Iron-rich Fe–O compounds at Earth’s core pressures

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Received: July 22, 2022; Accepted: November 13, 2022; Published Online: November 15, 2022; https://doi.org/10.1016/j.xinn.2022.100354
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GRAPHICAL ABSTRACT

PUBLIC SUMMARY
- A family of Fe-rich FeₙO compounds is revealed under Earth’s core conditions
- The FeₙO compounds feature close-packed Fe and O monolayers
- The separate O monolayer stabilizes FeₙO compounds at multi-megabar pressures
- The Earth’s inner core can contain more oxygen than expected due to FeₙO phases
- It alters our understanding of thermal evolution and seismic features of the core
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Received: July 22, 2022; Accepted: November 13, 2022; Published Online: November 15, 2022; https://doi.org/10.1016/j.xinn.2022.100354
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Citation: Liu J., Sun Y., Lv C., et al., (2023). Iron-rich Fe–O compounds at Earth’s core pressures. The Innovation 4(1), 100354.

Oxygen and iron are the most abundant elements on Earth, and their compounds are key planet-forming components. While oxygen is pervasive in the mantle, its presence in the solid inner core is still debatable. Yet, this issue is critical to understanding the co-evolution and the geomagnetic field generation. Thus far, iron monoxide (FeO) is the only known stoichiometric compound in the Fe–FeO system, and the existence of iron-rich FeO compounds has long been speculated. Here, we report that iron reacts with FeO and Fe2O3 at 220–260 GPa and 3000–3500 K in laser-heated diamond anvil cells. \textit{Ab initio} structure searches using the adaptive genetic algorithm indicate that a series of stable stoichiometric FeO compounds (with n > 1) can be formed. Like Fe–Fe and FeO–Fe2O3 compounds, these FeO compounds have close-packed layered structures featuring oxygen-only single layers separated by iron-only layers. Two solid-solution models with compositions close to FeO, the most stable Fe-rich phase identified, explain the X-ray diffraction patterns of the experimental reaction products quenched to room temperature. These results suggest that Fe-rich FeO compounds with close-packed layered motifs might be stable under inner core conditions. Future studies of the elastic, rheological, and thermal transport properties of these more anisotropic FeO solids should provide new insights into the seismic features of the inner core, inner core formation process and composition, and the thermal evolution of the planet.

RESULTS AND DISCUSSION

Experimental synthesis

We performed five high-P–T experiments to synthesize FeO compounds. We carried out synchrotron XRD experiments on the Fe–FeO system under high-P–T conditions using laser-heated diamond anvil cells at the Advanced Photon Source at the Argonne National Laboratory and the Shanghai Synchrotron Radiation Facility. The starting materials were mixtures of pure iron with FeO or Fe2O3 powder in a size range of submicron to a few microns (refer to details in the material and methods). Repetitive micro-second laser pulses were employed to heat the sample for a short period of ~1 s. This laser-heating strategy significantly reduced potential carbon diffusion from the diamond anvils into the sample chamber (see Note S1). The samples were well insulated from the diamond anvils by the KCl pressure-transmitting medium and were heated up evenly on both sides to reach high temperatures readily. No reaction was observed in the first three runs at 100–200 GPa up to 2600 K (Figure S1), consistent with previous experimental studies of FeO.7,20 In run 4, the Fe–FeO mixture was compressed firstly to 220 GPa at room temperature. Upon laser pulse heating to 2000–3000 K, diffraction peaks of both ε-Fe and B8-FeO merely became sharper, without the appearance of any new reflections. Further laser pulse heating to 3000–3200 K showed dramatic XRD pattern changes in a few seconds (left panel in Figure S2). The integrated diffraction peak intensities of the corresponding Fe and FeO phases reduced rapidly, indicating that iron reacted with FeO above 3000 K and 220–230 GPa. A similarly rapid chemical reaction happened in run five, starting from a Fe–Fe2O3 mixture that was compressed to 200–250 GPa at room temperature and exposed to repetitive laser pulse heating. After reaching ~3000 K, the peak intensities of the Fe and Fe2O3 phases decreased, while a set of additional diffraction peaks emerged (right panel in Figure S2). At least until 260 GPa and 3500 K, they remained unaltered before the anvils shattered upon further heating.

