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# Xenon iron oxides predicted as potential Xe hosts in Earth's lower mantle

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An enduring geological mystery concerns the missing xenon problem, referring to the abnormally low concentration of xenon compared to other noble gases in Earth's atmosphere. Identifying mantle minerals that can capture and stabilize xenon has been a great challenge in materials physics and xenon chemistry. Here, using an advanced crystal structure search algorithm in conjunction with first-principles calculations we find reactions of xenon with recently discovered iron peroxide  $\text{FeO}_2$ , forming robust xenon-iron oxides  $\text{Xe}_2\text{FeO}_2$  and  $\text{XeFe}_3\text{O}_6$  with significant Xe-O bonding in a wide range of pressure-temperature conditions corresponding to vast regions in Earth's lower mantle. Calculated mass density and sound velocities validate Xe-Fe oxides as viable lower-mantle constituents. Meanwhile, Fe oxides do not react with Kr, Ar and Ne. It means that if Xe exists in the lower mantle at the same pressures as  $\text{FeO}_2$ , xenon-iron oxides are predicted as potential Xe hosts in Earth's lower mantle and could provide the repository for the atmosphere's missing Xe. These findings establish robust materials basis, formation mechanism, and geological viability of these Xe-Fe oxides, which advance fundamental knowledge for understanding xenon chemistry and physics mechanisms for the possible deep-Earth Xe reservoir.

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The chemical reaction of inert xenon (Xe), a quintessential full-shell element, was earliest predicted by Pauling in 1933 and the first xenon compound was experimentally produced in 1962<sup>1</sup>. Then, more xenon compounds were experimentally synthesized at ambient pressure, containing some most electronegative atoms like fluorine<sup>2–5</sup> or oxygen<sup>6–9</sup>. Subsequently, scientists found that pressure can effectively improve the chemical reactivity of Xe<sup>10–17</sup>. At moderate pressures, solid xenon forms weakly bonded compounds with other species, e.g., with H<sub>2</sub>O<sup>10</sup> and O<sub>2</sub><sup>11,12</sup> at 1 and 3 GPa, respectively. Strikingly, several novel Xe compounds with unusual stoichiometries are found to be thermodynamically stable at high pressures, e.g., Xe oxides<sup>13,14</sup>, Xe nitrides<sup>15</sup>, xenon-hydrogen<sup>16</sup>, and Xe-Mg compounds<sup>17</sup>.

At ultra-high-pressure conditions, the high volatility, relative chemical inertia, and abundant isotopes of xenon make it a valuable tracer in the study of evolutionary dynamics and history of Earth. However, 99% of Earth's primordial Xe is mysteriously missing as characterized by its very low abundance compared to other noble gases in Earth's atmosphere<sup>18</sup>, which is known as the missing Xe problem<sup>19</sup>. Early hypotheses proposed that Xe might have escaped from the atmosphere after ionization<sup>20–22</sup>, or that it might be stored in the interior of Earth<sup>23–29</sup>. Attempts to incorporate Xe into ices, clathrates and sediments in the Earth's crust were not successful<sup>27–29</sup>. Laboratory experiments have succeeded in trapping Xe in quartz<sup>30,31</sup> and observing predicted stable xenon oxides<sup>13,14,32</sup>; but these results cannot explain the missing Xe mystery, because xenon oxides are unstable in equilibrium with metallic iron in lower mantle while xenon silicates decompose spontaneously at mantle pressures<sup>13</sup>. Reactions of Xe with iron and nickel in Earth's core were predicted as a viable scenario<sup>33</sup> and the predicted compounds were synthesized under core pressure and temperature conditions<sup>32,34</sup>. However, it remains highly intriguing and challenging to explore possible capture and stabilization of Xe by suitable minerals in Earth's mantle, which is of special significance because it was estimated that the loss of atmospheric Xe occurred about 100 million years from accretion, corresponding to the time of mantle differentiation event<sup>30</sup>.

Extensive past searches were unable to find chemical reactions of Xe with known mantle minerals. Recently discovered FeO<sub>2</sub> synthesized at lower mantle conditions<sup>35</sup> and stabilized above 74 GPa in theoretical calculation<sup>36</sup>, offer an intriguing new possibility. This newly identified iron peroxide is able to react with helium to form a rare helium-bearing compound that explains deep-Earth primordial helium deposits revealed by geochemical evidences<sup>37</sup>. This finding raises exciting prospects that FeO<sub>2</sub> may be able to react with Xe (actually *P-T* stability range of FeO<sub>2</sub> has not been completely established in experiments) at mantle conditions, thereby forming compounds capable of trapping Xe in Earth's interior. In this work, we have explored possible reactions of Xe with FeO<sub>2</sub> in contrast with known mantle constituents FeO, SiO<sub>2</sub>, MgO, CaO, and Al<sub>2</sub>O<sub>3</sub>. We find that FeO<sub>2</sub> has unique ability to react with Xe and form robust Xe-Fe oxides Xe<sub>2</sub>FeO<sub>2</sub> and XeFe<sub>3</sub>O<sub>6</sub> with surprisingly strong Xe-O bonding, while other mantle oxides do not react with Xe. We have further examined mass density and sound velocities of these Xe-Fe oxides, and the results support their viability in vast lower mantle region. These findings establish robust materials basis, formation mechanism, and geological viability of these Xe-Fe oxides, which advance fundamental knowledge for understanding xenon chemistry and physics mechanisms for the possible deep-Earth Xe reservoir.

