

## Variation of hydrogen bonded O...O distances in goethite at high pressure

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### ABSTRACT

In-situ synchrotron X-ray powder diffraction experiments on goethite were performed up to 24.5 GPa using a diamond-anvil cell at BL-18C in the Photon Factory, Japan. The compression behavior of goethite is anisotropic: the **a** axis, which is close to the direction of the hydrogen bond, is almost twice as compressible as the **b** and **c** axes. A second-order Birch-Murnaghan fit ( $K' = 4$ ) to the unit-cell volumes and pressures up to 24 GPa gave a bulk modulus  $K_0 = 111(2)$  GPa. The pressure medium apparently affects the compression behavior of goethite, as a sudden strain broadening occurs above 11 GPa, where solidification of the 4:1 methanol:ethanol pressure medium occurs. The crystal structure of goethite was refined by means of the Rietveld method at several pressures below 10 GPa. The main compression occurs in the “vacant channels” in the crystal structure, where the O-H...O bridges are located. The hydrogen-bonded O...O distance shortens with increasing pressure at the rate of about  $-0.023 \text{ \AA/GPa}$  and reaches  $2.60(1) \text{ \AA}$  at 9 GPa.

### INTRODUCTION

Goethite ( $\alpha$ -FeOOH) crystallizes in the orthorhombic system with space group *Pbnm* and is isostructural with diaspore (AlOOH) (Szytula et al. 1968). The structure of goethite can be described in terms of a slightly distorted hexagonally close-packed O atom arrangement with Fe atoms occupying two-thirds of the octahedral sites. There are two independent O sites, O1 and O2. The O1 atom is surrounded by three Fe atoms to form an almost planar triangle. The O2 atom is hydrogenated, and is surrounded by three Fe atoms and an H atom to form a distorted tetrahedral coordination. The hydrogen bonding connects with an O1 atom in an adjacent octahedron. The non-linear hydrogen bonding in goethite is known to be of moderate strength. As this is the most common type of hydrogen bond (Jeffrey 1997), it is important to understand their behavior as a function of pressure.

Numerous investigations of pressure-induced weak hydrogen bonding can be found in brucite-related minerals including hydrous silicates, based on spectroscopic (e.g., Kruger et al. 1989; Nguyen et al. 1994; Faust and Williams 1996), neutron diffraction (e.g., Parise et al. 1994, 1999; Kagi et al. 2000), and theoretical studies (e.g., Sherman 1991). However, a spectroscopic study of goethite by William and Guenther (1996) appears to be the only investigation that focused upon hydrogen bonding of moderate strength at high pressure. The theoretical study by Winkler et al. (2001) appears to be the only such study of diaspore, although equation-of-state studies of diaspore have been made (Ruoff and Vanderborgh 1991; Mao et al. 1994; Grevel et al. 2000). Furthermore, the bulk modulus of goethite is undetermined. In their study of goethite by Raman spectroscopy, William and Guenther (1996) observed two O-H

stretching vibrations and reported that one O-H stretching frequency decreased and the other increased with increasing pressure. The positive  $\Delta\nu_{\text{OH}}$  was attributed to repulsive interactions between cations and H. However, the theoretical investigation by Winkler et al. (2001) predicted only increased hydrogen bonding and a concomitant weakening of the hydroxyl bond with increasing pressure, implying the more usual negative pressure dependency of  $\nu_{\text{OH}}$ .

While good-quality X-ray diffraction data can yield approximate locations for H atoms, it is not possible to determine the details of their structural behavior because H is a very weak X-ray scatterer. However, the hydrogen-bonded O...O distances can be determined accurately by X-ray diffraction and so can provide useful information about the nature of hydrogen bonding, since the distances are often used as a criterion of hydrogen bonding. Moreover, compression of the hydrogen-bonded O...O distance may change the nature of hydrogen bonding, because it is considered that the quantum-mechanical charge-transfer contributions to the hydrogen bond energy become more important as this O...O distance shortens (e.g., Martens and Freund 1976). Nagai et al. (2000a, 2000b) reported on the pressure variation of the hydrogen bonded O...O distances in brucite and portlandite, based on the results of X-ray diffraction measurements. They suggested that a hydrogen bonded O...O distance of  $2.75 \text{ \AA}$  seems to be a kind of a critical distance, since the distance in brucite is not compressed below  $2.75 \text{ \AA}$  and portlandite transforms into an amorphous material when the distance becomes  $2.75 \text{ \AA}$ , which, perhaps significantly, corresponds to the  $\text{O}^{2-}\text{-O}^{2-}$  contact distance.

