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Soft X-ray Emission spectrometer on electron microprobe: towards the in-situ estimation of $Fe^{3+}/\sum Fe$ in silicates minerals and glasses

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Oxygen fugacity (fO_2), a measure of oxygen availability in a system – often called redox potential – is fundamental to Earth's evolution, influencing core formation, atmospheric chemistry, and ore deposit genesis. Iron, the most abundant multivalent element in magmas, is a proxy for magmas' fO_2. However, quantifying $Fe^{3+}/\sum Fe$ is hindered by costly, inaccessible, or destructive methods [1]. Bulk techniques like Mössbauer spectroscopy lack spatial resolution, preventing tracking of fO_2 evolution during magma ascent.

The University of Geneva has recently acquired a Soft X-ray Emission Spectroscopy (SXES) detector, attached to an electron microprobe, which provides in-situ full-spectrum parallel acquisition (~100 eV–2300 eV) with high signal-to-noise ratio, improving efficiency by reducing time per energy acquisition, and by minimizing sample damage. This method is particularly advantageous for analyzing minerals with low Fe concentrations or low self-absorption, which previously required prolonged exposure to achieve sufficient signal quality.

We present in situ $Fe^{3+}/\sum Fe$ analyzes of redox-sensitive silicates (clinopyroxene and amphibole) and volcanic glasses (natural and experimental) previously characterized by bulk Mössbauer spectroscopy and/or XANES [2-6]. Unlike the classic flank method relying on correlating Fe-Lb/Fe-La intensity ratio from two acceleration voltages with the ferric iron, we find that multiple SXES variables such as the area or the FWHM of the Fe-La peak measured at a single acceleration voltage (i.e., 7 keV) correlate strongly with the $Fe^{3+}/\sum Fe$ measured by bulk Mössbauer. Caveats due to bonding effects such as non-linearity between the iron content, soft X-ray line properties and self-absorption effect will be discussed.

Ultimately, this method will allow the characterization of the redox evolution of magmatic systems, adding a new dimension to our understanding of magmatic processes leading to volcanic eruptions, and the factors controlling the formation of ore deposits.

References

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