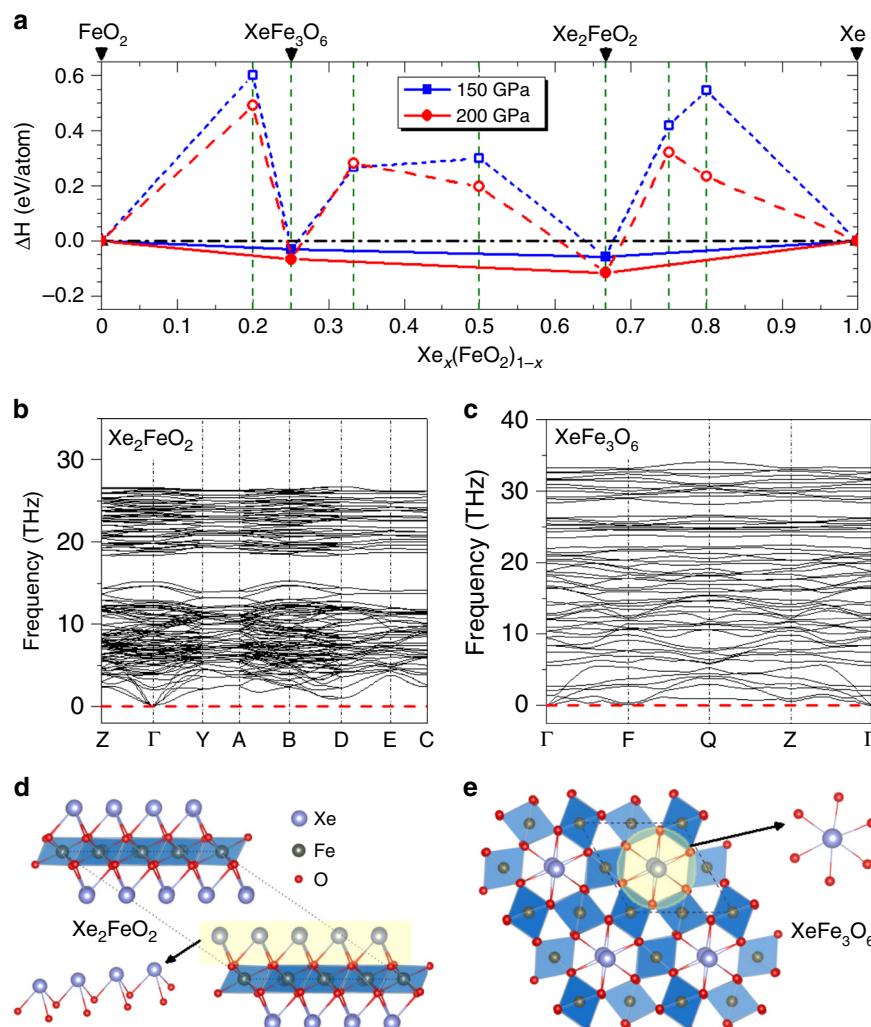
## Results

**Crystal structures.** We take the crystal phases identified by the structure search process at various FeO<sub>2</sub>: Xe ratios and compute

their enthalpy to determine the most viable structure at each composition, and based on the obtained results we construct the convex hull, as shown in Fig. 1a, which indicates stable products from reactions of FeO<sub>2</sub> and Xe. This exercise has led to the discovery of two Xe-Fe oxides, Xe<sub>2</sub>FeO<sub>2</sub> and XeFe<sub>3</sub>O<sub>6</sub>, that are stable against decomposition at 150 GPa and 200 GPa. The pressure-volume terms, associated with packing efficiency, make the major contribution to guarantee the thermodynamical stability of Xe<sub>2</sub>FeO<sub>2</sub> and XeFe<sub>3</sub>O<sub>6</sub> with formation enthalpies lying on the convex hull (Supplementary Fig. 1). These two Xe-Fe oxides are both still stable relative to all possible binary phases or pure simple substances of Xe-Fe-O<sub>2</sub>, which can be seen in Supplementary Information (Supplementary Figs. 2 and 3). The details Phonon dispersions calculated at 150 GPa (Fig. 1b, c) show that these compounds are dynamically stable and, as will be shown below, thermal effects further stabilize both oxides over a wider range of pressure at elevated temperatures at deep-Earth conditions. Here we first present a full analysis of structural and bonding characters of these two oxides at 150 GPa as a representative case study. The compound Xe<sub>2</sub>FeO<sub>2</sub> is crystallized in a monoclinic structure with *P2<sub>1</sub>/c* symmetry (Fig. 1d); its structural motif consists of stacked layers of corner-sharing octahedron with each Fe atom surrounded by six O atoms and the Fe atom is centered in a slightly distorted octahedron containing Fe-O bond lengths in a narrow range of 1.79–1.82 Å at 150 GPa. Each Xe atom in this structure has a coordination number of 3, bonding at the corners of FeO<sub>6</sub> octahedra with the Xe-O bond lengths in the range of 2.40–2.42 Å at 150 GPa, which are similar to those found in Xe<sub>2</sub>O<sub>3</sub> (~2.50 Å) and Xe<sub>2</sub>O<sub>5</sub> (~2.37 Å) at the same pressure<sup>38</sup>. Meanwhile, XeFe<sub>3</sub>O<sub>6</sub> is stabilized in a triclinic structure with *P-1* symmetry, containing two formula units per cell (Fig. 1e); its corner-sharing FeO<sub>6</sub> octahedra host Fe-O bonds with lengths of 1.73–1.81 Å at 150 GPa, forming a tubular structure, and each Xe atom has a coordination number of 6, located in the Fe-O tube with the nearest Xe-O distance of 2.08 Å, resulting in the vibrational mode of the lowest-frequency branch at F as shown in Fig. 1c. Further vibrational analyses are shown in Supplementary Fig. 4 and structural details of both Xe-Fe oxides at 150 GPa are listed in Supplementary Information (Supplementary Table 1).

## Discussion

**Chemical Bonding.** To assess bonding characters in the two Xe-Fe oxides, we have calculated their electronic density of states (DOS) at 150 GPa. The results shown in Fig. 2a, c reveal metallic nature of these compounds; crucially, in both cases the DOS in the vicinity of the Fermi level contain significant contributions from the Fe 3d, Xe 5p and O 2p states, indicating considerable Fe-O and Xe-O bonding interactions. We further calculated projected crystal orbital Hamiltonian population (pCOHP) that evaluates weighted population of wavefunctions on two atomic orbitals of a pair of selected atoms<sup>39</sup>. The results in Fig. 2b, d reveal characteristic Fe-O and Xe-O covalent bonding as indicated by the prominent features of strong low-energy bonding states together with some occupied antibonding states near the Fermi level in each case. It is noted that the occupied bonding states in Xe<sub>2</sub>FeO<sub>2</sub> occur deeper below the Fermi level compared to those in XeFe<sub>3</sub>O<sub>6</sub>, indicating higher stability of Xe<sub>2</sub>FeO<sub>2</sub>. Moreover, integrated COHP (ICOHP) provides an estimate of the overall bonding strength<sup>39</sup>. Calculated ICOHP values for the Fe-O and Xe-O bonds at 150 GPa are -1.45 eV/pair and -0.24 eV/pair in XeFe<sub>3</sub>O<sub>6</sub> and -1.01 eV/pair and -0.12 eV/pair in Xe<sub>2</sub>FeO<sub>2</sub>, respectively. These results show considerable Xe-O bonding compared to the strong Fe-O bonding, in sharp contrast to recently discovered He-FeO<sub>2</sub> compound where He atoms show little direct bonding<sup>37</sup> but instead serve as a Coulomb shield in



