Sound Velocities of Hot Dense Iron: Birch's Law Revisited

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Pressure velocities of hexagonal close-packed iron (hcp-Fe) were measured at pressures up to 73 gigapascals and at temperatures up to 1700 kelvin with nuclear inelastic x-ray scattering in a laser-heated diamond anvil cell. The compression-wave velocities ($V_p$) and shear-wave velocities ($V_s$) of hcp-Fe decreased significantly with increasing temperature under moderately high pressures. $V_p$ and $V_s$ under high pressures and temperatures thus cannot be fitted to a linear relation, Birch's law, which has been used to extrapolate measured sound velocities to densities of iron in Earth's interior. This result means that there are more light elements in Earth's core than have been inferred from linear extrapolation at room temperature.

The properties of Earth's iron-rich core have been inferred from estimates of iron density at high pressures and temperatures and from measurements of compression-wave ($V_p$) and shear-wave ($V_s$) velocities passing through the core (1–13). These data have indicated that Earth's core is less dense than pure iron by approximately 10% for the outer core and 3% for the inner core, suggesting the existence of light elements in the core. On the other hand, Birch's law, a linear sound velocity–density relation (2, 14, 15), has also been used to extrapolate measured sound velocities at high pressures and room temperatures to inner core conditions without considering the temperature effect (9, 12). This linear extrapolation has suggested that the inner core is mainly made of Fe-Ni alloy. The nuclear-resonant inelastic x-ray scattering (NRIXS) technique provides a direct probe of the phonon density of states (DOS) of the resonant isotope (16–18) using the 14.4125-keV transition of $^{57}$Fe. $V_p$ and $V_s$ of hexagonal close-packed (hcp) Fe have been measured up to 153 GPa at 300 K (10, 19). However, the effect of temperature on the sound velocity measurements of Fe in static studies is not well understood. Here we report the static NRIXS study of the sound velocities of hcp-Fe up to 73 GPa and 1700 K in a laser-heated diamond anvil cell (LHDAC), and we discuss the temperature effect on the sound velocities and Birch's law.

We conducted NRIXS experiments in an LHDAC at Sector 3 of the Advanced Photon Source (APS) at Argonne National Laboratory (20, 21). Energy spectra were obtained by tuning the x-ray energy (±70 meV) around the nuclear transition energy of 14.4125 keV and collecting the Fe K-fluorescence (the emission of an x-ray photon via the transition of an atomic electron into an unoccupied ls state) radiation that was emitted with time delay relative to the incident x-ray pulses. We used a quasiharmonic model to extract the phonon DOS from the NRIXS spectra (Fig. 1) according to the procedure described in (16–18). With the NRIXS technique, we measured the spectrum of the self-correlation function of the position of the Fe atoms (17). In the model, the atomic motions relative to the temperature-dependent averaged position are assumed to be harmonic under the given conditions of pressure, temperature, and other parameters. Thermal effects, such as expansion and change of force constants with atomic distances, were allowed to change but the vibrations were still assumed to occur in a harmonic potential. The average kinetic energy and force constant independently derived from the moments of the measured spectra were consistent with the values evaluated from the quasiharmonic model (17), indicating the validity of the model to our high-pressure/temperature data (22). The Debye sound velocity ($V_D$) was derived from parabolic fitting of the low-energy regime of the DOS (16–18), and the vibrational, elastic, and thermodynamic parameters were obtained by the integration of the DOS. We then calculated the thermal

