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Hydrostatic compression of iron and related compounds: an overview

David R. Wilburn[1] and William A. Bassett[2]

Department of Geological Sciences, University of Rochester
Rochester, New York 14627

Abstract

Compression data for iron were collected using X-ray diffraction on samples under hydrostatic pressure. Stress inhomogeneity effects were eliminated by the use of an encapsulated liquid pressure medium. Pressures were determined on the basis of both NaCl and ruby fluorescence methods; no significant difference was observed when both were used at the same time. Compression data for a gasketed sample of γ–Fe_2SiO_4 + NaCl were also reported. Comparisons of both data sets were then made with existing hydrostatic and non-hydrostatic data for materials compressed in the diamond cell. The bulk modulus (K_0) of iron reported here was found to be 1.64±0.07 Mbar if the pressure derivative of bulk modulus (K_0') was set at 4.0. The difference observed between bulk moduli calculated from hydrostatic and non-hydrostatic data is attributed to the presence of stress anisotropy in the latter case, and is apparently related to the shear strength of the sample. The discrepancies between the bulk moduli obtained under hydrostatic and non-hydrostatic conditions for α–Fe, α–Fe_2SiO_4, γ–Fe_2SiO_4, Fe_2O_3, Fe_3O_4, and SiO_2 appear to increase with increasing shear strength.

Introduction

The presence of iron in the earth's interior has led to a great deal of interest in the elastic behavior of iron and its compounds at high pressures. X-ray diffraction of samples while under high pressures has been utilized for the past 15 years to provide information on bulk moduli and their pressure derivatives. Many of the earlier studies used solid pressure-transmitting media, which have been shown to introduce some error (Jamieson and Olinger, 1971; Sato, 1977). Recently, investigators have reduced the possibility of such errors by immersing the sample in a liquid medium. In this paper, we compare the results from these investigations in terms of the effect of the pressure-transmitting media on bulk modulus.

Experimental procedures

Compression measurements on a wide number of samples of geophysical importance have been made using the opposed diamond anvil device developed by Bassett *et al.* (1967) based on an earlier design of Piermarini and Weir (1962). In this device a sample is placed between the flat, parallel faces of two single-crystal, 1/8 carat diamonds. After pressure has been applied to the sample by means of a piston-screw assembly, an X-ray beam is then directed through the diamonds and the sample. The cell is designed so that scattered X-rays are recorded on a cylindrical film.

In the case where a solid pressure-transmitting medium is used, the sample is mixed with a highly compressible material such as NaCl in a volume ratio of 1:1. The NaCl serves as both a pressure-transmitting medium and pressure standard. Pressures are then calculated from the observed cell volume of the NaCl, using either the Hildebrand equation (Weaver *et al.*, 1971) or the Decker equation (Decker, 1965). Deviation between these two methods falls within experimental error. The assumption made is that the pressure of the surrounding solid medium is equal to that of the sample. However doubt has recently been cast on this assumption (Jamieson and Olinger, 1971).

Since a liquid provides truly hydrostatic conditions, it is desirable to surround the sample with a liquid to ensure pressure uniformity. This procedure has been followed in a number of recent investigations. The results on iron, reported for the first time

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[1] Present address: U.S. Bureau of Mines, 4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213.

[2] Present address: Department of Geological Sciences, Cornell University, Ithaca, New York 14853.

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here, also utilized this technique. Except for our use of a gasket, the instrumentation used in this investigation is virtually the same as that used by Takahashi *et al.* (1968).

The iron sample was a finely-powdered iron sponge supplied by Johnson Matthey and Company, Ltd. The chemical purity of the iron was determined spectrographically. The following sample impurities were observed: Mn 3ppm, Mg 2ppm, Ni 2ppm, Si 2ppm, Al 1ppm, and Cu less than 1ppm. NaCl was standard reagent-grade.

The finely-powdered iron is immersed in a liquid and contained by a gasket between the diamond anvils. A methanol–ethanol mixture 4:1 by volume (Piermarini *et al.*, 1973) was selected as the pressure-transmitting medium. The gasket consists of a foil of tempered 301 stainless steel 0.25 mm thick (initial thickness) with a hole 0.2–0.4 mm in diameter. The anvil faces range from 0.5–0.7 mm across. A chip of ruby (0.05 mm across) is placed in the hole with the sample and alcohol mixture (Barnett *et al.*, 1973).