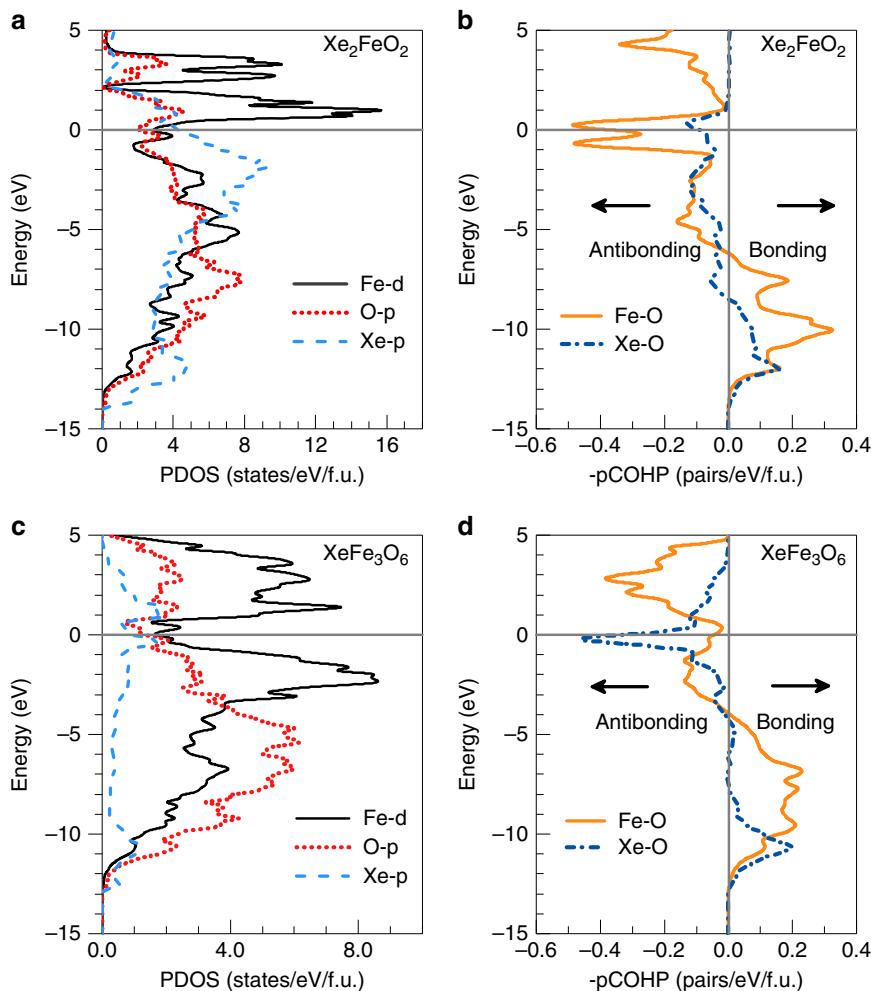
**Fig. 1 Energetic stability and structures of Xe-Fe oxides.** **a** The ground-state convex hull with solid lines for the  $FeO_2$ -Xe system constructed from calculated formation enthalpy ( $\Delta H$ ) data, identifying two stable Xe-Fe oxides,  $Xe_2FeO_2$  and  $XeFe_3O_6$ , at 150 GPa and 200 GPa. The solid and open symbols represent the stable structures lying on the convex hull and the unstable structures above the convex hull, respectively. **b** Phonon dispersions of  $Xe_2FeO_2$  at 150 GPa. **c** Phonon dispersions of  $Xe_3FeO_6$  at 150 GPa. **d** The structure of  $Xe_2FeO_2$  with a polyhedral and an enlarged view. **e** The structure of  $Xe_3FeO_6$  with a polyhedral and an enlarged view. Xe, Fe, and O atoms are, respectively, shown in purple, gray, and red spheres.

stabilizing the structure<sup>40</sup>. We also examined charge distribution in  $Xe_2FeO_2$  and  $XeFe_3O_6$  by a Bader charge analysis<sup>41</sup>, and the results reveal a considerable amount of highly unusual charge transfer from Fe and Xe to O atoms. At 150 GPa, the Bader partial charges in  $Xe_2FeO_2$  are +0.30, +1.40, -1.00 for Xe, Fe, and O, respectively; meanwhile, Bader partial charges in  $XeFe_3O_6$  are +1.35, +1.35, -0.90 for Xe, Fe, and O, respectively, at the same pressure. As a result, Xe atoms in  $XeFe_3O_6$  can donate more electrons than in  $Xe_2FeO_2$  and Xe atoms can display different valence states in  $FeO_2$ -Xe compounds. These significant charge transfers once again indicate strong bonding formation involving Xe, which is rare among noble gas atoms.

**Thermal effect.** Thermal effects play a crucial role in material stability at pertinent geophysical conditions, where temperatures reach 2000–4500 K. Here, we evaluate Gibbs free energy of  $Xe_2FeO_2$  and  $XeFe_3O_6$  by calculating lattice contributions to the entropic term using the quasiharmonic approximation to account for volume dependence of phonon frequencies due to temperature induced lattice expansion. In Fig. 3a we present relevant energetic terms affecting structure stability. It is seen that internal energy  $U$  values of the two Xe-Fe oxides are higher than those of

their separate constituents, namely Xe and  $FeO_2$ , but the  $PV$  terms are decisively favorable and dominant, producing the lower enthalpy  $H$  for the formation of both oxides. The temperature effect (i.e., thermal vibration of atomic positions) are favorable to reduce Gibbs free energy  $G$  of the Xe-Fe oxides even more relative to their separate constituents, further stabilizing the resulting crystal structures. Consequently, the threshold pressure above which these oxides are stable reduces considerably at increasing temperatures, thereby significantly expanding their stability field as will be seen in the phase diagram presented below.

**Phase diagram.** For a full assessment of temperature effects, we have performed extensive energetic and ab initio molecular dynamics (AIMD) simulations to evaluate structural stability and construct pressure-temperature ( $P$ - $T$ ) phase diagram for the Xe-Fe oxide system. We present in Fig. 3b, c the mean square deviations (MSD) of atomic positions in the Xe-Fe oxides at typical high  $P$ - $T$  conditions of 150 GPa and 3000 K, and the results show that the Fe, O, and Xe atoms all remain near their lattice sites, indicating stability of the crystal structure. Similar AIMD simulations were performed systematically to probe each phase and determine the boundary where temperature-driven



**Fig. 2 Electronic properties of the two Xe-Fe oxides at 150 GPa.** **a** Projected density of states (PDOS) of Fe-d, O-p, and Xe-p orbitals in  $\text{Xe}_2\text{FeO}_2$ . **b** Projected crystal orbital Hamiltonian Population (-pCOHP) of the newly predicted  $\text{Xe}_2\text{FeO}_2$  compound. The values of  $-\text{pCOHP} > 0$  signify bonding states and the values of  $-\text{pCOHP} < 0$  signify antibonding states. **c** PDOS of Fe-d, O-p, and Xe-p orbitals in  $\text{XeFe}_3\text{O}_6$ . **d** -pCOHP of the newly predicted  $\text{XeFe}_3\text{O}_6$  compound. The Fermi energy is set to zero of the energy.

instability sets as indicated by deviating MSD from equilibrium positions; meanwhile Gibbs free energies were computed and compared to determine the boundaries between different solid phases in the  $P$ - $T$  space. The resulting phase diagram (Fig. 4) spans a wide  $P$ - $T$  range covering the lower mantle and higher  $P$ - $T$  regions.