Here we present the first compression data for goethite and discuss how hydrogen bonding in goethite behaves as a function of pressure, based upon pressure variation of the hydrogen bonded O...O distance derived from in-situ synchrotron X-ray diffraction experiments.

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## EXPERIMENTAL METHODS

The sample material was powdered  $\alpha$ -FeOOH of 99% purity from Johnson-Matthey, Inc. No impurity phase was detected in X-ray powder diffraction spectra and unit-cell parameters of  $a = 4.6251(1)$ ,  $b = 9.9985(1)$ , and  $c = 3.0370(1)$  Å were obtained.

A pair of 0.35 mm culet diamonds and a pre-indented stainless steel gasket was used. A gasketed sample powder was compressed up to 24.5 GPa by a lever-and-spring type diamond anvil cell (Yagi and Akimoto 1982) with a few small ruby chips for pressure calibration by the ruby-fluorescence method. A 4:1 methanol:ethanol pressure medium was used. Angle-dispersive synchrotron X-ray powder diffraction experiments were performed using an image-plate detector on beamline BL-18C at the Photon Factory, Japan. Monochromatized X-rays of energy 20 keV were used and collimated to 40  $\mu$ m diameter (Kikegawa 1997). Exposure times were 0.5 to 3 hours.

The Debye-Scherrer rings of the sample showed quite homogeneous contrast and no diffracted spots could be observed. Thus, the two-dimensional image was integrated along each Debye-Scherrer ring and was converted to a one-dimensional diffraction pattern using the program PIP (Fujihisa and Aoki 1998). Diffraction data obtained at several pressures below 10 GPa were analyzed using the Rietveld structural refinement program RIETAN2000 (Izumi and Ikeda 2000). Since the scattering power of the H atom is negligibly small for X-rays, we refined the atomic coordinates of the Fe and O atoms only. Unit-cell parameters, scale factors, peak-width parameters, and an overall isotropic atomic displacement parameter were refined. Refinement of a preferred-orientation parameter showed almost no improvement in the refinement, so preferred-orientation effects were ignored.

## RESULTS AND DISCUSSION

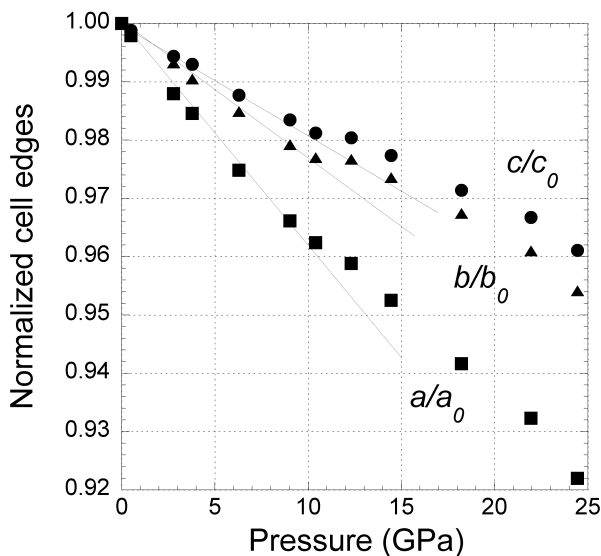
The unit-cell parameters were determined using a whole-pattern fitting method (RIETAN2000) and are listed in Table 1. As shown in Figure 1, the compressional behavior of goethite is anisotropic, with the **a** axis being more compressible than the **b** or **c** axes. Although small humps can be observed on each axial compression curve around 11 GPa, there is no evidence for major structural changes in diffraction patterns up to 24.5 GPa. These features could be due to non-hydrostaticity caused by the solidification of the 4:1 methanol:ethanol pressure medium, which occurs above 11 GPa (Piermarini et al. 1973). Indeed, a sudden strain broadening of diffraction peaks can be observed around the same pressure, as shown in Figure 2. Similar features were observed by Mao et al. (1994) in their high-pressure study of diaspore.

