

# Surface Oxidation of Rhodonite: Structural and Chemical Study by Surface Scattering and Glancing Incidence XAS Techniques

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## Introduction

Defining the mechanisms of reaction between mineral surfaces and aqueous fluids is critical to understanding and predicting many geochemical, environmental, and industrial processes [1]. Manganese is the second most abundant heavy metal in the earth's crust (after iron), and it is an important component in a wide spectrum of geochemical processes. In nature, II, III, and IV oxidation states of Mn predominate in an unusual range of multiple valance minerals, which are useful indicators of depositional variables such as temperature, [O<sub>2</sub>], [CO<sub>2</sub>], Eh, and pH. The mobility of Mn is largely controlled by its oxidation state, since higher oxidation states tend to hydrolyze and precipitate. Therefore, the mobility of Mn is favored by reducing conditions, and the Mn<sup>2+</sup> ion and its complexes constitute the principle transport species. Recent studies have examined Mn solution species [2] and the oxidation of Mn(II) at hematite, goethite, and albite surfaces [3]. However, little work has been carried out to investigate the fundamental reaction mechanisms involved in the oxidation of Mn at the surface of the representative Mn minerals. In this work, we use rhodonite as a model Mn-silicate mineral to investigate both chemical and structural changes at the mineral-fluid interface during reaction with an oxidizing fluid.

To determine changes in surface structure, specular and diffuse scattering profiles were collected from the rhodonite surface before and after two reaction stages. For chemical changes with depth resolution, glancing incidence x-ray absorption spectroscopy (GIXAS) was used. The reflectivity measurements allow for a determination of the surface roughening and thickness of any coherent product layer at the surface associated with the reaction. GIXAS yields information about the oxidation state and local coordination environment of Mn, with depth sensitivity controlled by the penetration depth of the x-rays in the material at a particular glancing angle of incidence. The process of collecting reflectivity and GIXAS data was repeated after several reaction steps to build up information on the rate of oxidation and surface roughening.

## Materials and Methods

A chemomechanically polished (siton) rhodonite wafer (40 × 25 × 3 mm) was fixed into a purpose-built sample

chamber. The sample chamber was made from Kel-F (a chemically inert polymer similar to Teflon®), with x-ray windows of Teflon-coated Kapton® and inlet/outlet holes for fluid or gas flow through the chamber. Prior to the reaction, Mn K-edge XANES spectra were acquired at several incident angles. Specular and diffuse scattering profiles were also collected from the pristine surface. Fluid-mediated oxidation of the rhodonite surface was carried out in two stages, both using pH 3.5 (HNO<sub>3</sub>) 0.1 M LiCl solution to simulate a natural oxidizing fluid. In the first stage (R), the sample was exposed to fluid for 1 h. In the second stage (F), it was exposed for an additional 2.5 h. Specular and diffuse scattering profiles were collected from the rhodonite surface after each stage. Mn K-edge XANES spectra were acquired at selected incidence angles after the first reaction stage and after the final stage.

Measurements were performed at the APS on beamline 13-ID. X-rays from the first harmonic of an APS undulator A were monochromatized by using a double-crystal Si(111) monochromator. The beam was focused to approximately 50 μm (vertical) × 100 μm (horizontal) by using Rd-coated focusing mirrors in the Kirkpatrick-Baez (K-B) geometry. The sample was positioned by using a general-purpose kappa-geometry diffractometer (Newport). XAS data were collected in fluorescence yield mode by using a 16-element Ge-detector (Canberra).

## Results

Specular reflectivity data from the pristine sample indicate that the unreacted surface had an rms roughness of 16.5 Å. Diffuse scatter profiles show a mosaic structure present in the unreacted surface. After the first reaction step, both the diffuse and specular profiles change significantly. The specular profile shows reflectivity oscillations (Kiessig fringes, Fig. 1). These may be interpreted as a reacted volume of 75-Å-thick mineral solid with an electron density of ~85% rhodonite. The mosaic structure of the surface has changed with mild etching of the surface. The increase in scattering intensity in the Yoneda wings indicates that the surface roughness may have increased slightly and that the correlation length between surface features has probably decreased.

After the final reaction, the most dynamic change occurs in the relative intensity of the Yoneda wings. Here

the low-angle Yoneda peak has grown significantly. Again, we interpret this increase in the magnitude of the Yoneda wing to be caused by a significant decrease in the surface correlation length. Furthermore, the reflectivity oscillations in the specular profiles have nearly disappeared after the additional 2.5 h of reaction. Disappearance of the reflectivity oscillations is most likely caused by more extensive leaching of surface Mn, leading to the destruction of the well-organized thin-film layer.