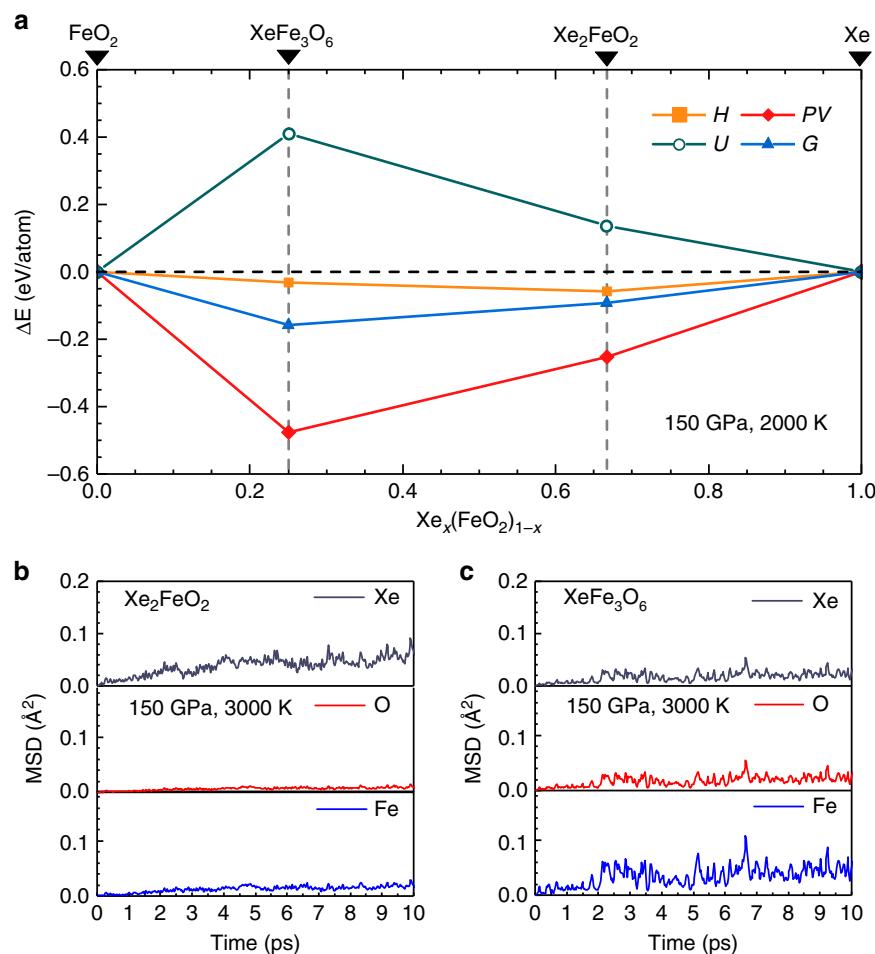
We now analyze the stability fields of the predicted Xe-Fe oxides under the ( $P$ ,  $T$ ) conditions conforming to geological constraints dictated by the geotherm that is also shown in Fig. 4. It is seen that  $\text{Xe}_2\text{FeO}_2$  is stable in the pressure range 110–120 GPa and temperatures around 2500 K inside the geotherm corresponding to the deep lower mantle region; meanwhile, both  $\text{Xe}_2\text{FeO}_2$  and  $\text{XeFe}_3\text{O}_6$  are stable between pressures 120–136 GPa and temperatures 2500–3600 K inside the geotherm corresponding to the lowest mantle to core-mantle boundary (CMB); finally, as pressure and temperature rise further,  $\text{Xe}_2\text{FeO}_2$  becomes the sole stable phase.

The above results suggest stable Xe-Fe oxides under the ( $P$ ,  $T$ ) conditions in vast deep-Earth regions. It is, however, necessary to assess the viability of the predicted Xe-Fe oxides in geological environments by examining their key material characteristics. To this end, we have run AIMD simulations to determine crystal structures at selected ( $P$ ,  $T$ ) conditions and used an AIMD-based strain-stress method<sup>42,43</sup> to calculate the elastic tensors, from

which elastic-wave velocities were determined by solving the Christoffel equation  $\det |T_{ik} - \delta_{ik} V^2| = 0$ , where  $\delta_{ik}$  is the Kronecker delta function,  $V$  is one of the seismic velocities, and  $T_{ik}$  is the Christoffel stiffness<sup>44</sup>.

**Mass density and sound velocities.** We examine mass density and mean compressional ( $P$ -wave) and shear ( $S$ -wave) sound velocities,  $V_P$  and  $V_S$ , respectively, at two representative ( $P$ ,  $T$ ) points: (120 GPa, 2500 K) for lower mantle, and (135 GPa, 3500 K) for CMB, and compare with geological data. We first examine  $\text{XeFe}_3\text{O}_6$ , whose stability field compared to the geotherm indicates its stability in the lower mantle and CMB regions, but higher temperatures destabilize this compound. The calculated densities of  $\text{XeFe}_3\text{O}_6$  are 8.86 and 9.06 g/cm<sup>3</sup> at the selected lower mantle and CMB ( $P$ ,  $T$ ) points, respectively, which lie within or close to the range of 4.95–9.90 g/cm<sup>3</sup> from the core rigidity zone (CRZ) model and the range of 5.57–8.91 g/cm<sup>3</sup> from the ultralow velocity zone (ULVZ) model<sup>45</sup>. The calculated  $V_P$  ( $V_S$ ) are 8.94(4.03) km/s and 9.20(4.26) km/s, respectively, which lie within the range of 8.20–10.70 km/s (1.00–5.00 km/s) for the ULVZs<sup>45</sup>. All these results indicate that  $\text{XeFe}_3\text{O}_6$  is a viable constituent at the lower mantle and CMB ( $P$ ,  $T$ ) conditions.

The calculated densities of  $\text{Xe}_2\text{FeO}_2$  are 9.78 and 9.87 g/cm<sup>3</sup> at the lower mantle and CMB points, respectively, which lie outside



**Fig. 3 Calculated energetic terms and the mean square deviations.** **a** Various energetic term ( $\Delta E$ ) for the two Xe-Fe oxides, enthalpy (H), pressure-volume (PV) terms, internal energy (U), and Gibbs free energy (G) at 150 GPa, 2000 K. **b** Mean square deviations (MSD) of Xe, O, and Fe atomic positions in  $\text{Xe}_2\text{FeO}_2$  at 150 GPa, 3000 K. **c** MSD of Xe, O, and Fe atomic positions in  $\text{XeFe}_3\text{O}_6$  at 150 GPa, 3000 K.

the range of 5.57–8.91 g/cm<sup>3</sup> from the ULVZ model and at the top of the range of 4.95–9.90 g/cm<sup>3</sup> from the CRZ model<sup>45</sup>. The calculated  $V_P$  ( $V_S$ ) are 7.83(4.21) km/s and 7.94(4.02) km/s at the lower mantle and CMB points, respectively. While these  $V_S$  values lie within the range of 1.00–5.00 km/s from the CRZ model or the range 2.91–6.17 km/s from the ULVZ model<sup>45</sup>, the  $V_P$  values are out of the range of 10.97–13.03 km/s from the ULVZ model or the range of 8.20–10.70 km/s from the CRZ model<sup>45</sup>. These results render  $\text{Xe}_2\text{FeO}_2$  a marginal lower mantle or CMB constituent at best.

