Measuring iron speciation with the electron microprobe and a commercial soft X-ray emission spectrometer

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Résumé

In metamorphic mineral assemblages, iron may show mixed valency between divalent and trivalent form. Direct, in-situ measurement of the proportion of trivalent iron Fe3+ / Fetotal is of interest because i) it is a proxy to oxygen fugacity during crystallization, ii) it has thermobarometric implications, and iii) it is necessary for correct estimation of formula units, especially in hydrous silicates with possibly vacant crystal sites such as phyllosilicates. Commercial diffraction gratings coupled to X-ray CCD cameras mounted on electron microprobes allow measuring emission lines in the soft X-ray region at micro-scale, directly over petrologic thin section. This includes the Lα and Lβ emission lines of iron, located near 720 eV. Previous studies have shown that these emission lines evolve with the ratio Fe3+ / Fetotal due to self-absorption effects.

Using Jeol's "SX-ES" apparatus, featuring an approximate 1 eV spectral resolution around 720 eV, we investigate the practical feasibility of quantifying Fe3+ / Fetotal in silicates routinely. A set of silicates with known iron content (_˜1 to _˜50 wt. %) and speciation (Fe3+ / Fetotal = 0 to 100 %) is used as external standards to find the best methodology. The silicate set is of synthetic and natural origin and includes three dozen crystals from twelve mineral groups where Fe3+ / Fetotal is known from stoichiometry or measured with XANES at the K level of iron.
A shift in Lα and Lβ emission lines of iron due to self-absorption is easily observed and allows distinguishing between ferrous and ferric minerals at similar Fe content, at least for concentrations above _˜3 wt. % Fetotal. Quantification is more difficult and requires modelling combining fitting emission lines and using ratios of spectral features such as intensity at fixed energies and/or energy at maximum intensity. The additional difficulties arise from low spectral resolution (in the range of the peak shift between ferrous and ferric minerals) and low signal/noise ratio in minerals with Fetotal < _˜5 wt. %. The approach shows excellent applicability to garnet with Fe3+ / Fetotal reproduced within uncertainties. Application to other silicates is in progress and differs from garnet where Fe2+ is dodecahedral.

Mots-Clés: iron speciation, electron microprobe, soft X rays

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