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Using Calibration Curves to Quantify Fe with the Soft Lα and Lβ X-ray Lines

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The electron probe microanalysis (EPMA) field has seen many important advances in the last decade. One of these novelties has been the introduction of the field emission gun (FEG), allowing bright and narrow electron beams and increased imaging spatial resolution. To better take advantage of these improvements for analytical spatial resolution, it is also necessary to reduce the beam energy, typically to 8 kV or lower. Thus, the combination of the reduced beam size and the reduced electron interaction volume allows the quantification of sub-micrometer features. However, by reducing the accelerating voltage, some of the main X-ray lines, traditionally used for quantification purpose, cannot be excited. For example, this is the case of the transition elements for which the main Kα X-ray line cannot be excited for accelerating voltages below 5-8 kV (the same situation can be found for some of the rare earth elements where the Lα X-ray line cannot be excited at such low accelerating voltages). Thus, quantifying these transition elements requires the use of X-ray lines that are in the domain of the soft X-rays, such as the Lα X-ray line.

Another great advancement that emerged in the EPMA realm was the development and commercialization of the Soft X-ray Emission Spectrometer (SXES). This detector consists of a variable spacing diffraction grating and a Peltier-cooled CCD camera [1] which allows the acquisition of a whole X-ray spectrum, similar to the energy-dispersive spectrometer, but in the soft X-ray energy range. The SXES combines an energy resolution comparable to the wavelength-dispersive spectrometers (WDS) and a detection efficiency close to the energy-dispersive spectrometers (EDS). The typical detection energy range varies between few tenths of eV to few keV. For example, the JEOL JS2000 extended range grating can detect X-rays in the range from 240 eV to 2800 eV and has a spectral resolution of 4.5 eV for the Mg Kα X-ray line. This grating can record the main characteristic X-rays of elements up to Cl (for the first order of diffraction). For heavier elements whose K lines are generally outside of the detected energy range, higher order of diffraction or non-conventional X-ray lines (i.e., soft X-ray lines) must be used, such as the Lα line for the transition elements.

For both these advances (the SXES and the increased analytical spatial resolution with the FEG), the use of the soft X-ray lines for quantification purpose is required. However, there is the complication that the behavior of the characteristic Lα and Lβ X-ray lines of the first-row transition metals is not fully understood. This is due to bonding effects that are different from one material to another and thus are likely to change the fundamental atomic parameters (binding energy, transition probabilities, ionization cross sections, mass absorption coefficients, ...) which in turn are modifying the X-ray line properties (shape, intensity, maximum position, ...). As an example, for pyrite and pyrrhotite, which have a "similar" matrix constitution, an increase of the Fe content should translate into an increase of the Fe Lα X-ray intensity. However, as shown in Figure 1, the opposite behavior occurs: pyrite, which has an iron content of 46.7 wt%, has a much stronger Fe Lα X-ray intensity than pyrrhotite, which has a higher iron content of 60.5 wt%.

We describe here a method to measure the iron concentration in Fe-bearing mineral families using simple calibration curves. The calibration curves were acquired by measuring the Fe Lα and Lβ X-ray lines on standards of well-known compositions and by calculating the total X-ray intensity corresponding the area

of these lines. For each Fe-bearing mineral families – in the present work: Fe-silicides, Fe-sulfides, olivines, Fe-garnets and chromites – area k-ratios were then obtained and plotted as a function of the Fe composition. It has been shown [2,3] that these calibration curves are independent of the spectrometers and can be used on any instrument equipped with WDS, EDS and SXES detectors without having to "rescale" them, as long as the accelerating voltage and the takeoff angle are the same as the ones used to acquire the curves, i.e., 7 kV and 40°, respectively. It is worth noting that because the Fe Lα and Lβ soft X-rays are subject to self-absorption (the electron ionization edges are within the extent of the X-ray lines), the traditional k-ratio method, consisting of measuring the maximum X-ray intensity and off peak channels to remove the continuum, is not spectrometer independent [2,3], but can still be used to derive spectrometer-dependent calibration curves.

The method was successfully applied to the quantitative analysis of Fe-bearing materials using different microprobe instruments and using different types of detectors: SXES, WDS and EDS. For each mineral family, the experimental data acquired with the different spectrometers are in very good agreement with each other, in absolute value. The area k-ratios generally vary smoothly as a function of the Fe content, letting each set of area k-ratios to be fitted by a polynomial with a good coefficient of determination. However, one exception arises: with the above-mentioned case of pyrite vs pyrrhotite (and also troilite), the Fe Lα+Lβ area k-ratios have the same values (Figure 2). In this particular situation, instead of summing the area of the Fe Lα and Fe Lβ X-ray lines to derive the calibration curve, independent Fe Lα and Fe Lβ area k-ratios were calculated and then averaged together. The derived calibration curves were utilized to measure the Fe content in unknown Fe-silicide, olivine, garnet and chromite samples at 7 kV with good accuracy. This method is also showing promising results on other mineral families and other transition elements, such as Cr [4].