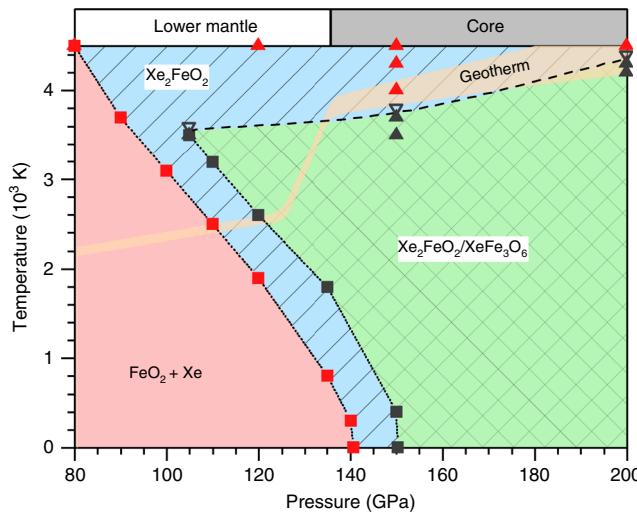
**Reaction of noble gases and deep-Earth constituents.** Finally, we highlight several significant aspects on the special role of FeO<sub>2</sub> in trapping Xe in deep Earth. First, we have systematically examined possible reaction of Xe with major deep-Earth constituents FeO, SiO<sub>2</sub>, MgO, CaO, and Al<sub>2</sub>O<sub>3</sub>, and the resulting convex-hull data (Supplementary Fig. 5) show highly unfavorable energetics in all the cases, offering an underlying cause for unsuccessful past attempts to find Xe-bearing minerals in Earth's mantle. Second, we have examined possible reactions of other noble gases Ne, Ar, and Kr with FeO<sub>2</sub>, and the results (Supplementary Fig. 6) indicate no tendency toward forming any stable noble-gas-Fe oxides up to 200 GPa. These results provide the possibility that Xe could be the sole inert element for reacting with deep-Earth constituents under mantle conditions. Moreover, while He-bearing compound FeO<sub>2</sub>He is found stable at CMB conditions, there is little direct bonding between He and Fe or O

atoms in the compound<sup>37</sup>. Compared to Kr, Ar, Ne, and He, Xe has the lowest ionization energy and electronegativity, and consequently Xe is the easiest noble-gas atom to open up its outermost closed shell and form direct bonding as found in  $\text{Xe}_2\text{FeO}_2$  and  $\text{XeFe}_3\text{O}_6$ .

In summary, we have identified two Xe-Fe oxides,  $\text{Xe}_2\text{FeO}_2$  and  $\text{XeFe}_3\text{O}_6$ , that are the first viable Xe-bearing compound at Earth's lower mantle conditions. These new compounds are predicted by extensive crystal structure search in conjunction with ab initio energetic calculations and molecular dynamics simulations. Mass densities and compressional and shear sound velocities calculated at deep-Earth conditions are compatible with pertinent ULVZ and PREM data, thus confirming viability of  $\text{Xe}_2\text{FeO}_2$  in geological environments. These results provide compelling evidence for a distinct deep-Earth Xe reservoir beyond previously proposed Xe-Fe and Xe-Ni intermetallic compounds in Earth's inner core, thereby greatly expanding the range and scope of Xe-bearing compounds in deep Earth. The Xe-Fe oxides may enrich the understanding of prominent geophysical and geochemical processes, such as seismic anomalies near the CMB and possibly new chemical reactions inside Earth's lower mantle.

## Methods

**Structural predictions.** Our structure search is based on a global optimization of free-energy surfaces using the CALYPSO methodology<sup>46,47</sup>, which has been successfully employed in predicting a large variety of crystal structures<sup>48–52</sup>. Evolutionary variable-cell calculations were performed at 120, 150, and 200 GPa with 1,



**Fig. 4 The Pressure-temperature (P-T) phase diagram of the Xe-FeO<sub>2</sub> system.** The dotted and dashed lines indicate phase boundaries and temperature-driven phase instability, which are determined by Gibbs free energy and ab initio molecular dynamics (AIMD) calculations, respectively. The square symbols show phase transition points based on relative Gibbs free energy, and the solid and open triangle symbols represent stable and temperature-driven unstable solid phases, respectively, determined by AIMD simulations. The P-T regions of stable Xe<sub>2</sub>FeO<sub>2</sub> are covered by slash lines and the P-T regions of stable XeFe<sub>3</sub>O<sub>6</sub> are filled by back-slash. The pressure boundary between the lower mantle and the core is shown at the top of the figure. Also shown is the geotherm of the Earth's interior<sup>65</sup>.

2, 3, and 4 formula units (f. u.) per cell. Most searches converge in 50 generations with about 2500 structures generated.

**Ab initio calculations.** First-principles total-energy and electronic property calculations were carried out using the density functional theory with the Perdew-Burke-Ernzerhof exchange-correlation functional in the generalized gradient approximation (GGA)<sup>53,54</sup> as implemented in the VASP code<sup>55</sup>, adopting frozen-core all-electron projector-augmented wave method<sup>56</sup> with 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>7</sup> 4s<sup>1</sup>, 2s<sup>2</sup> 2p<sup>4</sup>, and 4d<sup>10</sup> 5s<sup>2</sup> 5p<sup>6</sup> treated as valence electrons for Fe, O, and Xe, respectively. Correlation effects among the Fe 3d electrons were treated in the GGA + U approach<sup>57,58</sup>, adopting the recently proposed on-site Coulomb interaction  $U = 5.0$  eV and a Hund's coupling  $J = 0.8$  eV<sup>59–61</sup>. The spin-polarized and magnetic states were considered in obtaining the total-energy of the compounds containing iron. Zero-point energy was included in all reported calculations. A cutoff energy of 1200 eV for the plane-wave expansion and fine Monkhorst-Pack  $\mathbf{k}$  meshes<sup>62</sup> were chosen to ensure enthalpy convergence of better than 1 meV/atom.

**Phonon calculations.** To determine the dynamical stability, we performed phonon calculations by the direct supercell method using the Hellmann-Feynman theorem, as implemented in Phonopy code<sup>63</sup>. The harmonic interatomic force constants are calculated by  $3 \times 3 \times 3$  and  $3 \times 2 \times 2$  supercells for  $P2_1/c$ -Xe<sub>2</sub>FeO<sub>2</sub> and  $P-1$ -XeFe<sub>3</sub>O<sub>6</sub>, respectively. Forces were calculated for atomic displacements of 0.01 Å, with a convergence threshold of  $1 \times 10^{-5}$  eV/Å.

**Van der Waals interaction.** To examine the contribution of vdW interaction to the lattice energy, we have calculated the enthalpy of formation of Xe<sub>2</sub>FeO<sub>2</sub> at high pressures using the vdW-DF2 density functional<sup>64</sup>. Our results show that the enthalpy of formation is less sensitive to the contribution of vdW correction at high-pressure conditions for Xe-FeO<sub>2</sub> compounds, e.g., about 0.6 meV/atom for  $P2_1/c$  Xe<sub>2</sub>FeO<sub>2</sub> at 135 GPa, thus vdW interaction is not considered in the calculations of lattice energy.

## Data availability

The authors declare that the main data supporting the findings of this study are contained within the paper and its associated Supplementary Information. All other relevant data are available from the corresponding author upon reasonable request.

## Code availability

CALYPSO code is free for academic use, by registering at <http://www.calypso.cn>. The other scripts are available from the authors upon reasonable request.

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## Author contributions

Q.L., C.C., and Y.M. designed the research; F.P., and X.S. performed the calculations; F.P., X.S., C.L., Q.L., M.M., C.C., and Y.M. analyzed and interpreted the data, and contributed to the writing of the paper.

## Competing interests

The authors declare no competing interests.