The diffraction peaks of the new phases did not change significantly after quenching the sample to room temperature (see Figures 1 and S2). The quenched new phase(s) remain (meta)stable at room temperature upon decompression to ~160 GPa. To improve the quality of the quenched samples’
XRD patterns, we rotated the diamond anvil cell (DAC) by ±10° around the incident X-ray beam direction. This procedure significantly improved the XRD peak intensities relative to the background in these polycrystalline samples (Figures S3 and S4). The short 1-s data collection time makes this procedure very challenging at high P–T, and the high-temperature XRD patterns show a relatively higher background intensity (Figure S2). This was another reason for using the XRD patterns collected at room temperature and 220–245 GPa to identify the new phases. The new diffraction peaks from Fe + FeO and Fe + Fe₂O₃ reactions show consistent (Fe-only or O-only) hexagonal close-packed layers, similar to the end-member 0.2 meV/atom above it. All these new Fe-rich compounds have single species stacking layers (Figure 2A), which is the criterion used to select the stability of these structures. Therefore, O-only layers are not closely packed. All those atomic arrangements have high enthalpy. A previous computational search found an Fe₂O₆ hexagonal structure (P 6₃m) more similar to the Pb₀/mmc ground state revealed here. However, the enthalpy of the Fe₂m2 phase is still ~10 meV/atom higher than the Pb₀/mmc phase (Figure S8). Further calculations up to IC pressures confirm the stability of Pb₀/mmc Fe₂O₆ against the decomposition into Fe and FeO (Figure S8). The dynamic stability of these new phases is also confirmed at both 215 and 380 GPa (Figure S9).

Crystal structure prediction

To solve the XRDs, we first conducted crystal structure searches for FeₙO (n > 1) compounds using the adaptive genetic algorithm (AGA) at 215 GPa. By searching in a wide range of Fe-rich compositions (see material and methods for details), several new stoichiometric FeₙO phases are found to be more stable than the combination of two end members, ε-Fe and B8–FeO. Figure 2A shows the convex hull obtained from these crystal structure searches. Four compounds with FeₙO (space group Pb₀/mmc), Fe₂O₆ (P3m1), FeO₃ (R3m), and FeO₃ (R3m) stoichiometries are ground states at 215 GPa. The FeO₃ (R3m) phase is very close to the convex hull, with only 0.2 meV/atom above it. All these new Fe-rich compounds have single species (Fe-only or O-only) hexagonal close-packed layers, similar to the end-member phases ε-Fe (P6₃/mmc) and B8–FeO (P6₃/mmc) (Figure 2B). Furthermore, most low-enthalpy compounds also have hexagonal close-packed layers, as noted by the red symbol in Figure 2A.

To study the close-packing motifs in these phases, we selected structures whose formation enthalpies are within 26 meV/atom (~300 K) above the convex hull. The lattice parameter c of these structures displays nearly linear dependence on the number of layers in the primitive cell (Figure 2C), suggesting a similar layered motif in all these structures. By examining these structures’ stacking sequences, we found a simple compound formation rule. Only seven different three-layer stacking sequences out of 12 possible ones are present in these low-energy structures (see Figure 2D). The Fe–Fe–Fe layer sequence favors ABA stacking more than ABC, consistently with the stacking in ε-Fe. Layer sequences involving oxygen, e.g., Fe–O–Fe or Fe–Fe–O, favor ABC stacking over ABA. Five arrangements involving adjacent O–O layers, e.g., Fe–O–O or O–Fe–O with ABA stacking are absent among these structures. Therefore, O-only layers are well separated from each other. This stacking rule explains why the previously proposed FeₙO models are unstable, which included oxygen as substitutional and interstitial ions. The BiI₃-type (R3) model is hexagonal, but the oxygen layers are not closely packed. All those atomic arrangements have high enthalpy. A previous computational search found an Fe₂O₆ hexagonal structure (P 6₃m) more similar to the Pb₀/mmc ground state revealed here. However, the enthalpy of the Fe₂m2 phase is still ~10 meV/atom higher than the Pb₀/mmc phase (Figure S8). Further calculations up to IC pressures confirm the stability of Pb₀/mmc Fe₂O₆ against the decomposition into Fe and FeO (Figure S8). The dynamic stability of these new phases is also confirmed at both 215 and 380 GPa (Figure S9).