Figure 3 shows a plot of the pressure-volume data. A small hump can also be observed at about 11 GPa on this compression curve. This hump could arise from the same reason as discussed above. Fitting a second-order Birch Murnaghan EOS ( $K' = 4$ ) to the pressure-volume data in Table 1 gives a bulk modulus  $K_0 = 111(2)$  GPa, whereas fitting to pressure-volume data obtained below 11 GPa gives  $K_0 = 108.5(6)$  GPa. Values for the bulk modulus of diaspore reported in the literature are

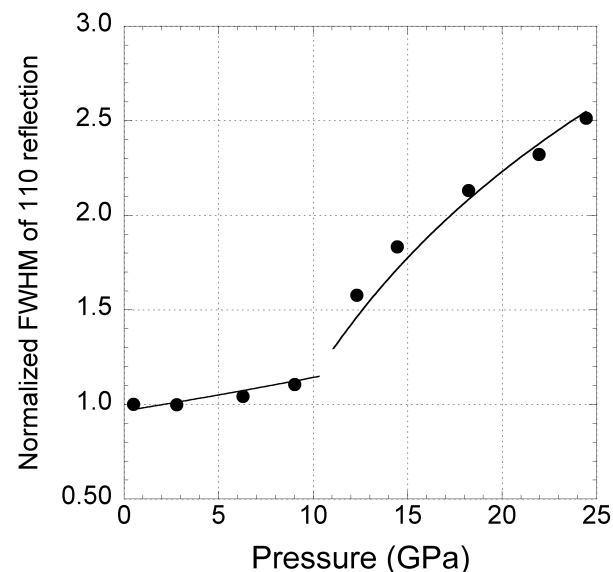
**TABLE 1.** Unit-cell parameters of goethite as a function of pressure

$P$ (GPa)	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
0	4.6250(1)	9.9900(2)	3.0370(1)	140.45(1)
0.5	4.6152(2)	9.9870(4)	3.0316(1)	139.73(1)
2.8	4.5692(2)	9.9428(5)	3.0163(1)	137.04(1)
3.8	4.5535(2)	9.9290(5)	3.0080(1)	135.67(1)
6.3	4.5086(2)	9.8759(6)	2.9910(1)	133.18(1)
9.0	4.4683(3)	9.8334(7)	2.9739(2)	130.67(1)
10.4	4.4510(4)	9.9671(9)	2.9672(3)	129.56(2)
12.3	4.4345(5)	9.803(1)	2.9662(4)	128.95(3)
14.5	4.4054(6)	9.773(2)	2.9566(5)	127.29(4)
18.2	4.3550(9)	9.713(3)	2.898(1)	124.27(5)
22.0	4.312(1)	9.666(4)	2.918(1)	121.64(8)
24.5	4.264(1)	9.610(5)	2.898(1)	118.74(5)

widely variable (e.g.,  $K_0 = 85$  GPa, Ruoff and Vanderborgh 1991; 225 GPa, Xu et al. 1994; 165 GPa, Mao et al. 1994; 134 GPa, Fasshauer et al. 1998; 134 GPa, Grevel et al. 2000). Such a spread of values is likely due to variable degrees of non-hydrostaticity in these studies. The value of  $K_0 = 134$  GPa obtained by Grevel et al. (2000) could be the most reliable because of the improved control of deviatoric stress in their experiments. It is interesting that, using the  $K_0 = 134$  GPa value, the value of  $K_0V_0$  for diaspore is almost identical to that of goethite obtained in this study. It is known that the value of  $K_0V_0$  is empirically almost constant in the same structural group (Anderson and Anderson 1970).



