

## Nonsteady State Hematite Dissolution: HAFM and STM Observations

Sherry D. Samson (ssamson@uwyo.edu)<sup>1</sup> & Carrick M. Eggleston (carrick@uwyo.edu)<sup>2</sup>

<sup>1</sup> Dept. of Geology and Geophysics, University of Wyoming, PO Box 3006, Laramie, WY 82071-3006, USA

<sup>2</sup> Department of Geology and Geophysics, University of Wyoming, PO Box 3006, Laramie, WY 82071-3006, USA

The dissolution of minerals is complex, involving adsorption of reactants (e.g., protons, ligands), the resulting changes in ligand exchange rates of surface metal centers, and possible restructuring of the surface at the atomic scale. Metal centers undergo a transition, via ligand exchange processes, from full and relatively static co-ordination in the bulk, through various forms of dynamic surface sites, to co-ordination by water, OH<sup>-</sup>, and perhaps other ligands in aqueous solution. Surface sites that detach to form aqueous ions thus exist by virtue of a host of foregoing processes that produce them. The depolymerisation sequence may correspond to terrace, step, and kink sites as in the dissolution of salts such as calcite and barite, but it remains to be shown that the relatively simple mechanism of ion detachment and attachment to kink sites applies to hematite and other oxides. Here, we use data from nonsteady state wet-chemical dissolution experiments, hydrothermal atomic force microscopy (HAFM), and scanning tunnelling microscopy (STM) to investigate how depolymerisation processes occur on hematite (001) surfaces. Nonsteady state experiments using downward pH-jumps to pH 1 following varying periods of ageing at higher pH (Samson and Eggleston, submitted), i.e., square waves in pH, demonstrate that hematite surface sites active for dissolution at pH 1 are regenerated very rapidly (within minutes, perhaps even within seconds) upon returns to higher pH from pH 1. Upon a jump from higher pH to pH 1, transients of initially elevated, but declining, dissolution rates are observed as this reservoir of active sites is dissolved more

rapidly than it can be replenished. A constant dissolution rate is achieved when the reservoir of active sites is depleted to the level characteristic of steady state at pH 1. Using HAFM, a pH-jump was imposed on a hematite sample in a flow-through cell in an attempt to observe in situ this transient dissolution phase. Initially the sample was imaged at 125 °C in deionised water, after which the inlet solution was changed to a 0.1 N HNO<sub>3</sub> solution. Throughout 12 hours of observation, at 125 °C and pH 1, no measurable dissolution of a 500 nm-wide terrace on the 001 face could be detected. Calculations based on our macroscopic dissolution rates suggest that even at steady state at pH 1 at 25 °C, approximately 36 nm of step retreat should occur in 12 hours. The absence of detectable step retreat under these conditions of low pH and elevated temperature suggests that hematite dissolution may not proceed by the same mechanism as the dissolution of salts such as barite and calcite. The HAFM data are compared to recent STM investigations that suggest that dissolution of iron from terraces could be responsible for the observed dissolution transients. The structural complexity of hematite surfaces may serve to diminish the kinetic distinction, with regard to dissolution, between kink sites and a variety of other possible adatom or "adsorbed" sites on terraces.

Samson SD & Eggleston CM, *Geochim. Cosmochim. Acta*, (submitted).