

## High Pressure X-Ray Diffraction Study on a Goethite using Synchrotron Radiation

방사광을 이용한 괴타이트에 대한 고압 X-선 회절연구

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**ABSTRACT :** High pressure X-ray diffraction study was carried out on a natural FeO(OH)-goethite to investigate its compressibility at room temperature. Energy dispersive X-ray diffraction method was employed using Mao-Bell type diamond anvil cell with Synchrotron Radiation. MgO powder was compressed together with goethite for the high pressure determinations. Bulk modulus was determined to be 147.9 GPa by the Birch-Murnaghan equation of state under assumption of  $K'_0$  of 4. This value was subjected to compare with its structural analogs and related materials.

**요약 :** 자연산 FeO(OH)-괴타이트의 압축성에 대한 X-선 회절실험을 상온에서 시행하였다. 방사광, 마오-벨 타입 다이아몬드 앤빌기기와 에너지 분산 X-선 회절법을 이용하였다. MgO 분말은 고압값을 결정하기 위하여 혼합하였다.  $K'_0$  을 4로 가정하였을 때, 버치-머내한 상태방정식을 이용하여 괴타이트의 체적탄성률은 147.9 GPa로 계산되었으며, 이 값을 구조유사체나 유관한 물질들과 비교하였다.

### INTRODUCTION

Hydrous minerals have been studied for their significance in modelling the water content at the mantle of the Earth interior. It's been reported that more than 5 times of H<sub>2</sub>O content of hydrosphere exists at the Earth's mantle (Liu, 1987). The equation of state (EOS) of various hydrous minerals have been measured by many high-pressure conditions (Simakov et al., 1974; Finger and Prewitt, 1989; Meade and Jeanloz, 1990; Duffy et al., 1991; Tyburczy et al., 1991; Fei and Mao, 1993; Xu et al., 1994; Mao et al., 1994). However, studies of Xu et al., (1994) and Mao et al., (1994) on diaspore which is in

the goethite structure are different very much each other in the bulk modulus (i.e.,  $K_0=230$  GPa, Xu et al., 1994;  $K_0=167.5$  GPa, Mao et al., 1994).

In the present paper, we report the EOS study results on a natural goethite-FeO(OH) under high pressure at room temperature conditions.

### EXPERIMENTS

#### Sample Preparation

A natural FeO(OH)-goethite has been collected at the Oksan (mountain) at the Gyeong-

**Table 1.** Chemical analysis by EPMA.

#	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe	O	Total
1	0.000	0.009	0.225	0.905	0.000	0.000	0.081	0.015	0.025	48.224	50.516	100.000
2	0.027	0.838	0.055	1.568	0.115	0.003	0.019	0.002	0.035	46.460	50.878	100.000
3	0.060	0.263	1.128	1.613	0.118	2.325	0.050	0.012	0.075	43.771	50.586	100.000
4	0.029	0.069	0.654	1.670	0.200	0.069	0.090	0.000	0.099	45.996	51.124	100.000
5	0.052	0.482	0.116	1.537	0.049	0.010	0.049	0.000	0.260	46.626	50.819	100.000
Av	0.034	0.332	0.436	1.459	0.096	0.481	0.058	0.006	0.099	46.215	50.785	100.000

sang Basin of Southeastern Korea. It has been reformed in a pseudomorph replaced pyrite in the anorthosite. This cubic crystal was ground into fine polycrystalline powder using agate mortar. Chemistry was determined by EPMA using the Cameca Quantitative Analysis Equipment (Table 1).

### Experimental Methods

Energy dispersive X-ray diffraction (EDXRD) method was employed using a Mao-Bell type diamond anvil cell (DAC) with Synchrotron Radiation (SR) at the Stanford Synchrotron Radiation Laboratory (SSRL). In the EDXRD principle, we have the relation;  $E_{\text{hkl}} \cdot d_{\text{hkl}} = h \cdot c / (2 \sin \theta) = 6.199 / \sin \theta$ . The relation is the function of the diffraction angle  $\theta$ . When  $\theta$  is fixed, this equation becomes constant (Giessen and Gordon, 1967);  $E \cdot d = \text{constant} = 57.003$ , and  $2\theta = 12.485^\circ$  in the present experiment set-up. From this equation, volume changes were calculated by the following relationships;  $(E_{\text{h}}/E_{\text{a}})^3 = (d_{\text{h}}/d_{\text{a}})^3 = V_{\text{h}}/V_{\text{a}}$  at different diffraction conditions, where 'a' and 'h' for ambient and high pressure conditions, respectively.

