

***In situ* observations of reductive dissolution of colloidal Lepidocrocite (γ -FeOOH) in ascorbic acid**

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Ferric iron oxides and hydroxides play a major role in the immobilization of contaminants in environmental systems, but when conditions in aquifers become more reducing, incorporated toxic elements can be released to the groundwater. Better understanding of reductive dissolution is essential for our ability to predict the movement of heavy metals in natural systems. Lepidocrocite, γ -FeOOH, found in soils and sediments most commonly near the redox boundary, is vulnerable to attack by natural reducing agents.

We have used the high resolution capabilities of Atomic Force Microscopy to investigate reductive dissolution of micrometer-scale crystals of lepidocrocite in a closed fluid cell containing 10 mM ascorbic acid ($C_6H_8O_6$) as a model organic reductant.

Figure 1 shows a subset of images taken during dissolution of one single lepidocrocite crystal. We were able to determine that the reductive dissolution rate is about $4 \times 10^{-3} \text{ g Fe m}^{-2}\text{h}^{-1}$, which compares very nicely with macroscopic rates. Dissolution on individual faces was fastest on the ends of the longest dimension and slowest on faces of the shortest dimension, so that length-to-width ratio changed as a function of time. Contaminants that are adsorbed preferentially to these faces can either be released to solution again during dissolution, or they can inhibit dissolution, enhancing prominence of a new face and thus promoting a new morphology.

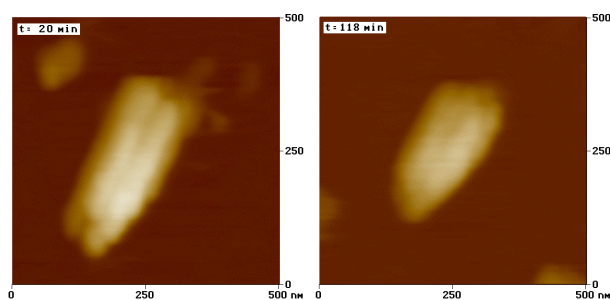


Figure 1: AFM images of one γ -FeOOH crystal during reductive dissolution – images taken after 20 min. of exposure to ascorbic acid (left) and 2 hours (right). Length/width/height ratio of the crystal is approximately (measured in nm) 385/180/16 (left) and 320/170/14 (right). Height is shown by graduated colour scale; bright is highest.

An isotope dilution, etch abrasion solution to the Akilia Island U-Pb age controversy

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Two-stage (3.65 and 3.85 Ga) zircon populations, with a minor 2.7 Ga component, in tonalite intrusions that were sampled to constrain the age of a mafic enclave, reported to contain ^{13}C -depleted graphite microparticles, Akilia Island, SW Greenland, have led to disparate interpretations (see review by Nutman et al., 2000). Nutman et al. (1997) ascribed the older age to the time of magmatic emplacement and the younger age to metamorphic growth, whereas Whitehouse et al. (1999) assigned magmatic growth at 3.65 Ga and the older age to inherited grains. Kamber and Moorbath (1998) suggest the latter explanation for the disparity between Rb-Sr, Sm-Nd, and Pb-Pb results versus ion probe ages throughout the region. Our initial analyses from the same sample sites (Krogh et al., 2000) supporting the younger age for magmatism are revised here based on our discovery that the few clear prisms analyzed have the same ages as the overgrowths and do not represent the main population of oscillatory zoned magmatic zircons.

The etch-abrasion method employed here exploits the extreme, radiation-induced solubility differences that render damaged domains visible, and leaves isotopically closed cores and tips, with the lowest U concentrations and the highest probability of concordance, unetched. Critical to this investigation is the fact that magmatic grains are typically highly zoned and turn white and friable where damaged zones are attacked, whereas metamorphic domains are not zoned and remain clear, so that the abundance distribution and habit of each stage is easily assessed.

Zircons from the tonalite sheet near the north contact with the mafic enclave are typically resorbed, 3:1 rounded prisms, with longitudinal cracks, and minor clear, pink overgrowths that together with highly etchable zones (3 hr NaOH 22°C) define the population as pre-metamorphic, primary magmatic. Metamorphic components comprise <10% of the population and occur as tips, rounded grains, and blocky prisms. Ages of 3760 \pm 4 Ma and 3658 \pm 3 Ma were obtained for the magmatic and metamorphic grains, respectively.

Zircons from the south contact sample only show two-stages of growth after etching (2.5 hr in HF at 220°C). Clear tips overgrow the dominant, zoned population and 5, 3:1 prisms and 3 equant grains of the latter type yield a colinear array (0.4% discordant) for an age of 3849 \pm 4 Ma to 2708 Ma (0.4% discordant). Overgrowth component (<10% of the population) gives a ca. 3670 Ma maximum age.

References

Nutman, A. et al. (2000), *Geochim. et Cosmochim. Acta* **64**, 3035-3060.