XRD solutions

First, we compared the predicted XRD patterns of the computationally identified FeₙO phases with the experimental ones. The four FeₙO phases in the convex hull can partially match the XRD lines of the quenched reaction products but do not provide a complete interpretation of the diffraction patterns (Figure S10). By including a few metastable FeₙO phases, the multi-phase aggregate XRD matches the experimental data better at both 220 and 245 GPa (Figure S11). Considering that all these FeₙO phases follow the same basic stacking rule, we anticipate the entropic stabilization of disordered solid solutions at high temperatures. To clarify this point, we set up reverse Monte Carlo (RMC) simulations of FeₙO (n > 1). The multi-phase aggregate XRD matches the experimental data better at both 220 and 245 GPa (Figure S11).

The XRD deviation, D_XRD, which is the criterion used to select preferred structures during the RMC sampling, is defined as D_XRD = \sqrt{(\langle \delta_{100} \rangle^2 + \langle \delta_{20} \rangle^2)}^2, i.e., the mean-square deviation between the simulated, \delta_{100} and \delta_{20}, and the experimental, \delta_{100} and \delta_{20}, peak intensities. The 2θ range analyzed is restricted to 9.2–10.2° at 220 GPa and 10.6–11.6° at 245 GPa, corresponding to the prominent peaks of the new reaction products.
in Figure 1. Figure 3B shows the D\textsubscript{XRD} values for the different supercell sizes and iron concentrations obtained in the RMC simulations. The smallest D\textsubscript{XRD} at 220 GPa points to a 42-layer structure with chemical composition Fe\textsubscript{29}O\textsubscript{13}, shown in Figure 3C. This structure's XRD matches all additional experimental peaks of the reaction products. Ab initio calculations show the formation enthalpy of this phase is only 28 meV/atom above the convex hull. This supercell's calculated equation of state agrees well with the experimental one (see Note S2 and Figure S12), confirming that this structure and composition are a reasonable solution for the experimental XRD. A similar RMC was performed to solve the XRD of the reaction products of Fe and Fe\textsubscript{2}O\textsubscript{3} at 245 GPa (Figure S13). A 38-layer structure solution with composition Fe\textsubscript{28}O\textsubscript{14} shown in Figure 3C. This structure

![Figure 2. Crystal structure of identified Fe\textsubscript{n}O compounds at 215 GPa](image)

(A) The formation enthalpy of AGA-searched compounds referenced by the dashed line shows their relative stability relative to the decomposition into ϵ-Fe and B8–FeO. The solid line indicates the convex hull formed by the thermodynamically stable compounds. Purple circles show structures with hexagonal close-packed layers. (B) Crystal structures of four Fe-rich compounds in the ground states. Gold and red solid symbols represent iron and oxygen, respectively. (C) Lattice parameter c of low-energy close-packed crystals as a function of the number of layers. (D) Frequency of structural and chemical order in the nearest neighbor layers of the low-energy close-packed crystals.

Figure 4 shows the electronic density of states of ϵ-Fe, Fe\textsubscript{3}O, Fe\textsubscript{2}O, and B8–FeO at 215 GPa and T\textsubscript{eq} = 3000 K. All Fe\textsubscript{n}O phases discovered are metallic. In ϵ-Fe, the Fermi level falls on a valley (Figure 4A), while in B8–FeO, it falls on a peak. Systematically, in Fe\textsubscript{3}O, the carrier density increases significantly with increasing oxygen content. In Fe\textsubscript{2}O, the Fermi level falls on a shallow valley, and the DOS has features resembling those of ϵ-Fe and Fe\textsubscript{3}O. Fe\textsubscript{2}O has two kinds of iron: those with (Fe\textsubscript{1}, Fe\textsubscript{2}, Fe\textsubscript{4}, Fe\textsubscript{5}) and those without (Fe\textsubscript{3}, Fe\textsubscript{6}) oxygen neighbors (see Figure 4). Fe\textsubscript{3}O's contribution to the DOS (red area in Figure 4B) resembles that of ϵ-Fe, while Fe\textsubscript{5}O's contribution (blue area in Figure 4B) resembles Fe\textsubscript{2}O's.