The size of diamond culet in both upper and lower anvils is 400  $\mu\text{m}$  each in diameter. Quality of diamond is gem level and the weight of each diamond reaches 0.3 carat (i.e., 60 mg). Sample was compacted into the circular hole of gasket between upper and lower diamond anvils. Fine powder of periclase (i.e., MgO) was mixed with goethite at the almost same ratio (i.

e., 1:1 in volume to goethite). Gasket material used is 'fully hardened T301' alloy metal plate and hole dimension is 200  $\mu\text{m}$  in diameter and 0.254 mm in thickness, respectively.

A schematic experimental set-up at the SSRL is shown in Fig. 1. Detailed view of the DAC and detecting apparatus set-up with multi-channel analyzer (MCA) system of 1024 channels was given elsewhere (Kim and Na, 1994). In this study, SR has been collimated to 50  $\mu\text{m}$  in diameter for pick-up the highest pressurized portion in the sample chamber.

In order to obtain a high detecting efficiency in the photon energy range of 10 to 50 KeV, an intrinsic Germanium solid state detector (i.e., ORTEC 573) was used. Its resolution is 141 eV at 5.9 KeV and degrades to 490 eV at 122 KeV. This detector operates at a low temperature (i.e., 77 K) with a bias voltage of 0.3 KV power supply. Detector was positioned  $\sim 60$  cm away from DAC to prevent it from oversaturation by SR. Using the various X-ray sources of Cu, Rb, Mo, Ag, Ba and Tb, energy calibration with respect to the channel has been completed.

Pressure of the compressed sample is essential for the volume determinations at the specific high pressure. Because of the technical difficulties of the laser induced ruby fluorescence pressure sensor, an internal pressure calibrant has been used for high pressure experiments (e.g., Ming et al., 1994). For goethite, MgO was selected for its least overlappings with those of specimen. From the photon energy shifts with pressure, lattice parameter variations (i.e.,  $a/a_0$ )

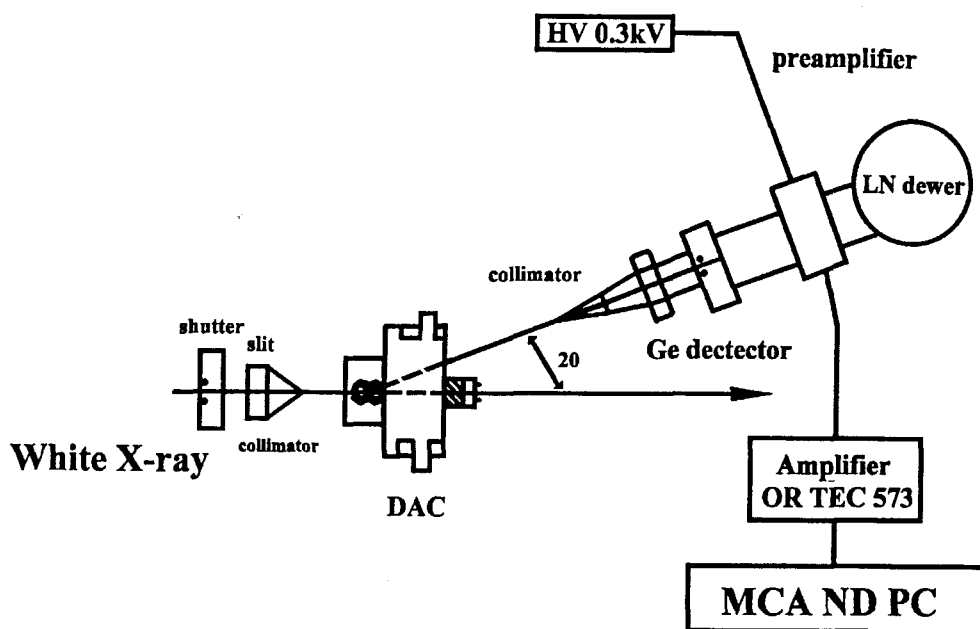


Fig. 1. A schematic experimental set-up at the SSRL.

were calculated and these data were used to determine the pressure value at the curve of MgO (Jamieson et al., 1982). A mixture of methanol-ethanol-water (MEW) in the volume ratio of 16 : 3 : 1, respectively was used as the pressure medium in the sample chamber. Pressure was increased up to 27.6 GPa at the room temperature condition in the present experiment.