## Additional information

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## **Supplementary information**

**for**

### **Xenon Iron Oxides Predicted as Potential Xe Hosts in Earth's Lower Mantle**

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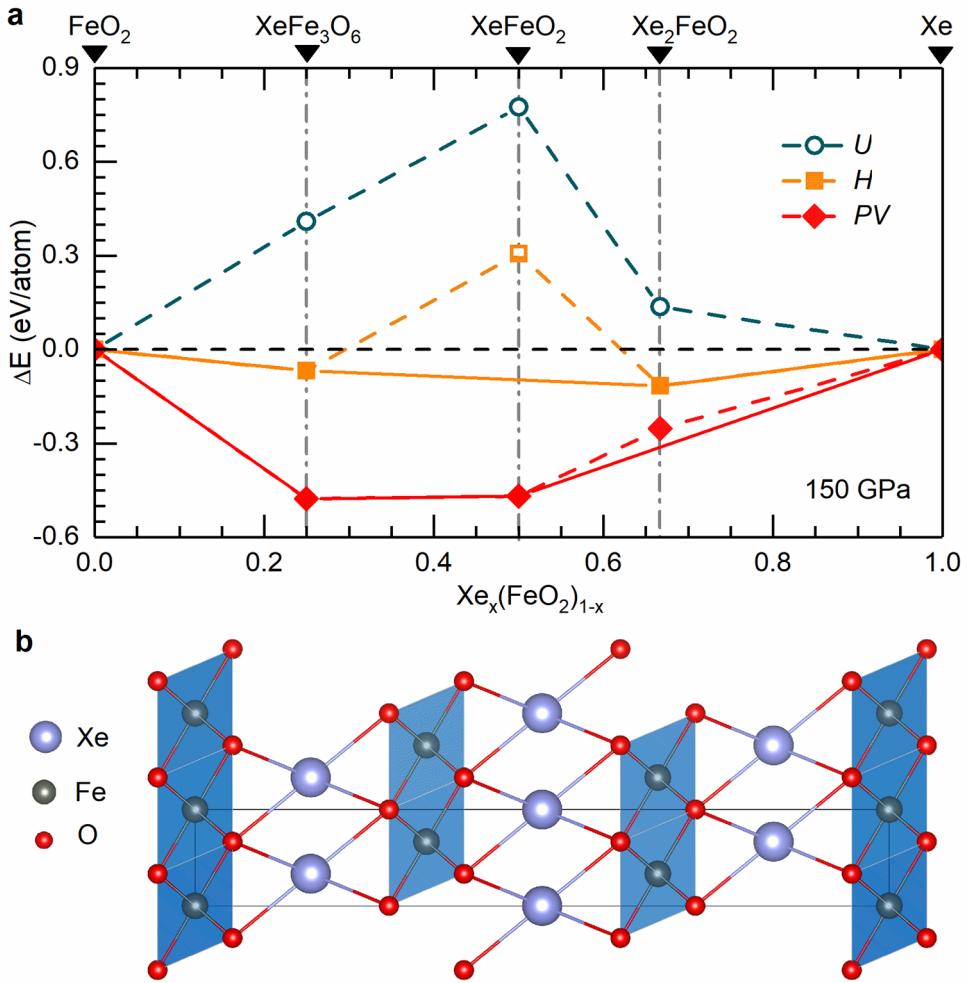
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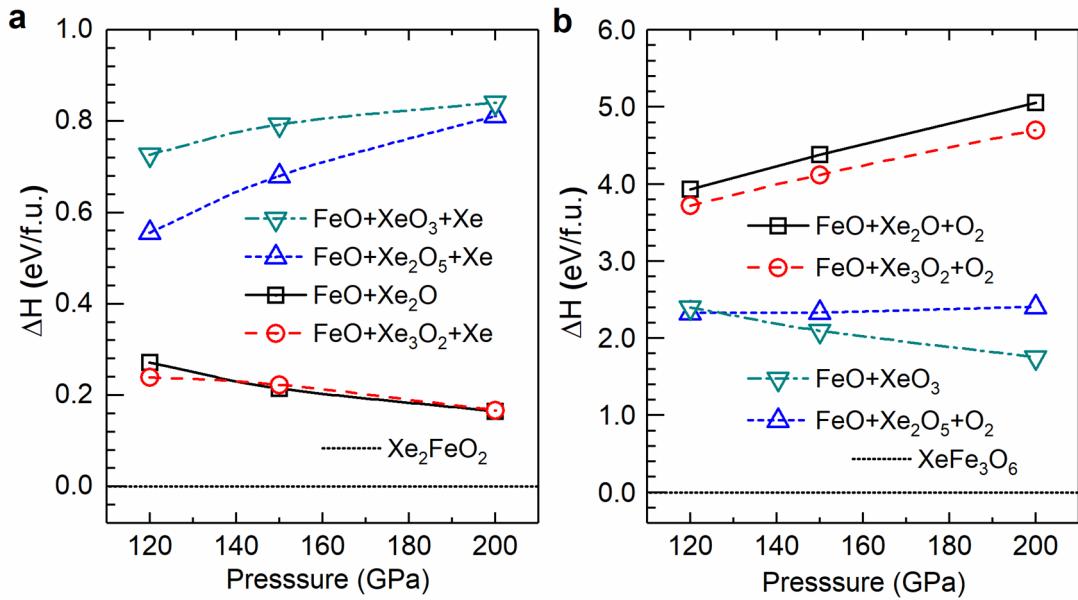
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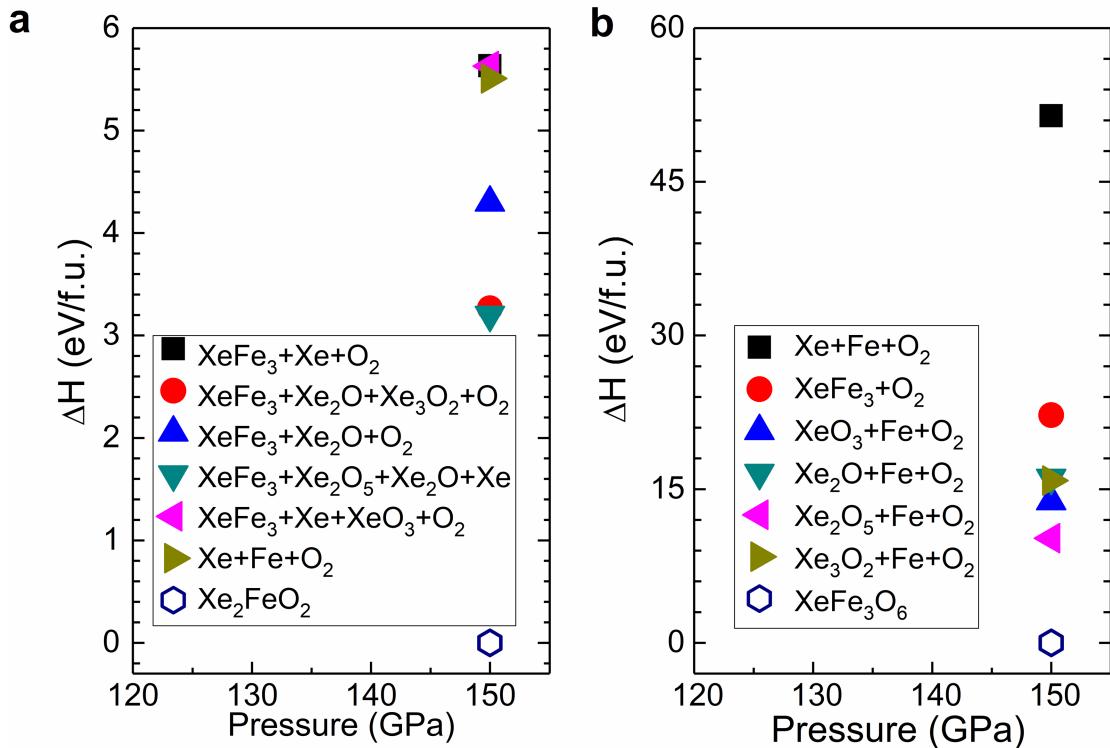
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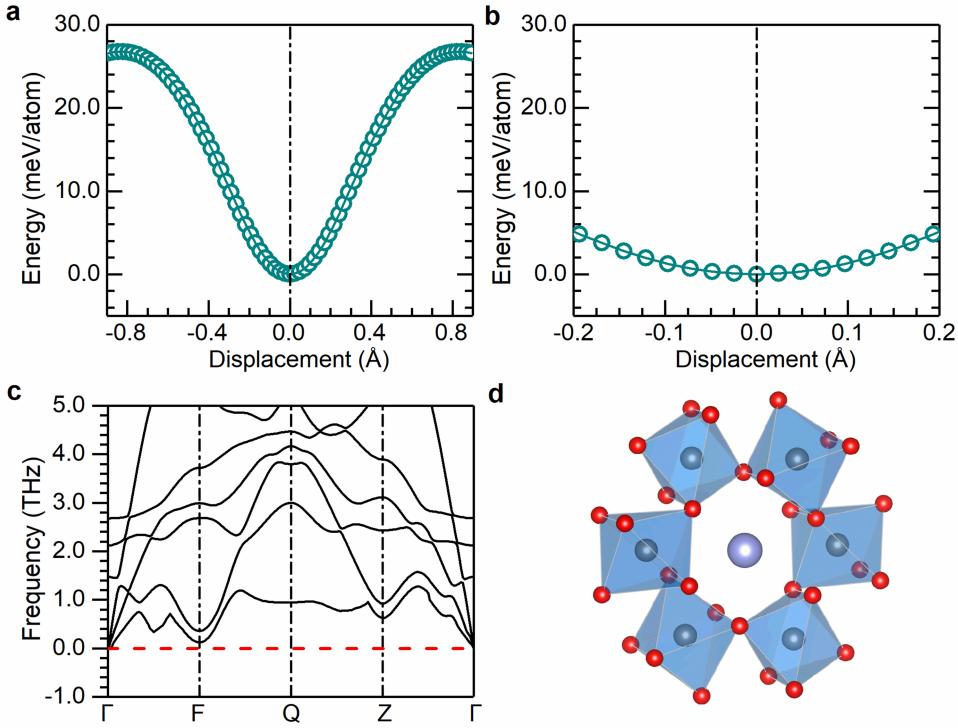
**Supplementary Figure 1. Calculated energetic terms of  $\text{FeO}_2$ -Xe compounds and the crystal structure of  $\text{XeFeO}_2$  at 150 GPa.** a The enthalpies  $\Delta H$ , the internal energies  $\Delta U$ , and the pressure-volume term  $\Delta(PV)$  for the Xe-Fe oxides. b The polyhedral views of theoretically predicted  $\text{XeFeO}_2$  structure. We discuss the energetic terms to examine the mechanism of thermodynamic stability for these  $\text{FeO}_2$ -Xe compounds. The pressure-volume terms, associated with packing efficiency, make similar contributions to lowering the enthalpy for  $\text{XeFe}_3\text{O}_6$  and  $\text{XeFeO}_2$ , while the unfavorable internal energy, associated with bonding enhancement, leads to a positive formation enthalpy for  $\text{XeFeO}_2$ . Although the value of pressure-volume term of  $\text{Xe}_2\text{FeO}_2$  is much lower than these of  $\text{XeFe}_3\text{O}_6$  and  $\text{XeFeO}_2$ , it still offsets the relatively weak negative effect of internal energy to enthalpy, thus yielding its thermodynamic stability with formation enthalpy lying on the convex hull.