The chemical bonding nature in the Fe\textsubscript{n}O phases is analyzed using electron localization function (ELF) and Bader charge transfer.32–34 Figure 5 shows the ELF cross-sections in the (110) plane containing both Fe and O atoms for ϵ-Fe, Fe\textsubscript{3}O, Fe\textsubscript{2}O, and B8–FeO. In ϵ-Fe, the ELF is relatively uniform. In B8–FeO, the valence electrons are more concentrated near oxygens, while Fe layers maintain a relatively uniform electron density. In Fe\textsubscript{2}O and Fe\textsubscript{3}O, adjacent Fe–Fe layers show similar ELFs to ϵ-Fe, while adjacent Fe–O layers have ELFs like those in B8–FeO. Table 1 shows Bader charge transfers in these compounds. Approximately 0.97 electrons transfer from Fe to O in B8–FeO. In Fe\textsubscript{2}O and Fe\textsubscript{3}O, O ions gain roughly the same number of electrons, but the electron loss per Fe in Fe\textsubscript{2}O is 0.47, i.e., half of that in FeO. In Fe\textsubscript{2}O, Fe without O neighbors (Fe\textsubscript{3}/Fe\textsubscript{6}) shows almost no electron loss, while Fe with O neighbors (Fe\textsubscript{1}/Fe\textsubscript{2}/Fe\textsubscript{4}/Fe\textsubscript{5}) shows an electron loss of 0.45, similar to Fe in Fe\textsubscript{2}O. Therefore, the electronic DOS, chemical bonding, and charge transfer in the Fe\textsubscript{n}O phases can be interpreted by recalling those in the end-member phases, i.e., ϵ-Fe and B8–FeO. This seemingly simple and sort-of-short-range interaction between Fe and B8–FeO...
suggests that several stoichiometries are possible in the Fe–FeO system, i.e., Fe₆O₇ phases containing O-only and Fe-only close-packed layers stacked in different ways that depend on n. An entropically stabilized alloy with a stacking disorder is likely to form at high temperatures.

**Geophysical implications**

Our high-P–T experiments show that Fe and FeO/Fe₂O₃ react at 220–260 GPa at temperatures higher than 3000 K. At the same time, our ab initio crystal structure prediction identifies several stable Fe₉O₁₄ phases with n > 1 at similar pressure conditions. These newly identified phases differ from previously suggested Fe₉O model13,14 and consist of single species (Fe-only or O-only) close-packed layers in various stacking sequences with an O-only single layer always separated by Fe-only layers. The best solutions for the experimental XRD peaks of the new phases quenched to room temperature point to structures lacking long-range chemical or stacking order. However, they still have average compositions close to Fe₂O₃, i.e., that of the most stable phase identified computationally in the Fe–FeO system. With this in mind, the new high-temperature reaction products are likely entropically stabilized solid solutions whose intrinsic disorder is retained upon quenching. Notably, these high-entropy phases may be favored over stoichiometric compounds (e.g., Fe₂O₃ and Fe₆O₇) at high IC temperatures. In general, the presence of oxygen layers should make Fe₂O₃ alloys more anisotropic from an elastic and thermal transport perspective compared with pure iron. These properties must be carefully investigated since they are essential for understanding the core’s thermal evolution and seismic features, including the IC’s age, energy source powering the geodynamo, and seismic heterogeneities.35,36

Oxygen has been proposed to be a likely light element alloyed with Fe in the liquid OC.8 It has been postulated that an oxygen-rich liquid OC adjoining an oxygen-deprived solid IC might account for the global seismic observations of the density jump across the IC–OC boundary.11 The successful syntheses of the solid Fe-rich Fe₂O₃ phases here suggest that the solid IC may also incorporate a significant amount of oxygen. The result is a less drastic oxygen partitioning between the OC and the IC and, consequently, a more complex origin of this density deficit contrast, with other elements also playing a significant role.8 In addition, forming solid Fe-rich Fe₂O₃ phases via IC nucleation and growth would affect the associated latent heat release from the IC to power the geodynamo through geological time.37

Oxygen has been present in every stage of Earth’s formation and evolution, and chemical interactions in the deep Earth involve oxygen transfer between the core and mantle.38–42 It has been suggested that the precipitation of MgO, FeO, and SiO₂ in the OC could have provided gravitational energy to drive early core convection and the Earth’s ancient magnetic field before the formation of the Earth’s solid core evolution.41–45

**Figure 3. Reverse Monte Carlo simulation of Fe₂O₁₄ structure** (A) Distribution of middle-layer spacings with different neighboring layers. Legs indicate chemical elements in the first and second nearest neighbor layers, e.g., “OFe–FeO” denoting that Fe layers are the first nearest neighbor and that O layers are the second nearest neighbors. The red curve is a Gaussian distribution fitting. (B) Oxygen concentration and XRD deviation (Dₑₓₑᵣₑ) of supercell structures from RMC simulation. Each point represents the final structure from one RMC simulation. The color bar indicates the number of atoms in the supercell. (C) The comparison between diffraction patterns by experiments at 220 GPa and the Fe₂O₁₄ supercell XRD produced by RMC simulations. The incident X-ray wavelength (X) is 0.2952 Å. Vertical ticks: Fe₂O₁₄ (black), B₂–FeO (orange), B₈–FeO (olive), B₂–KCl (magenta), and hcp–Re (blue). The lower panel shows the simulated crystal structure of Fe₂O₁₄.

