

In Situ X-Ray Study of Thermal Expansion and Phase Transition of Iron at Multimegabar Pressure

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The density of ϵ -iron has been calculated at pressures and temperatures up to 300 GPa and 1300 K, respectively. We observe ϵ to β phase transition at pressures between 135 and 300 GPa and temperature above 1350 K; the pattern can be interpreted in terms of double hexagonal close-packed structure. The density calculated at high pressure and temperature (330–360 GPa and 5000–7000 K) closely matches with preliminary reference Earth model density, thereby imposing constraint on the composition of the Earth's inner core.

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Iron is considered as the major component in the core of the Earth [1]. Therefore, physical properties of iron at the pressures and temperatures of Earth's core are very important for modeling composition and dynamics of the core [2,3]. While data on the static compression of iron at room temperature are available up to a pressure of 300 GPa [4], the data on thermal expansion of ϵ -Fe are very limited [5–7]. The results of *in situ* x-ray studies [6] in a multianvil apparatus at pressures 22–32 GPa indicate that thermal expansion of ϵ -Fe could be significantly higher than estimated before [7]. While there is evidence of a phase transition at high pressure and temperature of ϵ (hcp, hexagonal-close-packed) to β phase with double hcp (dhcp) [8,9] or orthorhombic structure [10,11], experiments performed with energy dispersive detectors and the laser heating technique led to a conclusion that the β -Fe is metastable [9,12]. Here we present the results of experiments on x-ray studies of ϵ -Fe in an externally heated diamond anvil cell (DAC) at pressure over 300 GPa and temperatures above 1300 K. By combining the present results with our earlier data [8], we could obtain the equation of state (EOS) for iron at multimegabar pressures, estimate density of iron at conditions of the Earth's core, and demonstrate that β -Fe with dhcp structure could be synthesized at pressures up to 300 GPa.

The experiments were performed on beam line ID 30 at the European Synchrotron Radiation Facility (ESRF) (Grenoble, France). In our experiments powder diffraction data were collected with fine incident x-ray beam ($8 \times 9 \mu\text{m}^2$ or less) of 0.3738 \AA wavelength on the Fast Scan imaging plate. The collected images were integrated in order to obtain the conventional diffraction spectrum.

We heat the samples externally in a Mao-Bell-type DAC [8,13]. Powdered samples (iron of 99.999% purity) were loaded into the $30\text{--}35 \mu\text{m}$ initial diameter hole in Regasket, which then confined between beveled diamonds with $40 \mu\text{m}$ ($50 \mu\text{m}$ in experiments with maximum pressure 240 GPa) culets. Pressure was determined with

powdered platinum (99.999% purity) as an *in situ* x-ray standard mixed in small proportion with the iron sample. It is likely that the platinum scale is accurate to a few percent [4,14].

In our analysis of the integrated x-ray spectra, we used the program GSAS [15] and PEAKFIT 4.0 (Fig. 1). The lattice parameter of Pt was determined with an accuracy better than 0.002 \AA with resulting uncertainty of 2 GPa at pressure up to 100 GPa and of 5 GPa up to 300 GPa [14].

We reached a maximum temperature of 1370(5) K at a pressure of 305(5) GPa. Diamonds failed on a further increase in temperature at ~ 240 GPa in the first experiment, and on the heating sample above 310 GPa in the second experiment, but the samples were saved for lattice parameter measurements of both α -Fe and Pt at room conditions. The lattice parameters matched their initial values before experiments within the experimental errors (0.0004 \AA)

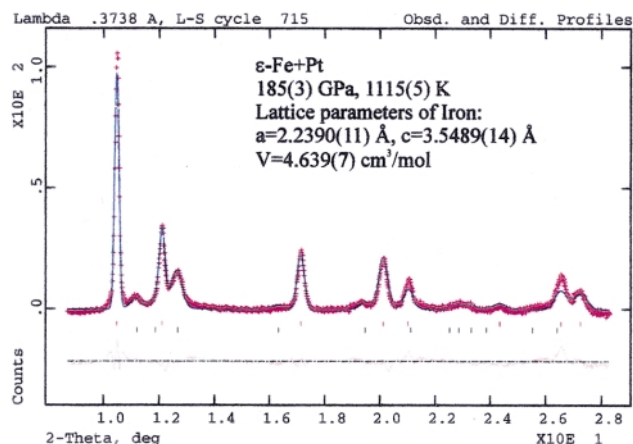


FIG. 1 (color). Typical example of analyzed integrated patterns of the spectrum collected at 1115(5) K and 185(3) GPa. GSAS program package [15] was used. The lower ticks mark positions of Fe and the upper one Pt pressure calibrant. Iron exhibits strong preferred orientation along the (001) direction. Background was subtracted.

