# Microscopic imaging of reduced zones on surfaces

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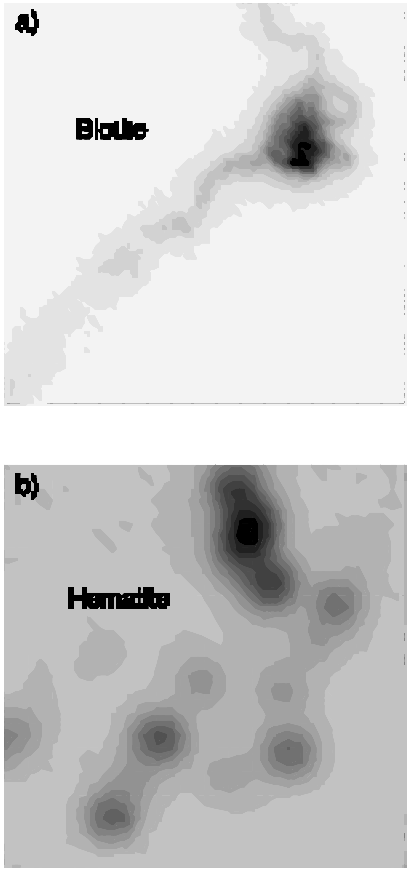
## Introduction

Although one of the key parameters in any mineral-water reaction is the reactive surface area of the mineral, accurate measurements are difficult to obtain. The difficulty is further compounded when one attempts to measure the surface coverage of the reduced form of a bulk constituent such as Fe. Surficial Fe(II) is subject to oxidation by atmospheric oxygen and does not yield a spectroscopic signature significantly different from that of Fe(III) in the bulk. To overcome this difficulty, we employed a reactive probe, Ag(I), to oxidize surface-accessible Fe(II) and precipitate Ag(m) in place, thereby preserving the spatial distribution of reactive surface sites in a form that is more stable to atmospheric oxidation and amenable to measurement. Furthermore, the K-edge x-ray properties of Ag [high-energy (25.4 keV), high fluorescence yield (83%), negligible absorption by air/water] make surface analysis by x-ray microscopy (XRM) practical.

## Methods and Materials

We prepared small specimens of biotite and hematite by reacting them with 0.01 M $Fe(NH_4)_2(SO_4)_2$ or a $HCO_3$-buffered 0.25 mM $Na_2S_2O_4$ solution, washing them three times with deionized $(DI)H_2O$, reacting them with 0.01 M AgF/HF, washing them three times with $(DI)H_2O$, and then drying them rapidly with a stream of inert gas. Specimens that had only contacted water or 0.01 M AgF/HF were also prepared. With the exception of the drying step, all preparation was performed under strictly anoxic conditions. Once the specimens were dry they were mounted on holders. The XRM analyses were performed using 25.6 keV light focus with a glass capillary having a 0.7 µm diameter exit. Spot size on the specimen varied with distance from the capillary tip and was adjusted to be approximately equal to the step size of the scan (typically 2.5–5 µm). In addition to transmission measurements, a 13-element Ge detector was used to detect Ag fluorescence produced by the sample.



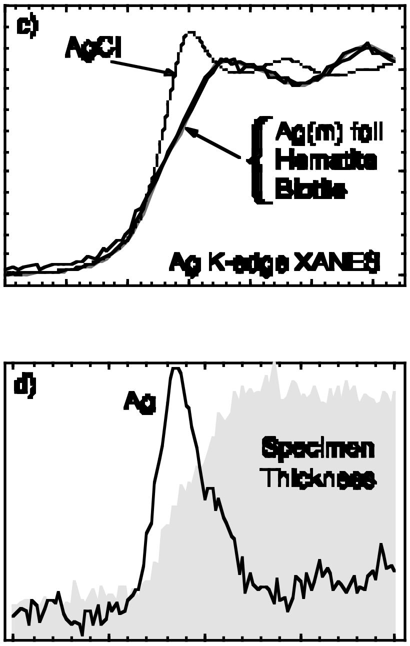


Figure 1: Surface XRM images (170 x 170 µm) of reduced zones (Ag density) on surfaces of a) biotite and b) hematite; c) normalized Ag-K-edge XANES spectra (25500–25565 eV) of reduced zones, Ag(m), and AgCl(s); and d) lateral scan (200 µm) across edge of reduced biotite showing Ag accumulation in frayed-edge sites.

of reaction suggestive of step edges with occasional high concentrations at defect sites. Large areas of the biotite yielded no measurable Ag. The hematite specimens showed reactive sites only after treatment with $Na_2S_2O_4$ and then yielded patterns suggesting small independent etch pits (Figure 1b). X-ray absorption near-edge structure (XANES) spectra collected at the reactive sites were identical to those for Ag(m) and significantly different from that for AgCl (Figure 1c), thus showing that the Ag accumulations were clearly the result of reduction of Ag by the mineral surface. Perhaps the most interesting feature is the highly localized nature of the reactions. For biotite, the reactive sites are predominately at the frayed edges of the particles and steps (Figure 1d). The similar ionic radii of $Ag^+$ and $K^+$ (the main interlayer cation in biotite) may account for the reactivity of these sites. Given the low solubility of $Ag_2S$, it is likely that this technique could also be used to image reduced zones produced by sulfate-reducing bacteria.

## Results and Discussion

The biotite specimens routinely yielded Ag on the surface as would be expected from the Fe(II) content of the mineral. Typical images (Figure 1a) suggested narrow contiguous zones

## Acknowledgments

Work supported by Laboratory Directed Research and Development funds through the Environmental Contamination Research Initiative at the Pacific Northwest National Laboratory (PNNL). The PNNL is operated for the U. S. Department of Energy (USDOE) by Battelle Memorial Institute under Contract No. DE-AC06-76RLO. Use of the Advanced Photon Source was supported by the USDOE, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.