**FIGURE 1.** Axial compression data. Solid squares, solid triangles and solid circles represent  $a/a_0$ ,  $b/b_0$ , and  $c/c_0$ , respectively. Solid lines are fitted to the data below 10 GPa to guide the eye.



**FIGURE 2.** Peak widths (FWHM) normalized by the value at 0.5 GPa as a function of pressure. Errors are about the size of the symbols. Solid lines are guides for the eyes.

## STRUCTURE REFINEMENTS

The diffraction peaks are quite sharp below 10 GPa. Exposures of three hours were needed to obtain statistically reliable diffraction data at 0.5, 2.8, 6.3, and 9.0 GPa. A representative example of a Rietveld refinement result is shown in Figure 4. All refinement results and selected bond lengths are listed in Table 2. The anisotropy of compression is now explained by the following crystallographic consideration on the basis of these data, with reference to the crystal structure of goethite shown in Figure 5. Edge-sharing Fe octahedra form so-called "double rutile strings" parallel to the *c* axis in a chequer-board array with channels between the strings running parallel to the *c* axis. Hydrogen-bonded O-H...O linkages form across the channels. The hydrogen bond vector has a significant component directed parallel to the *a* axis. Variations in the volume of the FeO<sub>6</sub> octahedron are listed in Table 2. The FeO<sub>6</sub> octahedron decreases by about 3% under compression from 0.5 to 9.0 GPa, whereas the unit-cell volume decreases by about 7% in the same

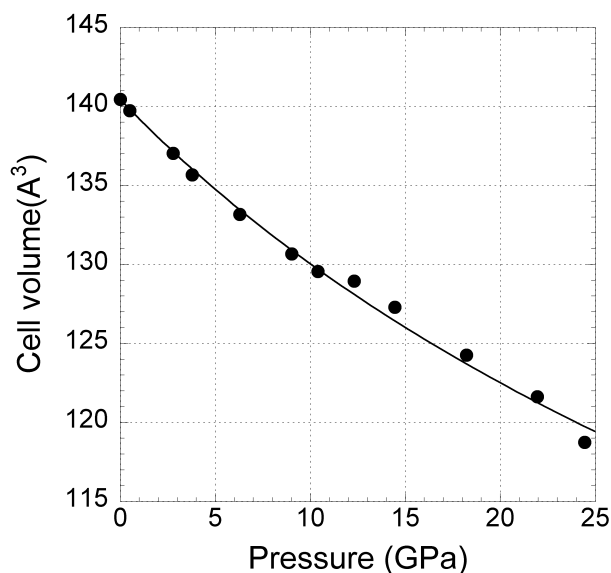


FIGURE 3. Unit-cell volume as a function of pressure. The solid curve is calculated from the second order Birch-Murnaghan equation of state [ $K_0 = 111(2)$  GPa,  $K' = 4$ ].

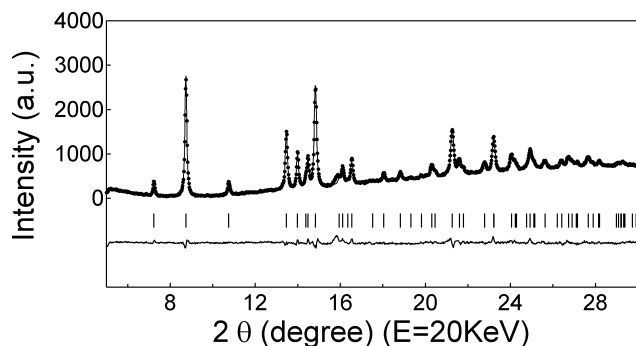


FIGURE 4. Observed (dots) and calculated (solid line) profile of goethite at 9.0 GPa. Differences between the observed and calculated intensities are plotted at the bottom and the vertical bars represent the positions of the diffraction peaks.

pressure range. This observation supports the notion that compression of channels controls the bulk compression that involves shortening the hydrogen bonds oriented nearly along the *a* axis.

