched standards are not available.

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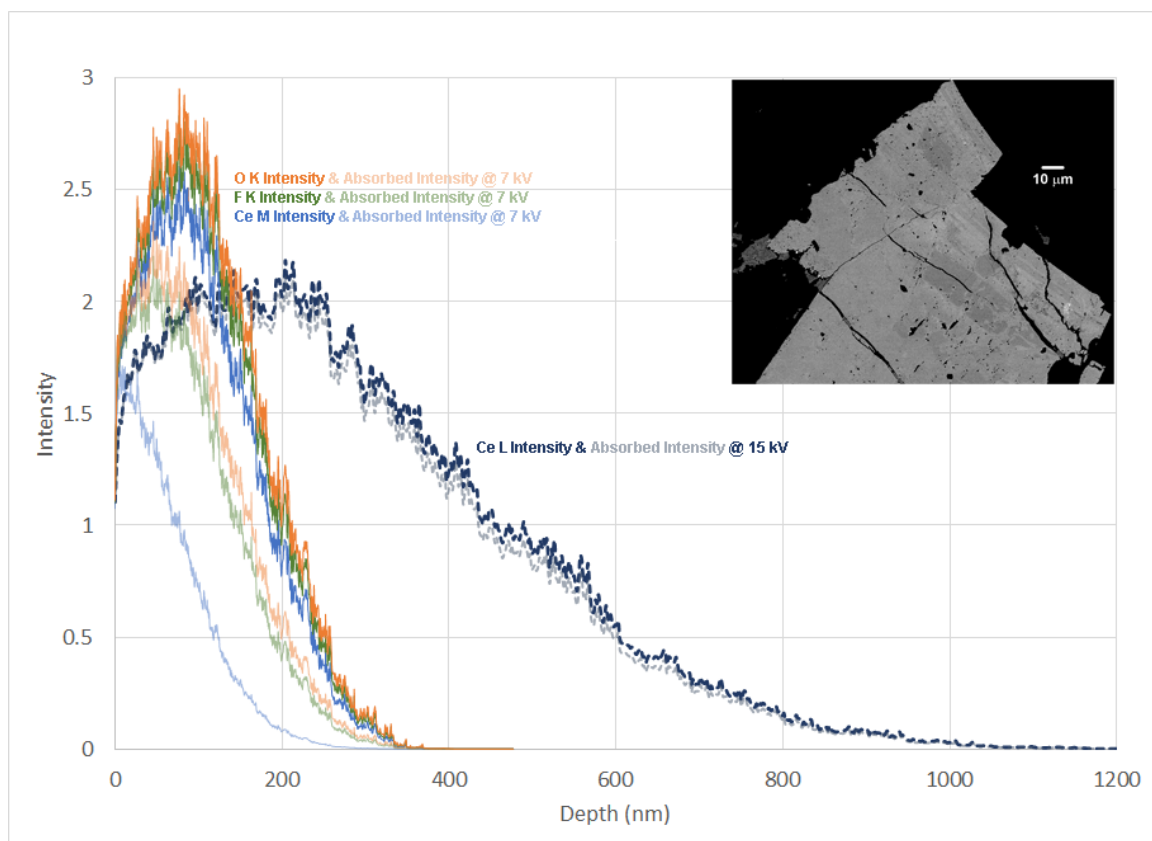
Figure 1. Depth distribution curves, φ(ρz), for Ce, F, and O at 7 keV and Ce at 15 keV. A backscattered electron image of bastnaesite shows the fine spatial variation of the composition.