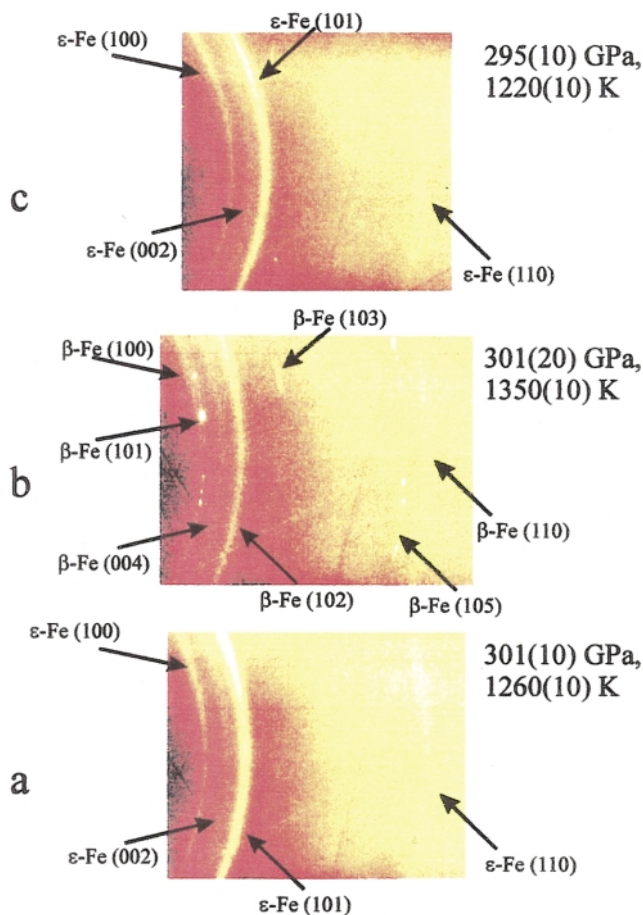


FIG. 2 (color). Examples of images collected on ID 30 beam line at ESRF with monochromatic 0.3738 Å radiation with fast image plate during electrical heating of iron powder: (a) at 1260(10) K temperature and 301(10) GPa pressure determined using ϵ -Fe equations of state; (b) at 1350(10) K and 301(20) GPa (uncertainty in pressure reflects unknown equation of state of β -Fe). Positions of all lines are presented in Table I and could be described in terms of dhcp structure with lattice parameters $a = 2.169(3)$ Å and $c = 6.936(22)$ Å; (c) at 1220(10) K and 295(10) GPa (determined using ϵ -Fe equations of state). All figures correspond to the same position of the x-ray beam spot near the center of pressure chamber. Appearance upon heating and disappearance upon cooling spotty lines of β -Fe (b) demonstrate the reversible nature of ϵ - β transformation.

indicating that there was no reaction between Pt and Fe in our experiments.

During heating at different pressures between 135 and 305 GPa, we observed the appearance of new spotty lines at temperature above 1325–1350 K [Figs. 2(a) and 2(b)]. Such lines could not be due to chemical reaction, because after experiments we lowered temperature and pressure to ambient condition and did not find any diffraction lines except for the lines of α -Fe and Pt. Upon cooling at temperatures below 1250 K, the spotty lines disappeared and only lines of ϵ -Fe remained [Fig. 2(c)]. This observation could be explained as due to a reversible transformation of ϵ to β iron with dhcp structure (Table I, Fig. 2) [8,9,16]. Detection of β -Fe at pressure above 300 GPa and high

TABLE I. Comparison of observed and calculated diffraction pattern of dhcp iron at 301(20) GPa and 1350(10) K [see Fig. 3(b)].

