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Quantitative nanoscale imaging of Fe and Mn redox in silicates by scanning transmission X-ray microscopy at the Fe and Mn $L_{2,3}$-edges.

FRANCK BOURDELLE[1], CYRIL DURAND[2], EMILY LLORET[2], ERWAN NICOLAS PAINEAU[3] AND LAURA AIRAGHI[4]

[1]CY Cergy Paris Université - GEC
[2]Université de Lille - LGCgE
[3]Université Paris-Saclay - LPS
[4]Université d'Orléans - ISTO

Presenting Author: franck.bourdelle@cyu.fr

The study of the biogeochemical cycling of Fe and Mn requires an understanding of the formation and transformation of Fe,Mn-bearing minerals, in particular Fe,Mn-silicates. The quantification of each Fe and Mn oxidation state in Fe and/or Mn-silicates (Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}, Mn^{4+}) is of primary importance to constrain this formation/transformation and the conditions of the medium (pressure-temperature-chemistry/redox). Different techniques have been considered for this purpose, including electron microprobe (EMP), X-ray photoelectron spectroscopy (XPS) or X-ray absorption near edge structure (XANES) spectroscopy at the K-edge.

However, Fe and Mn-bearing minerals often exhibit such small scale intracristalline heterogeneities to require investigations at the nanoscale and none of the methods cited above provide a nanometer-scale spatial resolution. These analytical obstacles often lead to approximate the charge of these metals in natural minerals. In the last decades, several (van Aken and Liebscher 2002) have proposed electron energy-loss spectroscopy (EELS) in transmission electron microscopy (TEM) as an efficient technique for quantifying the element oxidation state at a submicrometric scale. Nevertheless, this approach sometimes induces electron-beam damage such as metal reduction in fragile minerals like phyllosilicates (de Groot et al. 2010).

The XANES spectroscopy at the $L_{2,3}$-edges appears as a powerful alternative (Bourdelle et al. 2013, 2021). First, the incident X-ray energies are low at the Fe and Mn $L_{2,3}$-edges (630-730 eV) allowing high spatial resolution (< 30 nm at existing synchrotron facilities). Second, the X-ray incident beam is less destructive for samples than the TEM-EELS method. On the base of XANES analysis obtained by Scanning Transmission X-ray Microscopy (STXM), we present a new calibration that allow quantifying the Fe and Mn valence in submicrometric silicate particles. A protocol is proposed to construct quantitative maps of Fe and Mn valence with a spatial resolution of 20 nm. This approach was successfully applied on several case studies containing a mixing of Fe,Mn oxidation states, like Fe,Mn-phyllosilicates.

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