**MATERIALS AND METHODS**

**Sample preparation and characterization**

The starting materials of pure iron (C.A.S. #7439-89-6) mixed with FeO (C.A.S. #1345-25-1) or Fe₂O₃ (C.A.S. #1309-37-1) powders with grain sizes ranging from submicron to a few microns were prepared in an Fe/O ratio ~3:1. Each of the two mixtures was mechanically ground for 90 min in a glove box filled with Ar. Pairs of single- or double-beveled diamond anvils with culet sizes of 50–300 or 60–180–300 μm were used for the laser-heated DAC experiments. The sample disk of each Fe–O mixture was compressed to ~3–μm thick and 14–16 μm across and was selected and loaded into a sample chamber measuring 20–25 μm across consisting of a pre-indent Re gasket. Each sample platelet was sandwiched between two dried KCl platelets used as the pressure-transmitting medium and thermal insulation layers. The whole DAC sample assembly was sealed in a vacuum using a high-pressure gas loading system after being evacuated for 30 min before each sample chamber was compressed to high pressures. Before reaching a target pressure, XRD patterns were collected at ~30 GPa to confirm the presence of both iron and iron oxide.

**Synchrotron XRD experiments**

High-P–T XRD measurements were conducted at beamlines 13-ID-D of the Advanced Photon Source, Argonne National Laboratory. A highly monochromatized X-ray source with an energy of 42 keV (0.2952 Å) was used as the incident X-ray beam and focused
down to a 2- to 5-mm spot size (full width at half maximum) at the sample position. Each DAC was compressed to high pressure at room temperature in preparation for the laser heating experiments. The pressure was determined from the lattice parameters of hcp–Fe and B2–KCl, generally with an uncertainty of 2–5 GPa.46 At targeted pressures, two infrared laser beams were focused on 20- to 30-mm spots (full width at half maximum) on both sides of the sample. They were co-axially aligned with the incident X-ray beam using the X-ray-induced luminescence on the sample and/or ruby. We estimated the temperature of the heated samples by fitting measured thermal radiation spectra with the gray-body assumption function. The temperature uncertainty was within 100–200 K based on multiple temperature measurements on both sides.

AGA search

We searched for crystal structures of Fe-rich Fe₉O using the AGA,28,47,48 which combines ab initio calculations and auxiliary interatomic potentials described by the embedded-atom method in an adaptive manner to ensure high efficiency and accuracy. The structure searches were only constrained by the chemical composition, without any assumption on the Bravais lattice type, symmetry, atom basis, or unit cell dimensions. A wide range of different Fe-rich compositions (i.e., 2:1, 3:1, 3:2, 4:1, 4:3, 5:1, 5:2, 5:3, 5:4, 6:1, 6:5, 7:1, 8:1, 9:1) were selected with up to 25 atoms in the unit cell to perform the search. Each AGA run contains a genetic algorithm (GA) loop accelerated by interatomic potential and a density functional theory (DFT) calculation loop to refine the potential. The candidate pool in the GA search contained 64 structures. In each GA generation, 16 new structures were generated from the parent structure pool via the mating procedure. The structures in the pool were updated by keeping 64 of the lowest-energy structures. The structure search with a given auxiliary interatomic potential sustained 1000 consecutive GA generations. After one GA loop, 16 structures were randomly selected for the static DFT calculation to refine the potential. This process was repeated 80 times, followed by DFT structure optimization on unique crystal structures.