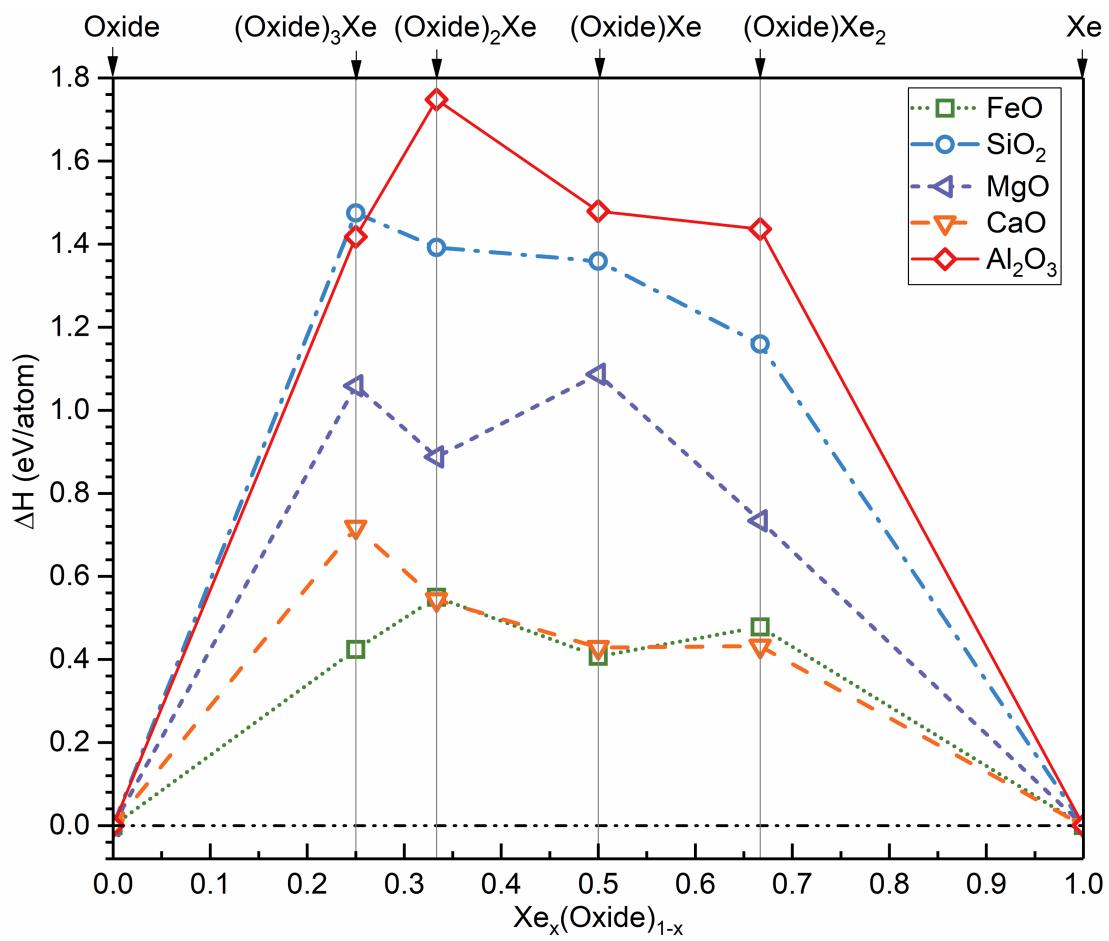
**Supplementary Figure 2. The relative stability of  $Xe_2\text{FeO}_2$  and  $Xe\text{Fe}_3\text{O}_6$  relative to  $\text{FeO}$  and  $\text{Xe}$  oxides, respectively.** The results in Supplementary Figure 1a shows that  $Xe_2\text{FeO}_2$  is at least 0.165 eV/f.u. more stable in energy relative the products of  $\text{FeO} + \text{Xe}_2\text{O}$ ,  $\text{FeO} + \text{Xe}_3\text{O}_2 + \text{Xe}$ ,  $\text{FeO} + \text{Xe}_2\text{O}_5 + \text{Xe}$ , and  $\text{FeO} + \text{Xe}_3\text{O}_2 + \text{Xe}$ . For  $Xe\text{Fe}_3\text{O}_6$ , the results in Supplementary Figure 2b shows that it is at least 1.749 eV/f.u. energetically much superior and against decomposition into a mixture of  $\text{FeO} + \text{Xe}_2\text{O} + \text{O}_2$ ,  $\text{FeO} + \text{Xe}_3\text{O}_2 + \text{O}_2$ ,  $\text{FeO} + \text{Xe}_2\text{O}_5 + \text{O}_2$ , or  $\text{FeO} + \text{XeO}_3$ .