Mn K-edge GIXAS data were collected from the pristine surface at incidence angles of 150, 300, and 600 mdeg (which are approximately  $\frac{1}{2}\theta_c$ ,  $\theta_c$ , and  $2\theta_c$ , respectively). After the first reaction stage, data were collected at 150, 170, 180, 225, 275, and 300 mdeg, and after the final reaction stage, they were collected at 150, 170, 190, 210, 250, 275, and 300 mdeg. The shape and position of the edge in the Mn K-edge spectrum is sensitive to the manganese oxidation state and coordination. The edge positions, determined from the first derivatives of the XANES spectra, are given in Table 1. Although at low angles, there is a slight shift in the edge energy after the first stage of the reaction, the magnitude is less than would be expected for a one-electron oxidation of all the manganese atoms, implying a mixture of oxidation states. At lower angles, the edge energy is slightly higher, showing a greater degree of Mn oxidation closer to the surface. The XANES spectra at four angles normalized to the height of the maximum peak shown in Fig. 2 clearly demonstrates the change in the average oxidation state of the manganese with depth. After the second reaction stage, the edge positions show some oxidation of the manganese, but there is no clear trend in oxidation state change with depth, which may be a result of the leaching of manganese preferentially from

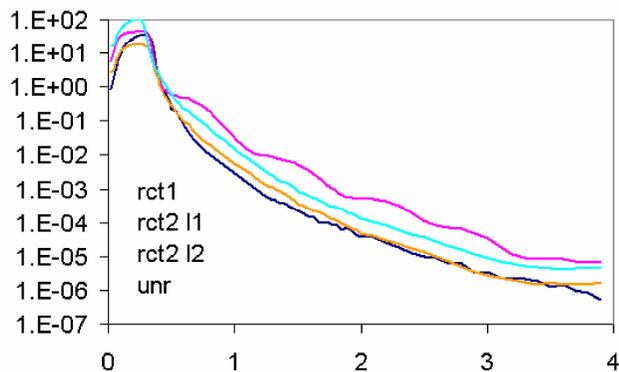


FIG. 1. Specular reflectivity profiles as a function of reaction time. Black curve is unreacted sample. Magenta curve with Kiessig fringes is after first reaction step. Blue and tan curves are both after the second reaction step but were taken at two different incident wavelengths.

Table 1. Mn K-edge positions measured from the first major peak in the first derivatives of the XANES spectra.

Rhodonite sample <sup>a</sup>	Angle (mdeg)	Estimated Depth (Å)	Edge Position (eV)
P	150	32.6	6544.5
P	300	140.0	6544.5
P	600	2550	6544.5
R	150	32.5	6545.0
R	170	34.1	6545.0
R	180	35.1	6545.0
R	225	42.0	6544.8
R	275	65.3	6544.7
R	300	140.0	6544.7
F	150	32.6	6544.9
F	170	34.1	6544.9
F	190	36.2	6544.9
F	210	39.1	6545.0
F	250	49.4	6545.0
F	275	65.3	6544.9
F	300	140.0	6544.7

<sup>a</sup>P = pristine, R = reacted (first stage), and F = final (second stage).

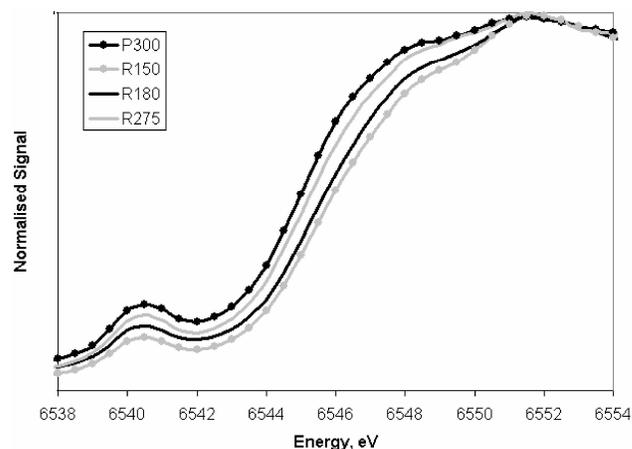


FIG. 2. XANES spectra of the rhodonite sample in glancing incidence. P300 refers to the pristine crystal at 300 mdeg incident angle. R150, R180, and R275 are all spectra taken after the first reaction step at progressively higher incident angles corresponding to progressively greater x-ray penetration depth. Incidence angles are 150, 180, and 275 mdeg, respectively.

the oxidized sites in the mineral surface with the more extended reaction time.

## **Discussion**

These preliminary results suggest that the combination of x-ray reflectivity and GIXAS provide the structural and chemical information necessary to elucidate the details of (potentially complex) reactions occurring at the mineral-fluid interface. The results presented here suggest that after a short reaction period, a leached layer is formed at the rhodonite surface with lower density than the bulk phase and partial oxidation of the Mn. A more extensive reaction appears to have destroyed the leached layer, although there is still evidence for the presence of oxidized Mn.

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