

Soft X-ray spectromicroscopy study of chemical heterogeneities in iron precipitates formed at or near bacterial cells

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Iron oxides formed in neutral-pH aqueous environments are frequently associated with bacteria, indicating the importance of microorganisms in geochemical cycling of iron species (Fortin and Beveridge, 2000). In this study, soft x-ray spectromicroscopy was used to investigate chemical heterogeneities of iron-containing precipitates formed at or near *Shewanella putrefaciens* (CN32) cell surfaces. Spectromicroscopic measurements at the iron L₃- and carbon K- edges with 30 nm spatial resolution provide direct evidence for chemical heterogeneities in biologically induced iron oxide precipitates both temporally and spatially. For example, adsorption or nucleation of Fe(III)- containing nanoparticles (e.g., ferrihydrite) was dominantly observed on *S. putrefaciens* cell surfaces at early stages (day 4) of batch culture experiments, whereas extensive coverage of the *S. putrefaciens* cells by Fe(II)- containing minerals (e.g., siderite (FeCO₃)) becomes more dominant in later culture stages (day 8, see Fig. 1). These direct observations of temporal and spatial heterogeneities of iron oxide precipitates in bacterial cell surfaces strongly support previous suggestion by Zachara et al. (2002) on the importance of local micro-environments in determining the fate of secondary iron minerals.

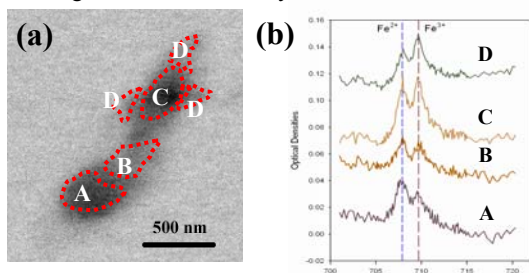


Fig. 1. (a) STXM images of single *S. putrefaciens* cell after 8 days in the presence of ferrihydrite coated quartz. (b) Fe L₃-edge NEXAFS spectra collected from different areas of bacterial cell shown in (a)

References

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Quantitative mapping of the ferrous to ferric ratio on a sub-micron scale using synchrotron spectromicroscopy

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Fundamental geological variables, including temperature, pressure and oxygen fugacity, may be estimated using the valence ratio of heterovalent transition metals, obtained via electron microprobe analysis or Mössbauer spectroscopy. In many rocks, meteorites and soils, however, the mineral inhomogeneities are too small to be analyzed with these traditional techniques. Recent transmission electron microscopes equipped with electron energy loss spectrometry (TEM-EELS) can determine the valence ratio in areas as small as 20 nm, and, separately, produce non-quantitative valence distribution maps. However, fully quantitative valence mapping on a sub-micron scale is not yet possible with TEM.

We developed a new method that couples x-ray absorption near edge structure (XANES) spectroscopy with high-resolution x-ray photoelectron emission microscopy (X-PEEM) [1]. Using previously established calculation methods [2,3], we produced high resolution chemical and elemental distribution maps and fully quantitative maps of the Fe(III)/ΣFe ratio from ilmenite containing hematite exsolution lamellae. This new modality is not limited to iron, and can also be applied to a variety of transition metal systems. X-PEEM analysis induces limited or no radiation damage to minerals, and does not require invasive or destructive sample preparations. This approach, therefore, is well suited for valuable and/or unique samples.

References

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