

Supplementary Material 1

The authors would like to emphasize, that the below-described methodology was tailored specifically for the Cameca SXFiveFE at University of Warsaw, Faculty of Geology (Poland). Each instrument has a unique set of diffracting crystals, which may differ in quality and, thus, analytical capabilities. The authors warn against any misguided application of the presented parameters to other EPMA instruments.

1. Detailed Explanation of the Selected Analytical Parameters

1.1. Fluorine Measurement

As indicated in Table S1, fluorine was measured on the LTAP crystal. It has approximately three times more counts than the TAP crystal. The alternatives are WDS LPC0 and EDS, however, these have also several shortcomings. Both LPC0 and EDS have low spectral resolution, which is sufficient for relatively F-rich minerals (e.g. apatite), but quite poor for Fe-REE-rich phases. Fe $L\alpha$ and Ce $M\zeta$ peak overlap with F $K\alpha$, which, with proper peak-overlap correction would not be a challenge. However, a first order M lines of REEs cover completely the background position for F $K\alpha$ from the left side of the spectrum (Figure 1) and, due to non-linear background continuum, the background cannot be correctly estimated under the peak position (with either linear or exponential background fitting model). It probably could be modelled with the Mean Atomic Number (MAN) background calibration method [3], however, the Cameca's PeakSight (v6.4) software, which we had used for this work still lacks this novel method. The (L)TAP crystal has enough of space for correct background measurements from both sides from the F $K\alpha$ peak (Figure 2).

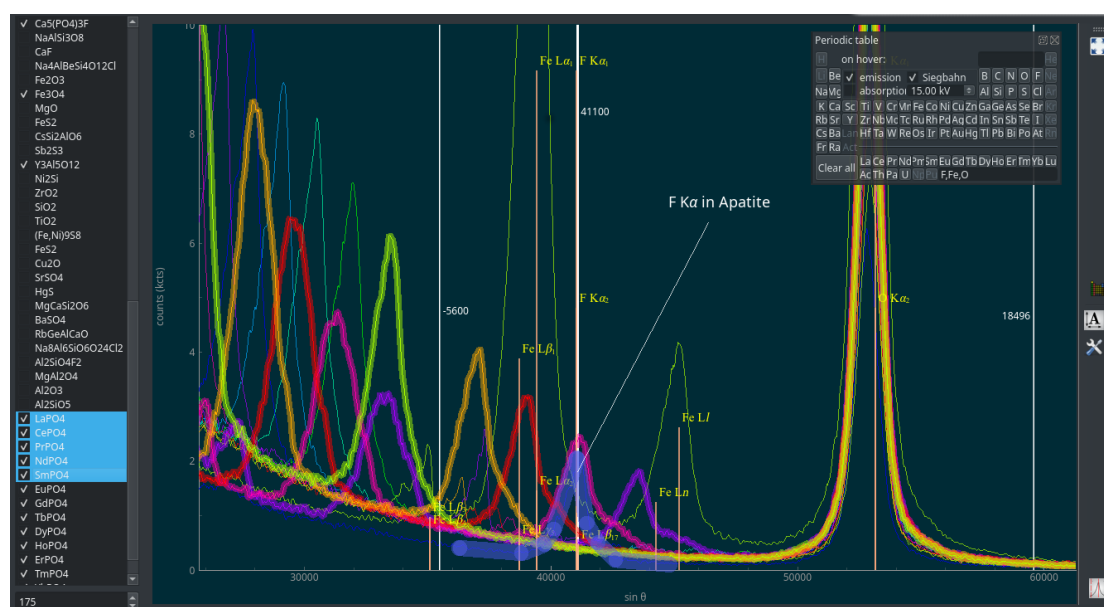


Figure 1. F $K\alpha$ situation with Fe L-lines and REE M lines on spectra acquired with LPC0 diffracting crystal. Note that left position at -5600 $\sin(\theta)$ 10k units at given large PC0 crystal is not free from overlaps, however small/normal PC0 crystal (depending from how tight the peaks can get) could be overlap free.