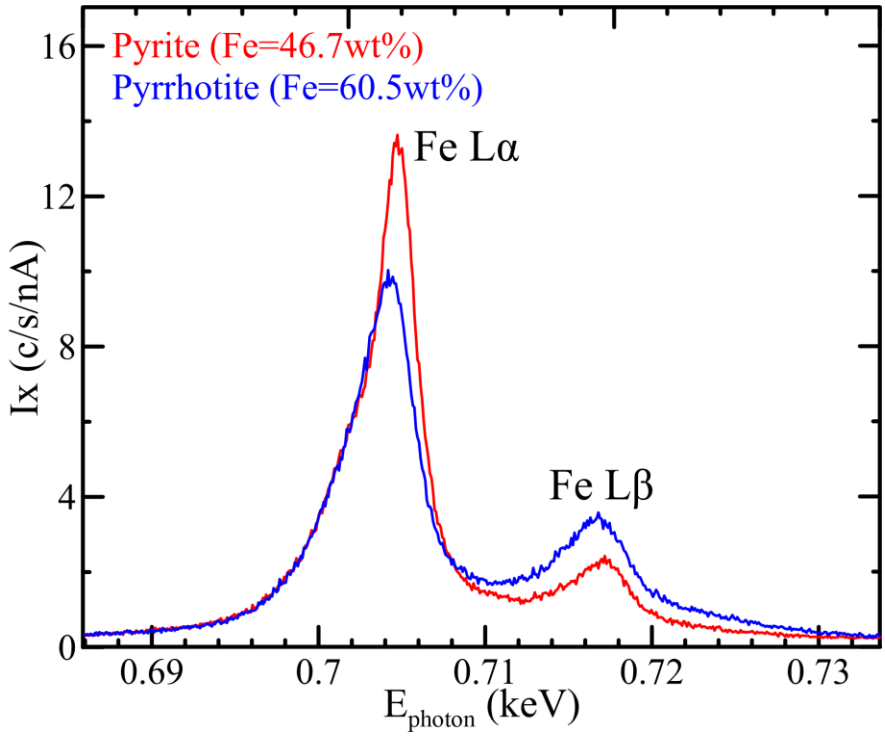

Figure 1. Figure 1: Fe Lα and Lβ X-ray lines measured on pyrite and pyrrhotite at 7 kV using a LTAP monochromator crystal.

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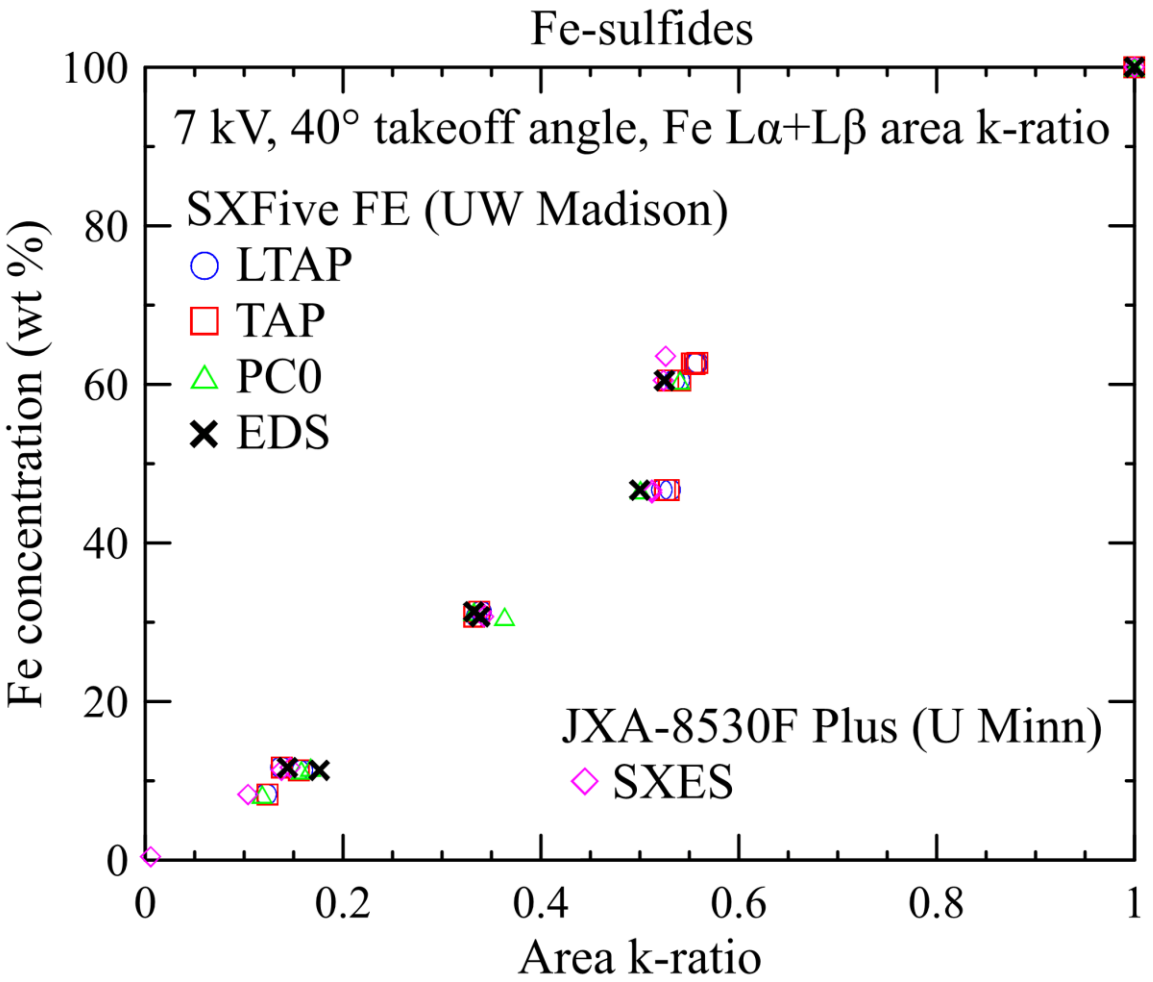

Figure 2. Figure 2: Area k-ratios of the Fe Lα-Lβ X-ray line measured on Fe-sulfides using different microprobes and spectrometers. The k-ratios are relative to pure Fe.

References

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