Ab initio calculations

We conducted ab initio calculations using the projector augmented-wave (PAW) method within DFT, as implemented in the VASP code.49–51 The exchange and correlation energies were treated with the generalized gradient approximation parameterized by the Perdew–Burke–Ernzerhof formula.52 PAW potentials with valence electronic configurations 3d⁷4s¹ and 2s²2p⁴ were used for the Fe and O atoms, respectively. The hard-core PAW potential with 3s²3p⁶3d⁷4s¹ for Fe was also tested. Both Fe PAWs show consistent results (see Note S4 and Figure S17). The Mermin functional was employed.53,54 A plane-wave basis set was used with a kinetic energy cutoff of 650 eV. During the AGA search, the Monkhorst–Pack sampling scheme was adopted for Brillouin zone sampling with a k-point grid of 2×3×3 Å⁻¹ and the ionic relaxations stopped when the forces on every atom became smaller than 0.01 eV/Å. The energy convergence criterion is 10⁻⁴ eV. Phonon calculations were performed using density functional perturbation theory implemented in the VASP code and the Phonopy software.55,56 with a k-point grid of 2×3×3 Å⁻¹ and supercells of 3×3×3 for Fe₉O (54 atoms), 2×2×2 for Fe₃O (64 atoms), 2×2×2 for Fe₃O₂ rhombohedral lattice (40 atoms), and 2×2×2 for Fe₅O₃ rhombohedral lattice (56 atoms).

RMC simulations

The RMC simulations were performed by randomly changing the chemistry (Fe/O ratio) and layer stackings in the supercells of the hexagonal lattice. There is no restriction
of the overall Fe/O concentration in the supercell. The only criterion to select preferred structures during the random sampling is based on the XRD deviation \( D_{\text{XRD}} = \sqrt{(I_{\text{exp}}(2\theta) - I_{\text{sim}}(2\theta))^2} \), which is the mean-square deviation of the intensities between simulated, \( I_{\text{sim}} \), and experimental, \( I_{\text{exp}} \), XRDs. The smaller the \( D_{\text{XRD}} \), the better the agreement with the experimental data. The acceptance rate during the RMC simulation follows the typical Metropolis acceptance rule as \( p = e^{-\Delta D} \), where \( \Delta D \) is the change of XRD deviation between two MC steps. \( \beta \) is a scaling factor that makes the overall acceptance rate around 20%. The structure is updated if the stacking changes during the RMC simulation. The interlayer distances were set using the most probable spacings shown in Figure 3A. According to Figure 2D, only seven out of 12 stacking sequences appeared in the low-energy structures found with the AGA search. Stackings other than the seven preferred ones in the RMC simulations were discouraged by assigning large \( \Delta D \) s. The RMC simulations used supercells containing 20 to 60 layers. Each simulation was repeated independently 30 times.

Data availability

All original data supporting the findings and structure files of this study have been deposited at https://doi.org/10.5281/zenodo.7155153.

Table 1. Bader charge analysis of the Fe3O phases

| Phase     | Fe     | O      |
|-----------|--------|--------|
| \( \varepsilon \)-Fe | 0      | -      |
| Fe3O \((P6_3/mmc)\) | Fe1/Fe2/Fe4/Fe5: +0.45 | -0.91 |
| Fe3/Fe6: +0.01  | -0.94  |
| Fe2O \((P3m1)\) | +0.47  | -0.94  |
| B8-FeO      | +0.97  | -0.97  |

The indices of Fe in Fe3O correspond to those in Figures 4B and 5.

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ACKNOWLEDGMENTS
This work is supported by NSFC grants nos. 42072052 and U1930401 and by National Science Foundation awards EAR-1918126 (R.M.W. and Y.S.), EAR-1918134 (K.H. and C.W.), and EAR-1901808 and EAR-1916941 (J. Lin). R.M.W. also acknowledges partial support from the Department of Energy, Theoretical Chemistry Program, through grant DE-SC0019759. Computational resources were provided by the Extreme Science and Engineering Discovery Environment (XSEDE) funded by the National Science Foundation through award ACI-1548562. This research also used resources of the Advanced Photon Source, a US Department of Energy Office of Science User Facility operated by Argonne National Laboratory under contract no. DE-AC02-06CH11357. The GeoSoilEnviroCARDS at the Advanced Photon Source is supported by the National Science Foundation - Earth Sciences award EAR-1634415 and the Department of Energy-Geosciences award DE-FG02-94ER14466. Some experiments are supported by the Synergic Extreme Condition User Facility (SECUF) and beamline BL15U1 at the Shanghai Synchrotron Radiation Facility (SSRF).

AUTHOR CONTRIBUTIONS
J. Lin, J. Liu, R.M.W., and Y.S. conceived the project. Y.S., F.Z., C.W., and K.H. performed ab initio calculations and crystal structure search. J. Liu, J. Lin, G.L., S.F., and V.B.P. carried out synchrotron experiments and data analyses. J. Liu, Y.S., and R.M.W. wrote the manuscript. All authors discussed the results and contributed to paper writing.

DECLARATION OF INTERESTS
The authors declare no competing interests.

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.xinn.2022.100354.

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