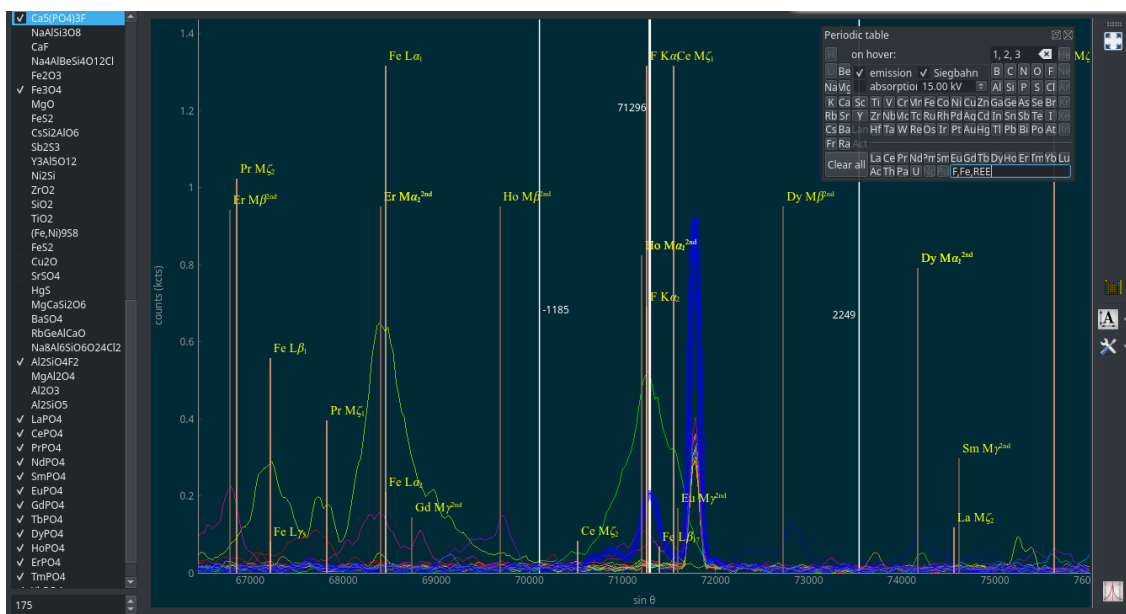


Figure 2: F K α situation with Fe L-lines and REE M lines on spectra acquired with TAP diffracting crystal. The broad green peak at F K α position is from synthetically pure topaz-F. Right to F K α there is higher order phosphorus Ka peak (the tallest peak). Some tiny phosphorus K-family satellite lines are also present close and over F K α , but they are very tiny and can be neglected here for this work.

The use of fluorapatite as a standard is not the best choice for F measurements. Such minerals as topaz or fluorite, have higher concentrations of F, however, the F K α peaks of these minerals show an energetic spread on the high-resolution region of TAP, where F K α from fluorapatite does not.

These problems were spotted thanks to the software being developed by the EPMA operator [1]. One of software functions allows for very rapid inspection of peak overlaps using the full WDS scans of standard materials for every element. This gives a complete overlook of situation and thus none of relevant (for the set of elements) peak-overlap corrections can be missed out from the analytical setup. All figures presented in this Supplementary Material are the screenshots of this software demonstrating the discussed overlap situations (Figures 1-3).

The F calibration measurements on the standard fluorapatite were performed at 10 nA current, 10 μ m beam size and using “time-0-intercept” function. Calibration measurements for other elements were made at 20 or 10 nA current with long counting times and at least 25 measurement points. The most critical factor with large diffracting crystals is the detectors dead time. SXFiveFE laboratory maintains a set of calibrations for different detector saturation rates (same calibration substance measured at different currents) and chooses those according to observed detector saturation rates for the measured line in the unknow substance. The internal dead time correction works properly up to about 10000 counts per second, but with more intensive measurements, different calibrations are needed. In case of a 50nA beam, proportional counter is still in the linear region even for most intensive lines and the counter dead time is correctly applied by internal EPMA corrections. The differing beam currents to each of the elements were not applied (e.g. 10 nA for F, P, Si, La, Ce and 50 nA for the rest), as single column/analytical condition is dictated by the SXFiveFE design. Changing the beam current (from 10 to 50 nA back and forth) introduces instabilities, as electron column of SXFiveFE has only a single condenser lens for setting the beam current – it needs to do much larger steps in power levelling than lenses working in pairs (the thermal equilibration of the lens requires a considerably longer time). Also, current drift cannot be corrected with beam regulator, as for this FEG-equipped (Field emission gun)

machine, the beam density is too high for beam regulator to work correctly at higher currents, and is not recommended to be used above 20 nA. The FEG on this machine is well maintained (monitored and adapted for its aging) and non-regulated beam drift and noise is below 0.5 % of beam current value for 24 h, or below 0.2 % for 10 minutes (at least twice better than vendor-specified limits) for all available current ranges (2 to 800 nA). For these reasons, all elements in allanite were measured at the same analytical conditions.