## RESULTS AND DISCUSSIONS

Peak search was done by the integration of the peak area occupied by the diffracted photon energy. Pressure was determined by the EOS of MgO (Jamieson et al., 1982), which are based on the weighted intensity ratio of MgO (200) and (220) by 2 : 1.

A series of spectra in the loading and unloading process is shown in Fig. 2. At 0.1 MPa, peaks of (110), (120), (130), (101), (040), (111), (121), (140), (211), (221) and (240) were used to calculate the lattice parameters of goethite:  $a = 4.665 \text{ \AA}$ ,  $b = 9.938 \text{ \AA}$ ,  $c = 3.005 \text{ \AA}$ . This value is

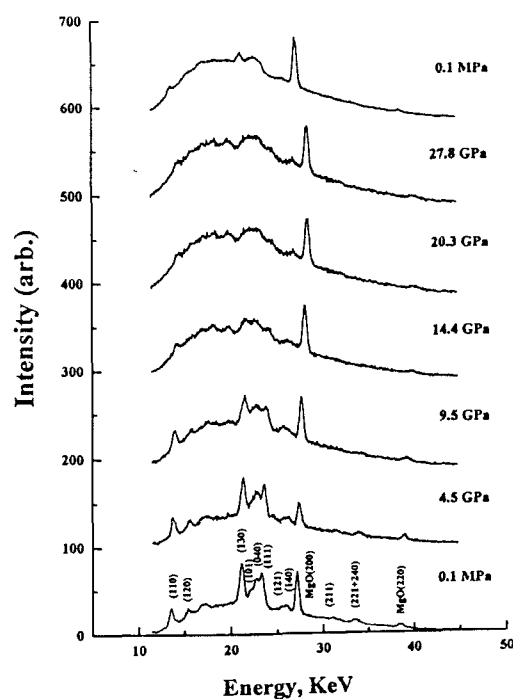


Fig. 2. A series spectra of goethite with pressures.

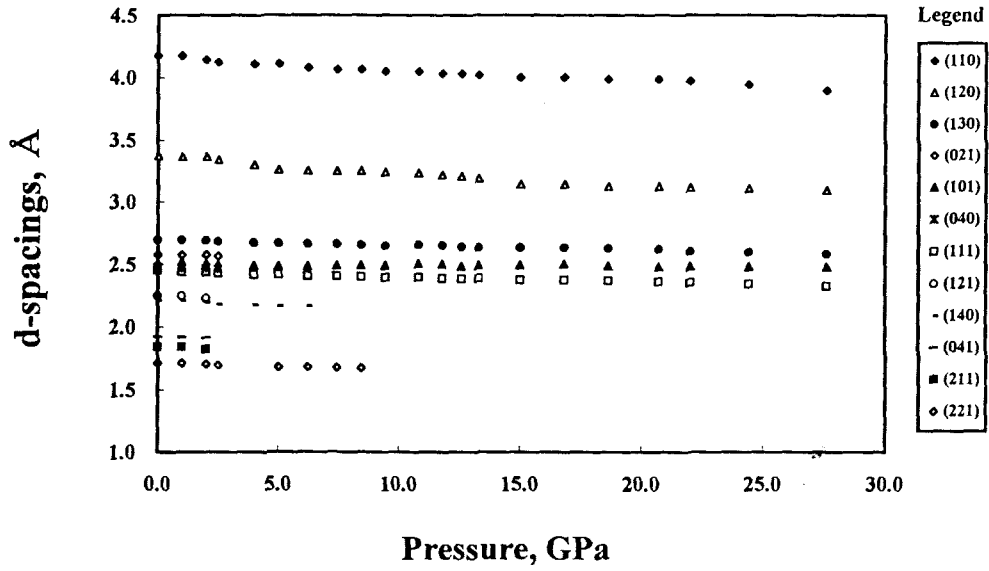


Fig. 3. Variations of *d*-spacings with pressure.

Table 2. XRD data on FeO(OH)-goethite with pressures.