Hkl	d_{obs} (Å)	I_{obs} (%)	d_{calc} (Å) ^a	I_{calc} (%) ^b
100	1.878	20	1.878	9
101	1.816	30	1.813	47
004	1.736	30	1.734	35
102	1.646	100	1.652	100
103	1.458	5	1.458	20
104	1.271	3	1.274	4
105	1.121	25	1.116	10
110	1.085	20	1.084	15

^aCalculated lattice parameters are $a = 2.169(3)$ Å, $c = 6.936(22)$ Å.

^bCalculated and observed intensities are in qualitative agreement. Quantitative comparison is difficult due to the effects of preferred orientation, recrystallization, poor crystallite statistics, and limited detected area (due to the slit in the Mao-Bell-type DAC).

temperature means that this phase could form the bulk of Earth's inner core (if no other new phase of iron is found at temperatures above 1400 K at high pressure).

In all, 109 data points were collected over the pressure range of 80 to 305 GPa and at temperatures between 300 and 1300 K to determine the EOS of ϵ -iron. When combined with our previous data [8] in the pressure range of 18–68 GPa and at temperatures up to 1700 K (79 data points), there is enough information to determine a thermal equation of state of ϵ -Fe at Earth's core conditions.

We used Birch Murnaghan EOS to describe our experimental data [17–20]:

$$P = 1.5K_{T,0}[(V_{T,0}/V)^{7/3} - (V_{T,0}/V)^{5/3}] \times \{1 - 0.75(4 - K_{T,0}^l)[(V_{T,0}/V)^{2/3} - 1]\}, \quad (1)$$

where $K_{T,0}$, $K_{T,0}^l$, and $V_{T,0}$ are the bulk modulus, its pressure derivative, and the volume of the unit cell at zero pressure and temperature T (in K), respectively;

$$K_{T,0} = 1/(b_1 + b_2T + b_3T^2).$$

The unit cell volume $V_{T,0}$ is given by the following expression: $V_{T,0} = V_0 \exp(\int \alpha_{T,0} dT)$, where V_0 and $\alpha_{T,0}$ are, respectively, the unit cell volume at zero pressure and the thermal expansivity at zero pressure and temperature T (K).

Table II and Fig. 3(a) show results of fitting of our data with (1). To discuss the accuracy of the determined

TABLE II. Thermoelastic parameters of ϵ -iron.

$V_0, \text{cm}^3/\text{mol}$	6.73(1)
$K_{300,0}^l$	5.81(6)
$\alpha_{300,0}, 10^{-5} \text{K}^{-1}$	6.93(37)
$b_1, 10^{-3} \text{GPa}^{-1}$	5.973(46)
$b_2, 10^{-6} \text{K}^{-1} \text{GPa}^{-1}$	1.380(17)
$b_3, 10^{-10} \text{K}^{-2} \text{GPa}^{-1}$	4.600(80)