1.2. Chosen X-ray Lines for Nd

The usual choice of the X-ray line for Nd is $L\beta_1$, whereas in this study we used $L\alpha$. There is a minor overlap of Nd $L\alpha$ with one of the Ce lines – $L\beta_1$. However, it is not a major problem and can be easily resolved with a well-known overlap correction procedure [2]. The Nd $L\beta_1$ line, on the other hand, although may appear as a better choice due to absence of any overlaps (Figure 3), has two significant drawbacks. One - there is little space for background measurements (especially when it is measured on LPET), and two – there is an interference with an absorption edge of the Ce L3 shell, directly at the peak centre position. This, in turn, renders the matrix correction completely unpredictable if the analyzed mineral contains Ce. The similar situation can be seen with Pr $L\beta_1$ where the peak centre is very close to the La L3 shell absorption edge. The choice of the correct X-ray line for Nd (as well as the remaining REE) is supported by no visible anomalies in chondrite-normalized REE patterns (Figure 4 in the main text). In contrast to the spot measurements, both Nd $L\alpha$ and $L\beta_1$ lines can be used for general element distribution mappings.

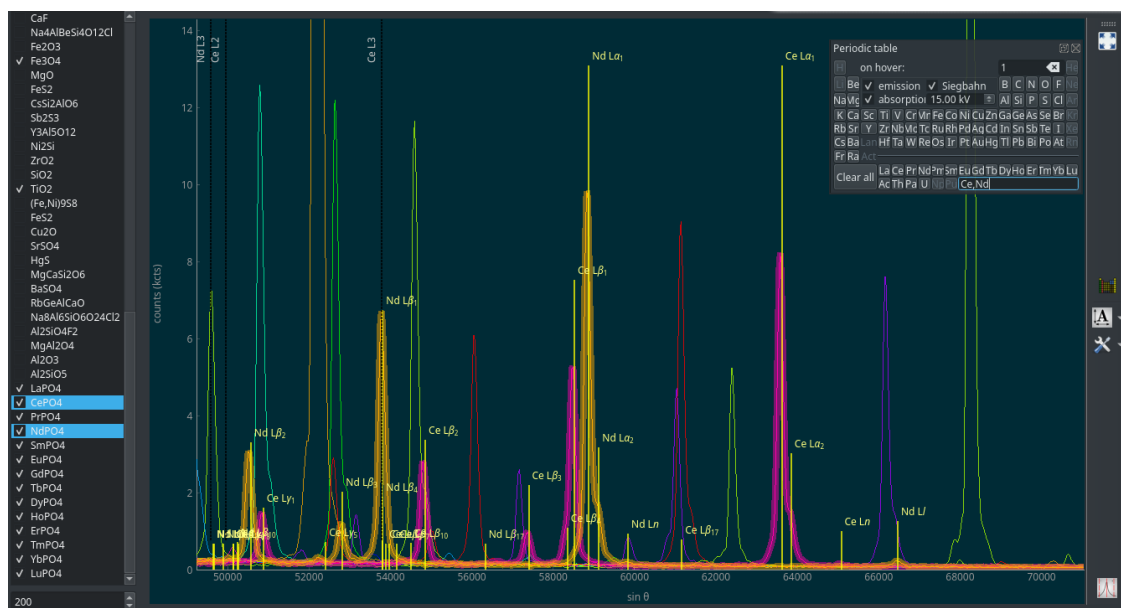


Figure 3. LREE spectral region acquired with LLIF crystal. Dark dashed lines dropped from the top mark absorption edges.

References

1. Jokubauskas, P. New software to improve the baseline accuracy of elemental composition measurements on SXFiveFE at University of Warsaw. *Mineralogia-Special Papers* **2019**, 49, 47.
2. Donovan, J.J.; Snyder, D.A.; Rivers, M.L. An Improved Interference Correction for Trace Element Analysis. *Microbeam Anal.* **1993**, 2, 23-28.

3. Donovan, J.J.; Singer, J.W.; Armstrong, J.T. A new EPMA method for fast trace element analysis in simple matrices. *Am. Mineral.* **2016**, 101, 1839–1853.