P, GPa	a	b	c	V	V/V <sub>0</sub>	a/a <sub>0</sub>	b/b <sub>0</sub>	c/c <sub>0</sub>
0.0001	4.665	9.938	3.005	139.30	1.000	1.000	1.000	1.000
0.6	4.679	9.932	3.002	139.48	1.001	1.003	0.999	0.999
1.8	4.631	9.915	2.996	137.53	0.987	0.993	0.998	0.997
3.2	4.527	9.912	2.996	134.41	0.965	0.970	0.997	0.997
4.5	4.510	9.936	2.993	134.13	0.963	0.967	0.999	0.997
5.4	4.443	9.915	3.005	132.38	0.950	0.952	0.998	1.000
6.1	4.445	9.901	3.000	131.92	0.947	0.953	0.996	0.998
7.2	4.424	9.915	3.008	131.94	0.947	0.948	0.998	1.001
8.1	4.419	9.885	3.004	131.20	0.942	0.947	0.995	1.000
9.5	4.374	9.905	3.010	130.43	0.936	0.938	0.997	1.002
10.6	4.359	9.947	3.025	131.18	0.942	0.934	1.001	1.007
12.0	4.335	9.973	3.028	130.88	0.940	0.929	1.003	1.008
12.1	4.336	9.900	3.007	129.02	0.926	0.930	0.996	1.001
13.1	4.307	9.886	3.028	128.92	0.926	0.923	0.995	1.008
14.4	4.246	9.925	3.032	127.77	0.917	0.910	0.999	1.009
16.8	4.249	9.919	3.037	127.97	0.919	0.911	0.998	1.011
18.4	4.218	9.916	3.031	126.78	0.910	0.904	0.998	1.009
20.3	4.226	9.869	3.018	125.87	0.904	0.906	0.993	1.004
21.8	4.228	9.751	3.007	123.99	0.890	0.906	0.981	1.001
24.6	4.200	9.750	3.006	123.11	0.884	0.900	0.981	1.001
27.8	4.165	9.724	3.003	121.62	0.873	0.893	0.978	0.999

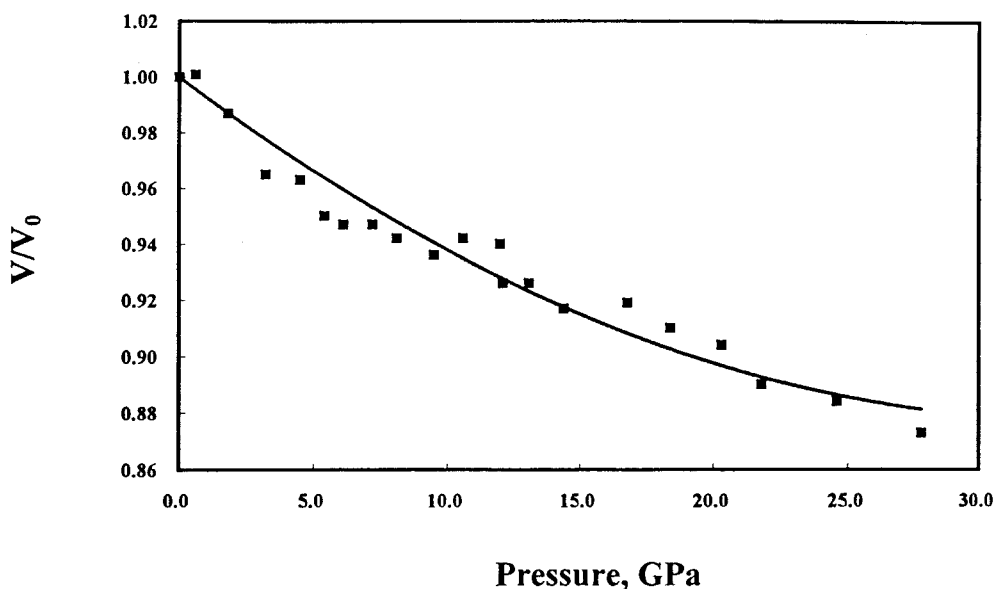


Fig. 4. The equation of state of goethite.  $V/V_0$

comparable with ASTM # 29-0713 (i.e.,  $a = 4.608 \text{ \AA}$ ,  $b = 9.956 \text{ \AA}$ ,  $c = 3.031 \text{ \AA}$ ). With increasing pressure, variations of d-spacings of each peak are given in Fig. 3. Only five sample peaks were used for calculation the lattice parameters over 10 GPa. This may be caused by the thinning of the specimen at high pressure as well as the enormous absorption of the diffracted radiation by diamond window. The variations of d-spacings of each peak were used to calculate the compression of the lattice parameters and volume of goethite at high pressures (Table 2). Mostly compression on the a-axis rules the volume compression. The c-axis does not shrink, but even expands with increasing pressure. This kind of behavior may be caused by the fact that along a-axis there exists the vacant space in the goethite structure, so shrink mainly along a-axis. Volume compression with pressure is shown in Fig. 4.

