

## A spectral library for Smithsonian rare-earth element phosphate standards using laser-induced fluorescence

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Innovation in raw material exploration relies on efficient and non-invasive technologies. Spectroscopy based methods have proven great potential to deliver instant and spatially continuous information on the composition of an investigated surface. Several studies successfully applied laser-induced fluorescence (LIF) for rare-earth element (REE) identification in natural rocks. However, the diagnostic assignment of detected emission lines remains a complex task, because of the highly variable composition of natural rocks. It needs a transfer of the profound knowledge from the field of applied physics and synthetic materials to the natural rock material under investigation. The evaluation of measured spectra and robust assignment of REEs requires reference data, yet usually based on tables of published emission lines, while data of complete reference spectra are not available. We present a library of reference spectra for all luminescent rare-earth elements using the Smithsonian rare-earth phosphate standards for electron microprobe analysis. We employ laser-induced fluorescence at three commonly used laser wavelengths (325 nm, 442 nm, 532 nm) to acquire reference spectra for REE phosphate minerals in the

visible to near-infrared spectral range (350 – 1080 nm). Excitation at all three laser wavelengths yielded spectra with distinct REE-related emission lines for EuPO4, TbPO4, DyPO4 and YbPO4. Lower energy laser excitation at 442 nm showed successful especially for suppressing non-REE-related broadband defect emission. Resulting REE-reference spectra include those from PrPO4, SmPO4 and ErPO4. For NdPO4 and HoPO4 most efficient excitation was achieved with 532 nm. The diagnostic emission lines of GdPO4 lie outside the detection range and none of the three laser wavelengths was appropriate for TmPO4 excitation.

Our results demonstrate the suitability of LIF for REE detection and especially the possibility of selective element excitation. Our reference spectra provide the full spectral information at high resolution (0.13nm) as a basis for an improved evaluation of REE-bearing natural rocks allowing for data analysis of emission line positions, emission line intensity ratios and splitting into emission line sub-levels. The spectral library data support the use of LIF for REE analysis in natural samples and its application in raw material exploration.