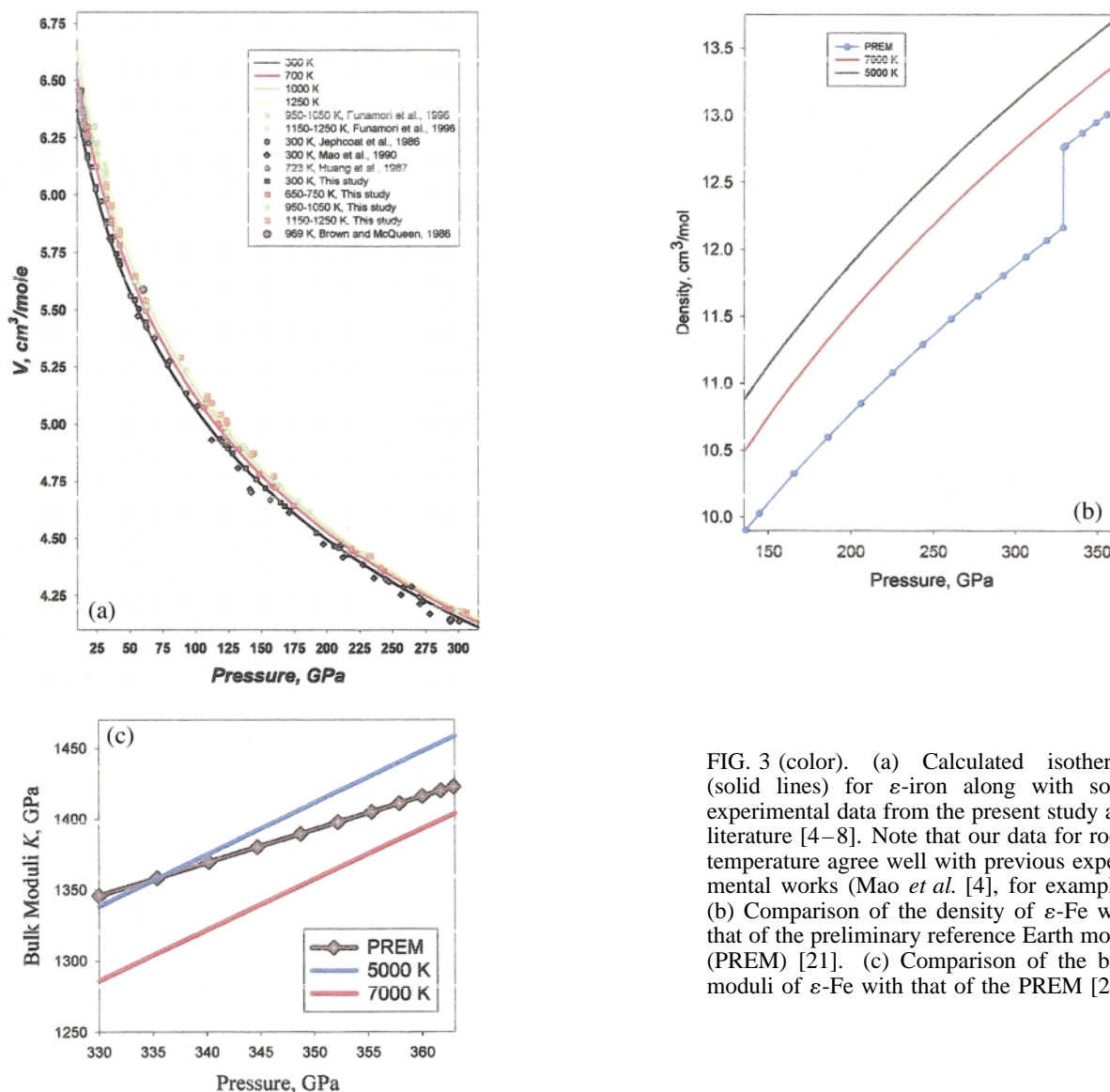


FIG. 3 (color). (a) Calculated isotherms (solid lines) for ϵ -iron along with some experimental data from the present study and literature [4–8]. Note that our data for room temperature agree well with previous experimental works (Mao *et al.* [4], for example). (b) Comparison of the density of ϵ -Fe with that of the preliminary reference Earth model (PREM) [21]. (c) Comparison of the bulk moduli of ϵ -Fe with that of the PREM [21].

thermoelastic properties, we should estimate the possible errors in the input experimental data. The errors in temperature measurements with thermocouple is ± 5 K. Errors in molar volume of ϵ -Fe are within ± 0.005 cm³/mol at 100 GPa and increase to ± 0.01 cm³/mol at 300 GPa. Uncertainty in pressure increases from 2 to 5 GPa at the highest pressure. The errors in pressure and temperature are reflected in statistical errors in determined thermoelastic parameters (Table I). Deviatoric stress in DAC, especially at very high pressures, could be a source of significant systematic errors in determination of lattice parameters [22,23]. However, for materials with moderate elastic anisotropy and for data collected in the angle dispersive mode, the systematic errors in the lattice parameters due to the uniaxial stress are “masked” in the errors of the fitting procedure [15,21,24]. Further, the effect of the stress is maximum for (00 l)-type reflections [21], which in our case are absent due to preferred orientation. In general, nonhydrostatic conditions of experiments could lead to overestimation of the molar volume at given pressure

[21,22]. With increasing temperature deviatoric stresses in DAC decrease [8] and, as a result, the changes in molar volume with temperature (and thermal expansion) could be underestimated.