Based on Table 2 and Fig. 4, bulk modulus (i.e.,  $K_T$ ) was determined by the Birch-Murghnan EOS (i.e.,  $P = 1.5 K_0 [X^{7/3} - X^{-5/3}] [1 - \xi (X^{-2/3} - 1)]$ , where  $X = V/V_0$ ,  $\xi = 3/4 (4 - K'_0)$  and

$K'_0 = (dK/dP)_1$ ) to be 147.9 GPa when  $K'_0$  is assumed to be 4. Goethite is different in  $K_T$  from most hydrous minerals such as  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ , which are crystallized in a layered structure (i.e.,  $K_T$  of  $\text{Mg}(\text{OH})_2 = 54.3 \text{ GPa}$ , Fei and Mao, 1993;  $K_T$  of  $\text{Ca}(\text{OH})_2 = 37.8 \text{ GPa}$ , Meade and Jeanloz, 1990). In this structure, the compression mainly takes place in such layers where hydrogen bonds connect. Hence, it causes the small bulk modulus. But, goethite is not a layered structure.

Crystal structure of goethite is in the orthorhombic system (i.e., Pbnm);  $\text{FeO}_3(\text{OH})_3$ -octahedra are linked by their apices to form chain.  $\text{Fe}^{3+}$  is octahedrally coordinated between O and  $(\text{OH})^{-1}$  which are arranged in hexagonal closed packing (h.c.p.) in the plane of b- and c-axis. Therefore, compression should take place along the bond of Fe and oxygen as well as hydroxide. In diasporite, Xu et al., (1994) explained that almost all compression occurs by shortening of Al-O bonds as in case of corundum (i.e.,  $\text{Al}_2\text{O}_3$ ). Bulk modulus of diasporite (i.e.,  $K_0 = 230 \text{ GPa}$ , Xu et al., 1994) was reported simi-

**Table 3.** Bulk moduli of goethite structures.

	$K_0$ GPa	Remark	References
	85.0	USM	Ruoff and Vanderborgh (1991)
AlO(OH)- diaspore	167.5	XRD	MaO et al. (1994)
	1703	XRD	Ruoff and Vanderborgh (1993)
	2300	XRD	Xu et al. (1994)
FeO(OH)- goethite	147.9	XRD	This study

\* XRD is X-ray diffraction measurement

USM is ultrasonic measurement

lar to corundum (i.e., 226 GPa, Sato and Akimoto, 1979). If this were really happened, it would be worthwhile extending similar comparisons to the structural analogs. Isostructural with corundum is hematite ( $\text{Fe}_2\text{O}_3$ ). Compared with  $\text{Fe}_2\text{O}_3$ , there are several values of bulk moduli available: 225 GPa (Finger and Hazen, 1980), 199 GPa (Wilburn and Bassett, 1978), 228 GPa (Bassett and Takahashi, 1974) and 178 GPa (Sato and Akimoto, 1979). Furthermore, ilmenite structure is closely related to the hematite structure; half the iron sites in hematite are occupied by  $\text{Fe}^{2+}$ , the other half by  $\text{Ti}^{4+}$ . There is a couple of bulk modulus available on  $\text{FeTiO}_3$ : 177 GPa (Wechsler and Prewitt, 1984) and 168 GPa (Liu et al., 1974).

Bulk moduli of diaspore and goethite were given in Table 3. In diaspore, the value of Xu et al., (1994) seems to be too high even if their compression were done in the non-hydrostatic conditions. From this point of view, the present value of 147.9 GPa of goethite which shows lower than those of hematite and ilmenite would be reasonable.

### SUMMARY

Hydrous minerals have been studied for their significance in modelling the water content at the interior of the Earth. The natural goethite- $\text{FeO}(\text{OH})$ , in the pseudoform of pyrite, was studied for its equation of state as well as any possible phase transformation(s) under high pressure at room temperature.

Polycrystalline goethite was compressed up to 27.8 GPa in the Mao-Bell type diamond anvil cell in con-

junction with Synchrotron Radiation at the SSRL. Bulk modulus of goethite was determined to be 147.9 GPa preliminarily using Birch-Murnaghan equation of state. This value was compared with those of diaspore and other hydrous minerals. In similar to other materials, most compression in goethite takes place along a-axis while c-axis does not shrink.