As in the earlier compression studies, a Mo*Kα* X-ray beam was directed through the sample, and diffracted X-rays were recorded photographically by placing a film cassette behind the sample. The diffraction pattern from an external flake of polycrystalline NaCl was recorded on the same film as a means of detecting and recording any variation in cell geometry.

Lattice parameters and cell volumes of the compressed iron were calculated from the (110), (200), (211), and in some cases (220) diffraction lines. The values listed in Table 1 are averages of the measured lines for a given run. The lattice parameters thus calculated are accurate to 0.07 percent, the volumes to 0.21 percent. Pressures are accurate to ±0.75 kbar.

Pressures were applied to the samples in cycles. Once an individual sample was loaded, the cell was taken up in pressure until the maximum pressure desired for that cycle was attained. A period of an hour or more was then allowed to elapse to permit relaxation of the gasket, and then pressure on the sample was measured by the ruby technique. The X-ray diffraction procedure was then employed to obtain compression data and NaCl pressures, then the pressure was remeasured using the ruby method.

Table 1. Experimental data. The effect of pressure on the lattice parameter a, and the resulting volume change V/V_0, of iron at (25±5)°C. Hydrostatic conditions are present.

Cycle	NaCl V/Vo	P(Kbar)	Ruby λ/λo	P(Kbar)	Iron a(bcc)Å	V/Vo
3	0.997	1	1.000	<2	2.866	1.000
1	0.964	10	1.0005	10	2.860	0.993
1	0.905	30	1.0015	29	2.850	0.983
5	0.886	39	1.0020	39	2.845	0.978
2	0.877	43	1.0023	43	2.842	0.975
5	0.861	51	1.0027	52	2.838	0.970
3	0.852	56	1.0030	57	2.835	0.968
5	0.831	69	1.0036	69	2.828	0.960
4	-	-	1.0040	75	2.829	0.961
6	-	-	1.0043	82	2.822	0.954
4	0.792	98	1.0051	98	2.819	0.951
4	0.785	101	1.0053	101	2.814	0.946
4	0.781	107	1.0057	108	2.811	0.943

Table 2. Bulk modulus, K_0 and $(\partial K/\partial P)_T$, K_0' of iron.

Ko	Ko'	Investigator
1.64	5.06	Voronov & Vereshchagin (1961)
1.64	5.94	Rotter & Smith (1966)
1.73	4.0	Takahashi et al. (1968)
1.64	4.0	This work

Once the desired information was obtained for a given pressure, pressure was released slightly until the next desired pressure was attained. This procedure was then repeated until all desired pressures were attained. At this point the pressure in the cell was released, and the cell was X-rayed again at one bar pressure in order to determine the room pressure values for lattice parameter and cell volume. This technique was employed so that the thickness of the sample (<0.25mm) was as nearly constant as possible over all pressure runs for a given cycle.

Results

A summary of all relevant data can be found in Table 4. Experimental data for iron are reported in Tables 1–3 and Figure 1. The value of the 1-bar isothermal bulk modulus, K_0, was calculated by means of a least-squares fit of the experimental data to the Birch-Murnaghan equation of state:

$$P = \tfrac{3}{2}K_0\left[\left(\frac{V}{V_0}\right)^{-7/3} - \left(\frac{V}{V_0}\right)^{-5/3}\right]$$

$$\left\{1 - \tfrac{3}{4}(4 - K_0')\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right] + \cdots\right\}$$

Table 3. Values of the isothermal bulk modulus, K_0, of iron obtained for given values of K_0' from the Birch-Murnaghan equation of state.