Thermal expansion at 22 GPa is $4.31 \cdot 10^{-5}$ K⁻¹ and at 32 GPa is $3.65 \cdot 10^{-5}$ K⁻¹. Thus, our values of thermal expansion are in good agreement with data by Funamori *et al.* (1996), $3.88 \cdot 10^{-5}$ K⁻¹ at 22 GPa and $3.16 \cdot 10^{-5}$ K⁻¹, especially if we take into account uncertainty of 30% in the Funamori *et al.* (1996) data (mainly due to the changes in the volume of iron before and after heating).

The average thermal expansivity $\bar{\alpha} = \ln(V_T/V_{300})/T - 300$ at 202 GPa and 5200 K is $9.13 \cdot 10^{-6}$ K⁻¹ which is close to the value obtained in shock compression measurements [$(9.1 \pm 2.0) \cdot 10^{-6}$ K⁻¹ [25]] and theoretical calculations [$1.0 \cdot 10^{-5}$ K⁻¹ [26]]. Bulk moduli of ϵ -Fe at 211 GPa and 300 K is 1110 GPa in good agreement with recently reported value 1071(107) GPa [27].

The equation of state for the β -iron phase is not studied yet, but available information from previous [8] and present studies (Table I, Fig. 2) suggest that the density of β -Fe may be very close to the density of ε -Fe.

Figures 3(b) and 3(c) show a comparison of the density and bulk moduli of ε -Fe with that of the core according to the preliminary reference earth model (PREM) [28]. Despite a significant discrepancy in the estimation of the temperature of Earth's core, the most realistic values fall between 5000 and 7000 K. The PREM bulk moduli for inner core fall between calculated bulk moduli for 5000 and 7000 K isotherms [Fig. 3(c)]. At 5000 K density of ε -Fe is 5% higher than PREM density of the inner core, and at 7000 K, just 2.5% higher. More than ten years ago Brown and McQueen [29], based on shock wave experiments on iron, wrote "...predicted velocities and densities for iron on geotherm are slightly large (by 10% or less) than average values for inner core. Such deviations may reflect both poor seismic resolution and uncertain thermal corrections for the equation of state of iron." Our present work provides reliable thermal equation of state of ε -Fe based on static compression data and our conclusion generally supports the earlier shock wave data [29], except for the fact that the difference in density of ε -Fe and PREM density at the inner core conditions is 2 to 4 times less than the earlier estimate [29]. As discussed above, possible systematic errors in our experiments (deviatoric stresses, for example) could decrease the measured values of thermal expansion, and, as a result, the real density of ε -Fe at Earth's core conditions could be even lower than that shown in Fig. 3(b). Future determination of shear moduli of iron at Earth's inner core conditions combined with data on density and bulk moduli obtained in the present study could provide strong constraints on the composition and temperature of the deep interior.