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### REFERENCES

- Bassett W. A. and Takahashi T. (1974) X-ray diffraction studies up to 300 kbar, in *Advances in High Pressure Research*, edited by R. H. Wentorf, 165-247, Academic Press, New York.
- Duffy T. S., Ahrens T. J., and Lange M. A. (1991) Shock wave equation of state of brucite  $\text{Mg}(\text{OH})_2$ , *J. Geophys. Res.*, 9, 14319-14330.
- Fei Y. and Mao H. K. (1993) Static compression of  $\text{Mg}(\text{OH})_2$  to 78 GPa at high temperature and constraints on the equation of state of fluid  $\text{H}_2\text{O}$ , *J. Geophys. Res.*, 98(B7), 11875-11884.
- Finger L. W. and Hazen R. M., (1980) Crystal structure and isothermal compression of  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$  to 50 kbars, *J. Appl. Phys.*, 51(10), 5362-5367.
- Finger L. W. and Prewitt C. T. (1989) Predicted composition for high-density hydrous magnesium silicates, *Geophys. Res. Lett.*, 16, 1395-1397.
- Giessen B. C. and Gordon G. E. (1967) X-ray diffraction: New high-speed technique based on X-ray spectrography, *Science*, 159, 973-975.

- Jamieson J. C., Fritz J. N., and Manghnani M. H. (1982) Pressure measurement at high temperature in X-ray diffraction studies: Gold as a primary standard, *Advances in Earth & Planet. Sci.*, 12, *High-Pressure Research in Geophysics*, eds S. Akimoto, M. H. Manghnani, 27-48.
- Kim Y. H. and Na K. C. (1994) High pressure X-ray diffraction studies on a graphite using Synchrotron Radiation, *J. Petrol. Soc., Korea*, 3, 34-40.
- Liu L., Bassett W. A., and Takahashi T. (1974) Isothermal compression of a spinel phase of  $\text{Co}_3\text{SiO}_4$  and magnesian ilmenite, *J. Geophys. Res.*, 79, 1160-1164.
- Liu L. (1987) Effects of  $\text{H}_2\text{O}$  on the phase behavior of the forsterite-enstatite system at high pressures and temperatures and implications for the Earth, *Phys. Earth Planet. Inter.*, 49, 142-167.
- Mao H. K., Shu J., Hu J., and Hemley R. J. (1994) High pressure X-ray diffraction study of diaspore, *Solid State Comm.*, 90(8), 497-500.
- Meade C. and Jeanloz R. (1990) Static compression of  $\text{Ca}(\text{OH})_2$  at room temperature: Observations of amorphization and equation of state measurements to 10.7 GPa, *Geophys. Res. Lett.*, 17, 1157-1160.
- Ming L. C., Jayaraman A., Shieh S. R., Kim Y. H., and Manghnani M. H. (1994) An in-situ high pressure X-ray diffraction study of  $\text{PbHfO}_3$  to 52.5 GPa at room temperature and pressure-induced phase transformations, *J. Phys. Chem. Solids*, 55 (11), 1213-1219.
- Ruoff A. L. and Vanderborgh C. A. (1991) Hydrogen reaction of ruby at high pressure: Implication for claims of metallic hydrogen, *Phys. Res. Lett.*, 66, 754-757.
- Ruoff A. L. and Vanderborgh C. A. (1993) Hydrogen reaction of ruby at high pressure: Implication for claims of metallic hydrogen, *Phys. Res. Lett.*, 71, 4279.
- Sato Y. and Akimoto S. I. (1979) Hydrostatic compression of four corundum-type compounds:  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$ , *J. Appl. Phys.*, 50(8), 5285-5291.
- Simakov G. V., Pavlovskiy M. N., Kalashnikov N. G., and Trunin R. F. (1974) Shock compression of twelve minerals, *Izvestiya Earth Phys.*, 10, 11-17.
- Tyburczy J. A., Duffy T. S., Ahrens T. J., and Lange M. A. (1991) Shock wave equation of state of serpentine to 150 GPa: implications for the occurrence of water in the earth's lower temperature and mantle, *J. Geophys. Res.*, 96, 18011-18027.
- Wechsler B. A. and Prewitt C. T. (1984) Crystal structure of ilmenite ( $\text{FeTiO}_3$ ) at high temperature and at high pressure, *Am. Mineral.*, 69, 176-185.
- Wilburn D. R. and Bassett W. A. (1978) Hydrostatic compression of iron and related compounds: an overview, *Am. Mineral.*, 63, 591-596.
- Xu J. A., Hu J., Ming L. C., Huang E., and Xie H. (1994) The compression of diaspore,  $\text{AlO}(\text{OH})$  at room temperature, *Geophys. Res. Lett.*, 21, 161-164.