Ko	Ko'	Ko	Ko'
1.77	1	1.60	5
1.72	2	1.58	5.5
1.68	3	1.57	6
1.64	4	1.53	7

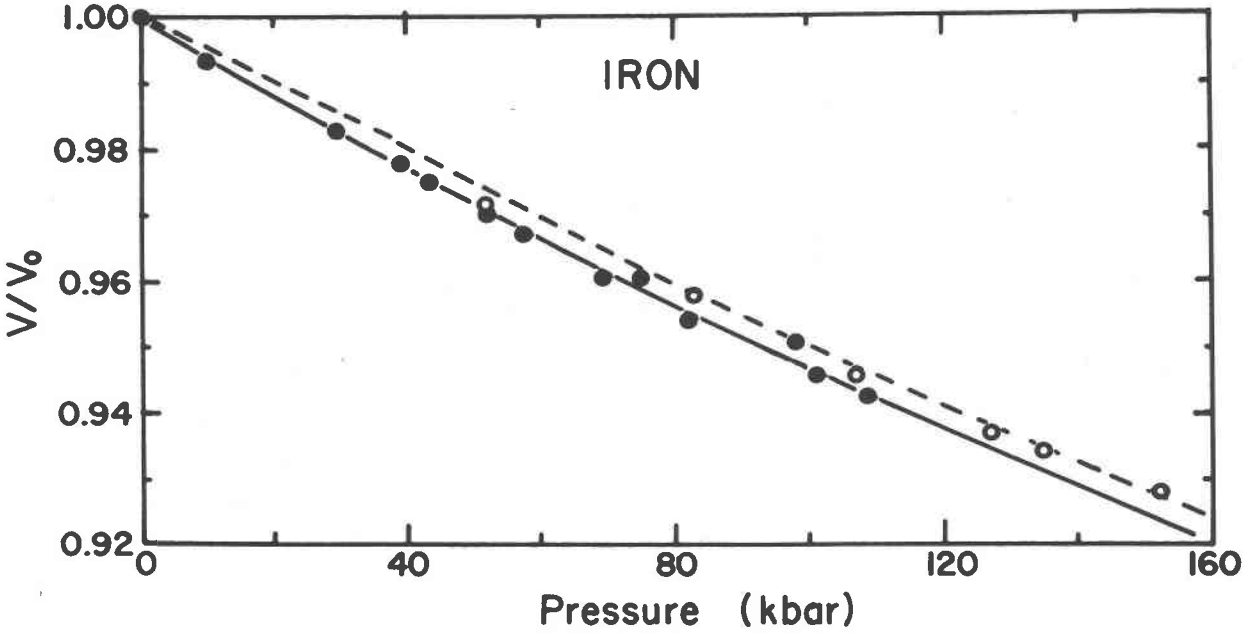

Fig. 1. Compression data for iron. The closed circles are data points measured by hydrostatic compression. The open circles are data points measured under ungasketed, non-hydrostatic conditions (Takahashi *et al.*, 1968). The two highest pressure points are for α–iron that has metastably persisted into the ϵ–iron stability field. The solid curve is a least-squares fit of the hydrostatic data to the Birch-Murnaghan equation. The dashed line is an interpretation of the data of Takahashi *et al.* assuming that the strength of the sample increases up to a point and then remains fairly constant with increasing pressure (Kinsland and Bassett, 1976).

where V and V_0 are the volume at pressure P and 1 bar respectively, and K_0' is the value of $(\partial K/\partial P)_T$ evaluated at 1 bar. If the assumption is made that K_0' is equal to 4, an assumption that is justified for oxides and silicates, the resulting bulk modulus (K_0) was found to be equal to 1.64±0.07 Mbar. Table 3 shows additional values for K_0, with the assumption of other values for K_0'.

Discussion

As can be seen in Table 2, the bulk modulus reported in this paper is slightly lower than the recalculated value of Takahashi *et al.* (1968), which is based upon non-hydrostatic data. The difference between these two values is believed to be significant, although the errors are such that a small amount of overlap exists between bulk moduli.

The static K_0 reported here is consistent with ultrasonic bulk moduli reported by Voronov and Vereschagin (1961) and Rotter and Smith (1966); however, there is a significant difference among K_0' values. It should be noted, however, that variation of K_0' among the ultrasonic measurements appears to be as much as 20 percent, indicating that the accuracy of this parameter is less well known than that of the bulk modulus.

For each compound tested, the bulk modulus determined from hydrostatic techniques was found to be less than the corresponding K_0 for that material measured under ungasketed conditions (Table 4). Consequently, the compression curve calculated for the hydrostatic data lies below the curve based on

Table 4. Bulk moduli for some materials in different media.

