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## Laser-induced fluorescence (LiF) spectroscopy for detecting REE cross-contaminations in the Smithsonian rare-earth element phosphate standards

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Spectroscopy based methods have proven great potential in efficient, non-invasive material characterization. Recording the material-specific optical properties delivers instant information on the composition of an investigated sample surface without chemical sample preparation and may be operated in spatially continuous mode. In minerals, laser-induced fluorescence (LiF) provides a promising method to address the challenges of robust and efficient rare-earth element (REE) detection. The method is based on the characteristic electronic transitions within the incompletely filled f-shell of REE. The corresponding emission shows distinct features (spectral fingerprints) in the visible and near-infrared (VNIR) range of the electromagnetic spectrum that allow to distinguish between individual REE and mineral matrix luminescence. Only REE with completely filled or empty f-orbitals miss characteristic luminescence (i.e. Y<sup>3+</sup>, Sc<sup>3+</sup>, La<sup>3+</sup>, Lu<sup>3+</sup>), while the emissions of Gd<sup>3+</sup> lie at lower wavelengths than the observed VNIR range.

We test the suitability of LiF in applications of REE identification by (1) building a spectral LiF library from a sample set of luminescent REE phosphates and (2) evaluating observed emissions in samples of non-luminescent REE, and (3) comparing indicated REE cross-contamination to results of neutron activation analysis (NAA). As samples, we use the Smithsonian REE phosphate standards for electron microprobe analysis. The synthetic material delivers a simple, well-defined host composition, is well investigated and NAA results are available on additional trace REE concentration resulting from the material production procedure. The trace REE concentrations are at the order of 10<sup>-4</sup> given in mass fraction. We employ laser-induced fluorescence at three commonly used laser wavelengths (325 nm, 442 nm, 532 nm) to acquire our REE sample spectra and record LiF signals in the visible to near-infrared spectral range (350 – 1080 nm).

The comparison of spectra from non-luminescent REE phosphates shows clear similarities in emission patterns that can be assigned to specific luminescent REE using the spectral LiF library. Our results demonstrate the suitability of LiF for REE detection along with the benefits of selective element excitation and highlight the high sensitivity of the LiF method. The detected emissions in the non-luminescent samples indicate a detection limit below mass fractions of 10<sup>-4</sup>, when

compared to NAA results, but also show that not all REE are equally responsive. Here, the co-existence of REE with complex interactions such as charge transfer contributes to the observed emission pattern. Adding to the spectral LiF library data and expanding investigations to further mineral hosts will facilitate new applications of LIF for REE analysis in natural samples and its implementation in raw material exploration.