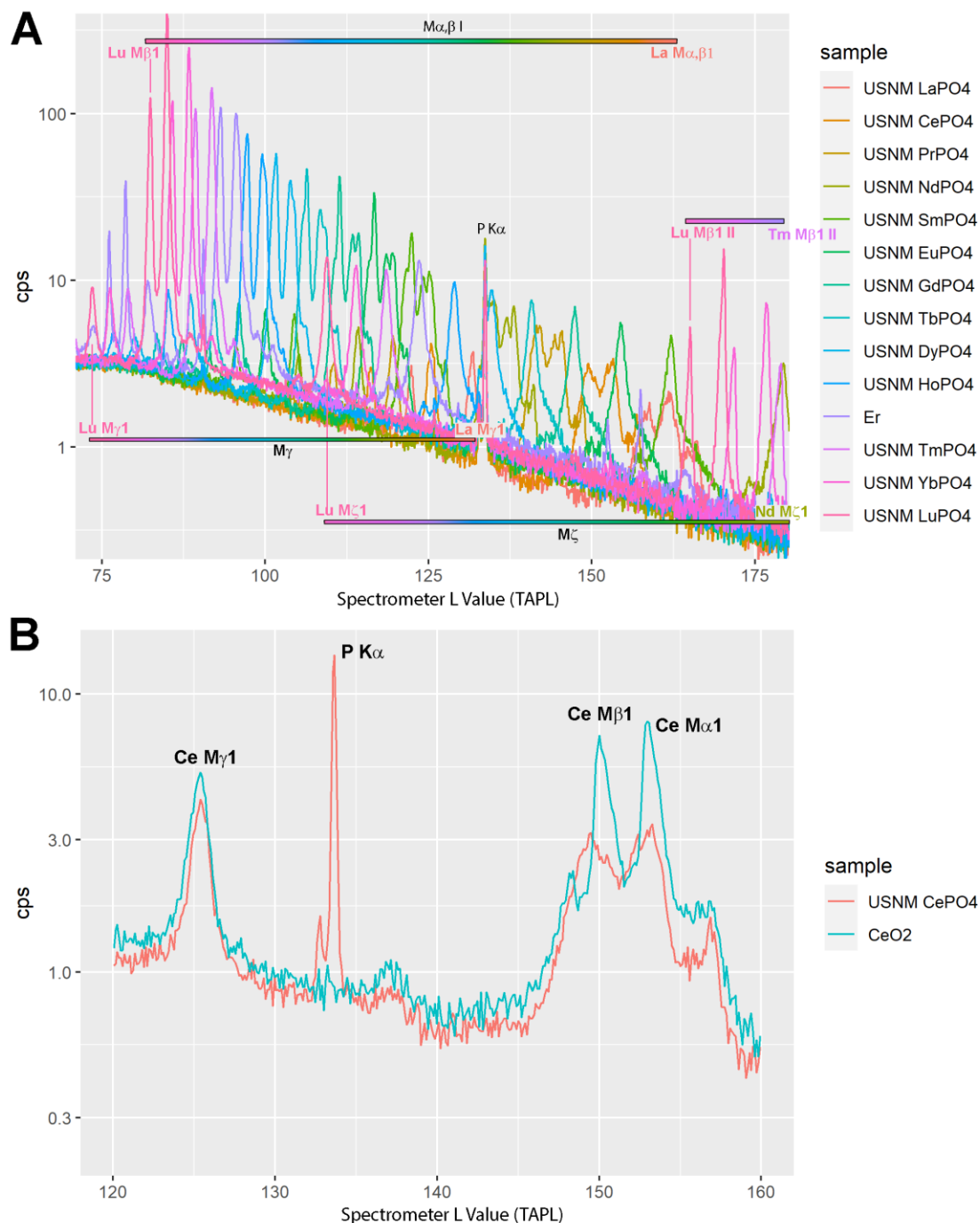
Figure 2. A. Wavescans on the USNM REE phosphates demonstrate multiple peak overlaps due to Mα, Mβ, Mγ, and Mζ x-ray lines. B. Spectrometer scans across the Mα, Mβ, and Mγ peaks in CePO4 and CeO2 demonstrate clear changes in peak position and shape for the Mα and Mβ x-ray lines but no resolvable change in the Mγ x-ray line.

References
[1] H. Lowers and G. Swayze, Microscopy and Microanalysis 26 (S2) (2020), p. 1884. doi:10.1017/S1431927620019704
[2] Drouin. D. et al., Scanning, 29 (2007), p. 92. doi:10.1002/sca.20000