The Fe-O1 bonds are significantly longer than those of Fe-O2. This difference can be explained in terms of the large sum of bond strengths received by hydrogenated O2. Figure 6 shows that the Fe-O2 bonds shorten more rapidly than the Fe-O1 bonds. Assuming that the strength of the O2-H hydroxyl bond decreases with pressure, the sum of bond strengths received by O2 should decrease, which would result in shortening of the Fe-O2 bonds. A theoretical calculation for diaspore by Winkler et al. (2001) supports this assumption, although the positive pressure dependency of the frequency of one of the two hydroxyl vibrations observed by William and Guenther (1996) remains unexplained.

TABLE 2. Refined atom coordinates ( $z = 1/4$ ) and selected interatomic distances (Å)

<i>P</i> (GPa)	10 <sup>-4</sup> *	0.5	2.8	6.3	9.0
Fe <i>x</i>	-0.045	-0.0485(4)	-0.0491(4)	-0.0472(5)	-0.0457(5)
<i>y</i>	0.145	0.1466(2)	0.1460(2)	0.1454(2)	0.1444(2)
O1 <i>x</i>	0.288	0.288(1)	0.288(1)	0.295(1)	0.306(1)
<i>y</i>	-0.199	-0.1968(6)	-0.1964(8)	-0.1960(8)	-0.1961(9)
O2 <i>x</i>	-0.198	-0.198(1)	-0.200(1)	-0.203(1)	-0.207(1)
<i>y</i>	-0.053	-0.0541(6)	-0.0538(8)	-0.0538(8)	-0.0520(8)
$U_{iso}^{\dagger}$ (Å <sup>2</sup> )		0.8(1)	0.6(1)	0.4(2)	0.3(2)
$R_{wp}$ (%)		4.54	5.95	6.01	5.54
$R_p$ (%)		2.91	3.35	3.63	3.57
$R_{Bragg}$ (%)		3.92	4.91	5.89	6.5
Fe-O1		1.990(6)	1.969(7)	1.936(7)	1.90(1)
		1.926(4)	1.928(5)	1.932(5)	1.955(5)
Fe-O2		2.120(6)	2.103(7)	2.089(7)	2.06(1)
		2.108(4)	2.100(5)	2.080(5)	2.076(4)
$V(FeO_6)$ (Å <sup>3</sup> )		10.75(2)	10.65(2)	10.49(2)	10.47(4)
O2-H...O1‡		2.793(5)	2.732(9)	2.66(1)	2.60(1)

\* Values at 10<sup>-4</sup> GPa were reported by Szytula et al. (1968).

† Refined overall  $U_{iso}$  value.

‡ The distance between donor and acceptor O atoms of the O-H...O group. See Young (1993) for definitions of the discrepancy indices.

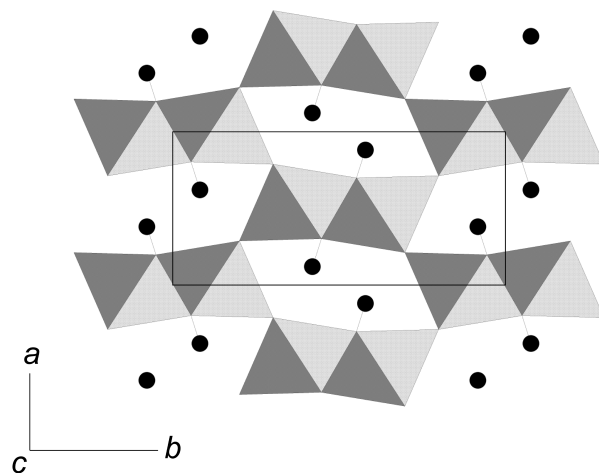


FIGURE 5. A polyhedral representation of the crystal structure of goethite viewed along the *c* axis and showing the O2-H...O1 bridges across the channels. The shortest H...H distance at ambient conditions is 2.47 Å.