References and Notes
12. Note that a synthetic $\mu_2$-PF$_6$-peroxocobalt(II) complex has been shown to directly hydroxylate an aromatic ring on a noncoordinating substrate (32).
13. A lower yield of the products is observed for electron-deficient substrates.
14. Materials and methods are available as supporting material on Science Online.
15. Both catechol and quinone are produced upon acidic workup of the solution mixture, which supports A as a reactive species during hydroxylation.
19. A resonance Raman spectrum resulting from 600-nm excitation shows a C-C stretch at 1280 cm$^{-1}$, which supports a phenolate to Cu charge-transfer assignment.
21. No vibrations characteristic for P complexes ($\sim 300$ or $\sim 730$ cm$^{-1}$) are observed.
25. EXAFS analysis typically cannot distinguish between atoms that differ in Z by 1 (e.g., O and N) (33). Given the $\alpha$ range of the EXAFS data ($\alpha = 3$ to $12.5$ Å$^{-1}$), any difference in $\alpha$ less than 0.17 Å between ligands in the first coordination shell (2 $\alpha < 1$ Å) could not be resolved.
27. An electrostatic aromatic substitution mechanism for a bis-$\mu_2$-oxocobalt(III) complex has been proposed in a case in which a ligand aryl group is hydroxylated (34).
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Materials and Methods
SOM Text
Figs. S1 to S8
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References
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Studies of bulk sound velocities of hcp-Fe reveal that the effect of temperature on the sound velocities is significant, especially at high pressures. The Birch-Murnaghan equation of state (EOS) is used to calculate the isothermal bulk modulus at high pressures, which is sensitive to the differences in the EOS data. The adiabatic bulk modulus at high pressures is calculated using the Birch-Murnaghan EOS. The adiabatic bulk modulus at high pressures is compared to the extrapolated sound velocities of hcp-Fe at high pressures and temperatures. The effect of temperature on the sound velocities is significant at high pressures, with a decrease in sound velocity of 7% for each 1000 K increase in temperature. The experimental results show that the extrapolated sound velocities at high pressures and temperatures are consistent with those of a previous NRIXS study at high pressures and 300 K. The extrapolation of shear wave of hcp-Fe in the Earth Reference Model (PREM) is consistent with the experimental results. The effect of temperature on the sound velocities is significant, and the extrapolated sound velocities at high pressures and temperatures are consistent with those of a previous NRIXS study at high pressures and 300 K.
Deep-Sea Temperature and Circulation Changes at the Paleocene-Eocene Thermal Maximum

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A rapid increase in greenhouse gas levels is thought to have fueled global warming at the Paleocene-Eocene Thermal Maximum (PETM). Foraminiferal magnesium/calcium ratios indicate that bottom waters warmed by 4° to 5°C, similar to tropical and subtropical surface ocean waters, implying no amplification of warming in high-latitude regions of deep-water formation under ice-free conditions. Intermediate waters warmed before the carbon isotope excursion, in association with downwelling in the North Pacific and reduced Southern Ocean convection, supporting changing circulation as the trigger for methane hydrate release. A switch to deep convection in the North Pacific at the PETM onset could have amplified and sustained warming.

PETM was a short-lived global warming event about 55 million years ago (Ma) that may provide insights into the environmental consequences of rising greenhouse gas levels (1, 2). A reduction in the carbonate content of deep-sea sediments (2) and a large negative excursion in marine and terrestrial carbon isotope (δ13C) records (1–3) are associated with the PETM and indicate the addition of 13C-depleted carbon to the oceans and atmosphere. A possible source of this carbon was the dissociation of ~1000 to 2100 gigatons (Gt) of methane hydrate in ocean sediments (4), most or all of which would have oxidized, raising atmospheric CO2 by 70 to 160 parts per million by volume (ppmv) (5, 6). Benthic foraminiferal taxa exhibit increased extinction rates during the PETM, probably because of deep-sea oxygen deficiency and a decrease in seawater carbonate ion concentration (2).

The climatic response to rising greenhouse gas levels in the past has been debated because of equivocal ocean temperature reconstructions based on foraminiferal oxygen isotope ratios (δ18O), which are a function of both temperature and seawater δ18O (δ18Ow). To circumvent this ambiguity, the Mg/Ca temperature proxy has been applied to planktonic foraminifera, and it documented a 4 to 5°C warming of sea-surface temperatures (SST) across the PETM in the subtropical (7) and tropical ocean (8, 9).

We investigated the evolution of deep-sea temperatures, high-latitude SST, and circulation patterns using foraminiferal Mg/Ca and stable isotope ratios (9, 10) in order to examine the causes and consequences of the δ13C excursion and the PETM. We used Mg/Ca ratios of benthic foraminifera to develop estimates of bottom water temperatures (Tb) for deep sites in the subtropical South Atlantic (Site 527) and tropical North Pacific (Site 1209) oceans, and for a site at intermediate depths in the equatorial Pacific Ocean (Site 865) (table S1). These temperatures should reflect surface conditions in high-latitude regions of deep-water formation. We integrated these data with SST records (7, 8) to study the spatial pattern of warming and changes in the