	Bulk Moduli (Mbar)		
Sample	Liquid Medium (Mbar)	Solid Medium in Diamond Cell	% Difference *
Stishovite	2.8 - 3.0 [a] #	3.44 ± 0.27[g]	17.4***
	2.81 - 3.01[b] **		20.7***
Magnetite	1.55 ± 0.12[c]	1.83 ± 0.10[h]	18.0
Hematite	1.99 ± 0.06[c]	2.28 ± 0.15[i]	14.6
Ringwoodite	1.97 ± ? [b]	2.12 ± 0.10[j]	7.6
	1.89 ± 0.12[d]		12.2
Fayalite	1.24 ± 0.02[e] *	1.35 ± 0.15[k]	8.9
Iron	1.64 ± 0.07[f]	1.73 ± 0.05[l]	5.7

a. Olinger (1976)
b. Sato (1977)
c. Bassett et al. (1977)
d. Wilburn & Bassett (1976)
e. Yagi et al. (1975)
f. This work
g. Liu et al. (1974)
h. Mao et al. (1974)
i. Bassett & Takahashi (1974)
j. Mao et al. (1969)
k. Takahashi (1970)
l. Takahashi et al. (1968)

* Ko' = 5.0
\# Ko' = 3.0-6.0
** Ko' = 0.0-5.0
*** From Ko values using Ko' = 4.0

corresponding ungasketed data. This systematic departure leads to the conclusion that the ungasketed samples are under non-hydrostatic conditions. Furthermore, because the samples and experimental apparatus used in both techniques are otherwise essentially equivalent, any deviation of experimental results can be solely attributed to this change in experimental technique.

There may be a minor error introduced in these comparisons due to the fact that the bulk moduli were based on compression data collected over different pressure ranges for different ungasketed samples. This is a matter that would need to be taken into consideration before attempting to make these relationships sufficiently quantitative for correcting non-hydrostatic data.

The question remains as to whether the use of a liquid surrounding the sample is absolutely necessary. Perhaps the gasket filled with dry NaCl provides a sufficiently isotropic stress field to produce a nearly hydrostatic environment. To test this possibility a series of pressure runs was conducted on γ–Fe_2SiO_4 using identical samples and instrumentation employed by both Mao *et al.* (1969) and Wilburn and Bassett (1976). In these experiments, however, the γ–Fe_2SiO_4 (ringwoodite) + NaCl samples were loaded into a gasket placed between the diamonds, as described previously but with no liquid added. Data generated from these experiments are included in Table 5 and Figure 2.

The compression curve based on data collected this way fell above the curve based on hydrostatic measurements but below the curve based on non-hydrostatic, ungasketed measurements. A bulk modulus of 2.07 Mbar was calculated from this set of data, assuming a K_0' of 4.0. As expected, this value falls between the hydrostatic value of 1.89 Mbar and the non-hydrostatic value of 2.12 Mbar. These data suggest that the gasket by itself does not provide complete hydrostaticity, but since it does serve to contain the sample, it does limit extrusion of the sample from between the diamonds, thereby decreasing the effect of stress anisotropy. In the non-hydrostatic, ungasketed case, differential sample extrusion may lead to bridging of the grains, which results in a greater anisotropic distribution of stress.

Table 5. Experimental data. The effect of pressure on the lattice parameter and resulting volume change of γ–Fe_2SiO_4 at (25±5)°C. Sample is gasketed but hydrostatic conditions are not present.

Cycle	NaCl V/Vo	P(Kbar)	Ruby λ/λo	P(Kbar)	a(Å)	γ-Fe_2SiO_4 V/Vo
6	0.997	1	1.000	<2	8.236	1.0004
3	0.920	24	1.0013	25	8.199	0.987
1	0.869	46	1.0024	46	8.176	0.979
3	0.834	67	1.0035	68	8.150	0.969
2	0.816	79	1.0042	79	8.135	0.964
5	0.811	83	1.0044	83	8.141	0.966
1	0.789	99	1.0052	100	8.113	0.956
4	0.742	145	1.0077	144	8.064	0.939
6	0.733	156	1.0081	154	8.063	0.939

The geometry of the diamond cell is such that the diffraction lines from an ungasketed sample represent *d*-spacings which are abnormally large, since their orientation is one of least stress. Consequently, volumes calculated from these *d*-spacings are too large. A bulk modulus calculated from these data would also be anomalously high. A detailed discussion of this stress state can be found in Kinsland and Bassett (1976) or Wilburn and Bassett (1976).