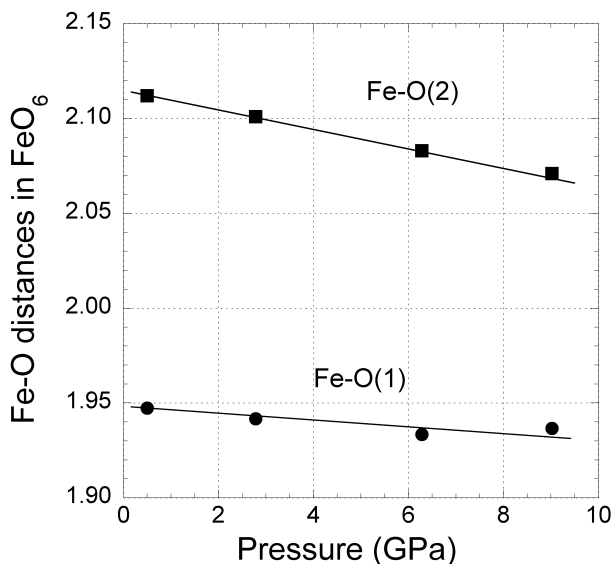


FIGURE 6. Fe-O bond lengths in  $\text{FeO}_6$  octahedra as a function of pressure. Average Fe-O1 and Fe-O2 bond distances are plotted. Solid lines are guides for the eyes.

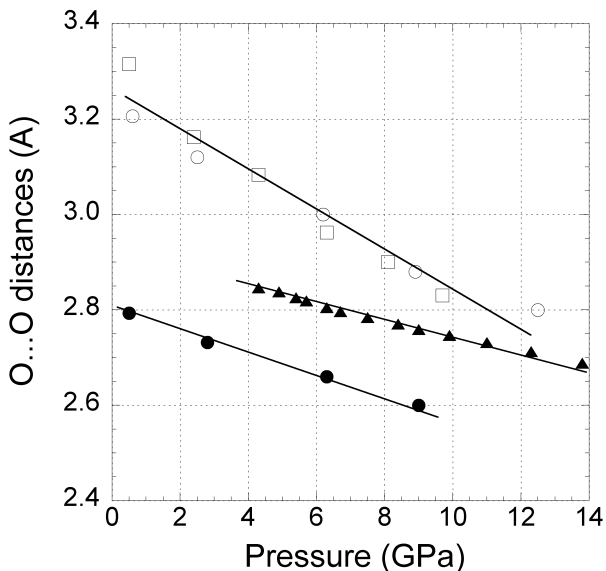


FIGURE 7. Hydrogen bonded O1...O2 distances (solid circles) in goethite are plotted as a function of pressure. Hydrogen bonded O...O distances in ice-VII (solid triangles) (Hemley et al. 1987), brucite (open circles), and portlandite (open squares) (Nagai et al. 2000a, 2000b) are also plotted as references. Solid lines are guides for the eyes.

The pressure dependency of the hydrogen-bonded O...O distance in goethite is  $-0.023 \text{ \AA/GPa}$  in the pressure range from 0.5 to 9.0 GPa. This value is much smaller than the value of  $-0.056 \text{ \AA/GPa}$  reported for both brucite and portlandite (Nagai et al. 2000a, 2000b), but it is close to the  $-0.019 \text{ \AA/GPa}$  reported for ice (e.g., VII: Hemley et al. 1987; VIII: Besson et al. 1993). Figure 7 shows the variation of the hydrogen-bonded O...O distances in goethite (this study) and ice-VII (Hemley et al. 1987). In general, a hydrogen-bonded O...O distance less

than  $2.5 \text{ \AA}$  suggests a category of moderate-strength hydrogen-bonding and that proton tunneling between donor O and acceptor O will be enhanced. In ice-VII, the hydrogen-bonded O...O distance at that pressure would be about  $2.4 \text{ \AA}$  at 62 GPa (Hemley et al. 1987) and Aoki et al. (1996) found the hydrogen-bond symmetrization at that pressure. Assuming similar behavior of contraction of the hydrogen-bonded O...O distance in goethite, it is expected that the distance would be less than  $2.4 \text{ \AA}$  at about 40 GPa. Furthermore, linear extrapolation to high pressure of the compressions of the Fe-O1 and Fe-O2 bond lengths indicates that these converge at about 40 GPa. Such convergence means that the bond strengths received by O1 become comparable to those of O2 and suggests the possibility of hydrogen bond symmetrization—an interesting possibility for future research.

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