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- [1] F. Birch, *J. Geophys. Res.* **57**, 227 (1952).
 [2] F. Birch, *Geophys. J. R. Astron. Soc.* **4**, 295 (1961); *J. Geophys. Res.* **69**, 4377 (1964).
 [3] R. Jeanloz, *J. Geophys. Res.* **84**, 6059 (1979); T. A. Ahrens and M. L. Jonson, in *A Handbook of Physical Constants* (American Geophysical Union, Washington, D.C., 1995), 143 pp.
 [4] H. K. Mao, Y. Wu, L. C. Chen, J. F. Shu, and A. P. Jephcoat, *J. Geophys. Res.* **95**, 21 737 (1990).
 [5] E. Huang, W. A. Basset, and P. Tao, *J. Geophys. Res.* **92**, 8129–8135 (1987).
 [6] N. Funamori, T. Yagi, and T. Uchida, *Geophys. Res. Lett.* **23**, 953–956 (1996).
 [7] A. Jephcoat and P. Olson, *Nature (London)* **325**, 332–335 (1987).
 [8] S. K. Saxena, L. S. Dubrovinsky, P. Häggkvist, Y. Cernius, G. Shen, and H. K. Mao, *Science* **269**, 1703–1704 (1995); L. S. Dubrovinsky, S. K. Saxena, and P. Lazor, *Phys. Chem. Miner.* **25**, 434–441 (1998); *Geophys. Res. Lett.* **24**, 1835–1838 (1997); *Eur. J. Miner.* **10**, 43–47 (1998).
 [9] C. S. Yoo, J. Akella, A. Compbell, H. K. Mao, and R. J. Hemley, *Science* **270**, 1473–1475 (1995); C. S. Yoo, P. Soderlind, and A. Compbell, *Phys. Lett. A* **214**, 65 (1996).
 [10] D. Andrault, G. Fiquet, M. Kunz, F. Visocekas, and D. Hausermann, *Science* **278**, 831 (1997).
 [11] L. S. Dubrovinsky, S. K. Saxena, P. Lazor, and H.-P. Weber, *Science* **281**, 5373 (1998).
 [12] G. Shen, H. K. Mao, R. J. Hemley, T. S. Duffy, and M. L. Rivers, *Geophys. Res. Lett.* **25**, 373 (1998).
 [13] S. Rekh, L. S. Dubrovinsky, and S. K. Saxena, *High Temp.-High Press.* **31**, 299–305 (1999).
 [14] N. C. Holmes, J. A. Moriarty, G. R. Gathers, and W. J. Nellis, *J. Appl. Phys.* **66**, 2962–2967 (1989); W. J. Nellis, J. A. Moriarty, A. C. Mitchell, M. Ross, R. G. Dandrea, N. W. Ashcroft, N. C. Holmes, and G. R. Gathers, *Phys. Rev. Lett.* **60**, 1414–1417 (1988).
 [15] A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LAUR, 86-748, 1994.
 [16] The difficulties associated with synthesis and identification of β -Fe were discussed in our previous works [8,11]. Major problems are as follows: detection of spotty lines with the energy dispersive method, interaction of oxides (periclase, corundum, etc.) pressure medium with iron in laser heated spot, and temperature distribution, and thermal stresses in laser heating technique. Those problems were overcome in the present study by using an angle dispersive x-ray area detector (imaging plate) and the electrical heating technique.
 [17] O. L. Anderson, *Equations of State of Solids for Geophysics and Ceramic Science* (Oxford University Press, New York, 1995), 405 pp.
 [18] N. A. Dubrovinsky, L. S. Dubrovinsky, and S. K. Saxena, *Geochim. Cosmochim. Acta.* **61**, 4151–4158 (1997).
 [19] N. Funamori, T. Yagi, W. Utsumi, T. Uchida, and M. Funamori, *J. Geophys. Res.* **101**, 8257–8269 (1996).
 [20] S. K. Saxena, *Geochim. Cosmochim. Acta* **60**, 2379–2395 (1996).
 [21] A. Singh and T. Le Bihan, *J. Appl. Phys.* **75**, 4956–4963 (1994).
 [22] A. Singh, C. Balasingh, H.-K. Mao, R. Hemley, and J. Shu, *J. Appl. Phys.* **83**, 7567–7575 (1998).
 [23] R. J. Hemley, H.-K. Mao, G. Shen, J. Badro, P. Gillet, M. Hanfland, and D. Häusermann, *Science* **276**, 1242–1244 (1996).
 [24] L. S. Dubrovinsky, P. Lazor, S. K. Saxena, P. Häggkvist, P.-H. Weber, and T. LeBihan, *Phys. Chem. Miner.* (to be published).
 [25] T. S. Duffy and T. J. Ahrens, *Geophys. Res. Lett.* **20**, 1103 (1993).
 [26] L. Stixrude, E. Wasserman, and R. E. Cohen, *J. Geophys. Res.* **102**, 24 729–24 739 (1997); E. Wasserman, L. Stixrude, and R. E. Cohen, *Phys. Rev. B* **53**, 8296–8309 (1996).
 [27] H. K. Mao, J. Shu, G. Shen, R. J. Hemley, B. Li, and A. Singh, *Nature (London)* **396**, 741 (1998).
 [28] A. M. Dziewonski and D. L. Anderson, *Phys. Earth Planet. Inter.* **25**, 297–356 (1981).
 [29] J. M. Brown and R. G. McQueen, *J. Geophys. Res.* **91**, 7485–7494 (1986).