The degree of deviation depends upon the amount of anisotropic stress imposed upon the sample. This in turn can be related to the shear strength of the sample and the pressure to which the sample is loaded. In the case where the shear strength of the sample is much greater than that of the NaCl with which it is mixed, the expected difference in K_0 would be large. This appears to hold true for materials such as stishovite (Fig. 3). The deviation in K_0 should be small, on the other hand, for a material whose shear strength is close to that of NaCl. The data for iron, which has a low shear strength, are consistent with this suggestion.

This relationship is shown more quantitatively in Figure 3 as a plot of bulk modulus discrepancy versus the contrast of shear strength between the sample and the surrounding NaCl. Although not conclusive, this plot suggests that the greater the contrast in shear strength between sample and NaCl, the greater the bulk modulus discrepancy.

Conclusions

All of the pressure measurements in this study made by the NaCl and ruby methods agreed within experimental error (Tables 1 and 5).

Results of the investigations discussed in this paper indicate that data collected on ungasketed samples in the diamond cell may be in error due to the presence of an anisotropic stress distribution. This leads to calculated bulk moduli for ungasketed samples which are too high. The magnitude of the error appears to increase with increasing difference between the shear strength of the sample and the surrounding NaCl.

At present the relationship is very indefinite. With

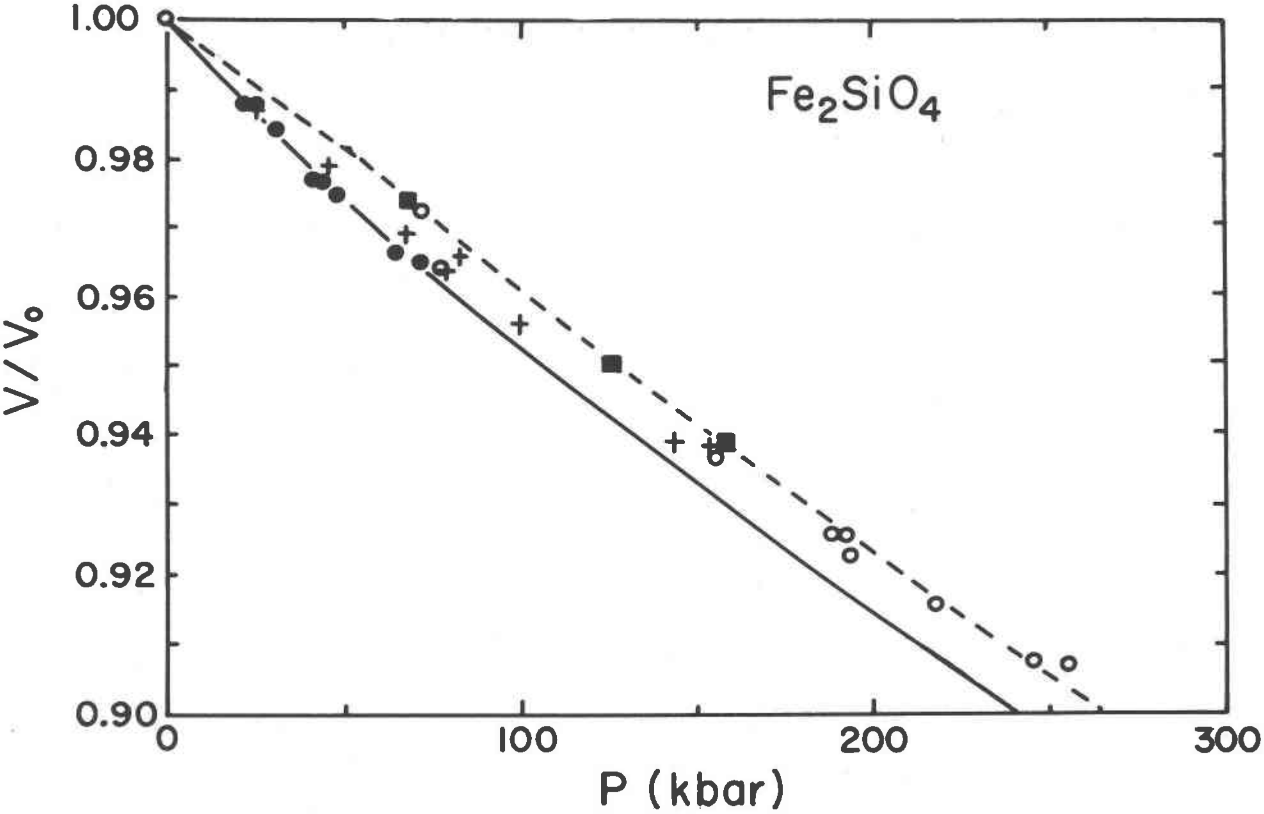

Fig. 2. Compression data for γ-Fe$_2$SiO$_4$. The closed circles are data points obtained by hydrostatic compression. The open circles are data points obtained under ungasketed, non-hydrostatic conditions (Mao *et al.*, 1969). The squares are data points obtained under ungasketed, non-hydrostatic conditions (Wilburn and Bassett, 1976). The pluses are data points obtained under gasketed conditions with a solid pressure medium (this work). The solid curve is a least-squares fit of the hydrostatic data to the Birch-Murnaghan equation. The dashed line is an interpretation of the data from Mao *et al.* assuming that the strength of the sample increases up to a point and then remains fairly constant with increasing pressure (Kinsland and Bassett, 1976).

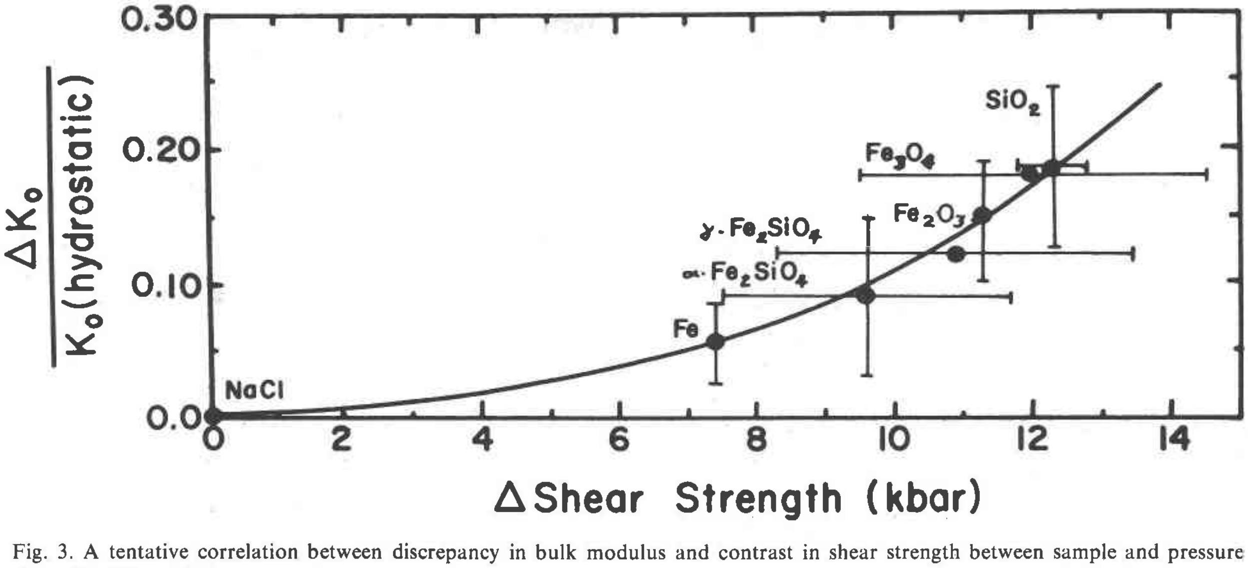

Fig. 3. A tentative correlation between discrepancy in bulk modulus and contrast in shear strength between sample and pressure medium (NaCl) at 40 kbar.

more data, however, it may be possible to derive a method for correcting compression data collected under non-hydrostatic conditions in the diamond cell. This would be of value not only for correcting older measurements but also for making measurements at pressures greater than those that permit the use of a liquid.

Gasketing of the sample without the use of a liquid reduces the error somewhat but does not provide an adequately isotropic stress field to eliminate the error.

Future compression work by X-ray diffraction should take these effects into consideration.

Acknowledgments

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