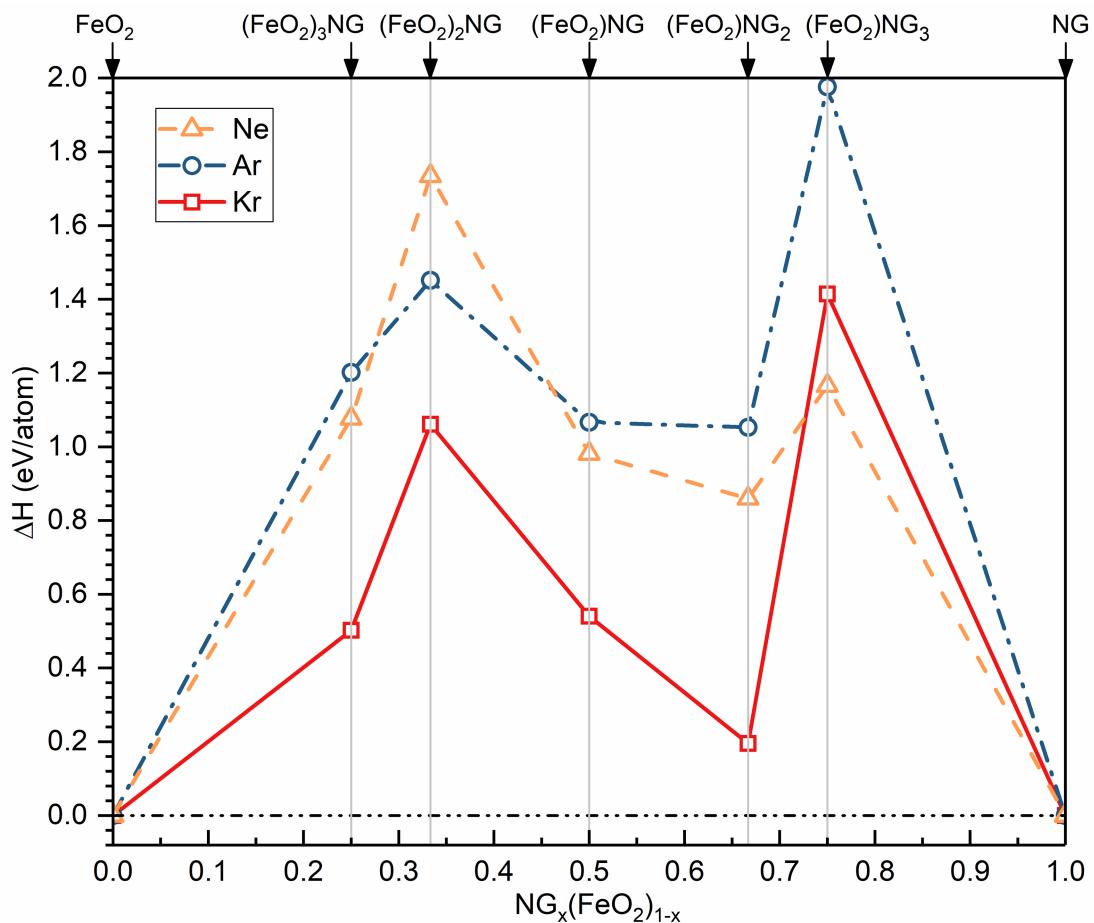
**Supplementary Figure 3. The relative stability of  $\text{Xe}_2\text{FeO}_2$  and  $\text{XeFe}_3\text{O}_6$  relative to  $\text{Xe}_x\text{Fe}_y/\text{Fe}$  and  $\text{O}/\text{Xe}$  oxides, respectively.** Our results show that  $\text{Xe}_2\text{FeO}_2$  [Supplementary Figure 3a] is at least 3.265 eV/f.u. in energy more stable than the products of  $\text{XeFe}_3 + \text{Xe} + \text{O}_2$ ,  $\text{XeFe}_3 + \text{Xe}_2\text{O} + \text{O}_2$ ,  $\text{XeFe}_3 + \text{Xe}_3\text{O}_2 + \text{Xe}_2\text{O} + \text{O}_2$ ,  $\text{XeFe}_3 + \text{Xe}_2\text{O}_5 + \text{Xe}_2\text{O} + \text{Xe}$ ,  $\text{XeFe}_3 + \text{XeO}_3 + \text{Xe} + \text{O}_2$ , or  $\text{Fe} + \text{Xe} + \text{O}_2$ . Supplementary Figure 3b reveals that  $\text{XeFe}_3\text{O}_6$  remains stable (even reach ~10.0 eV/f.u.) relative the products of  $\text{Fe} + \text{Xe} + \text{O}_2$ ,  $\text{XeFe}_3 + \text{O}_2$ ,  $\text{Fe} + \text{XeO}_3 + \text{O}_2$ ,  $\text{Fe} + \text{Xe}_2\text{O}_5 + \text{O}_2$ ,  $\text{Fe} + \text{Xe}_3\text{O}_2 + \text{O}_2$ , or  $\text{Fe} + \text{Xe}_2\text{O} + \text{O}_2$ .



**Supplementary Figure 4. The vibrational analyses for  $\text{XeFe}_3\text{O}_6$ .** a The internal energy difference at various Xe positions along the channels (the vibration eigenvector of the vibrational mode of the lowest-frequency) of the Fe-O framework at 150 GPa and zero temperature. The original structure is located at an energy minimum on the energy surface, signifying its dynamical stability. b The internal energy difference of  $\text{XeFe}_3\text{O}_6$  at various Xe positions along the channels near the equilibrium position. c The theoretical phonon spectrum at the low-frequency region. d The snapshot for the Fe-O framework with Xe atom in the channel. The vibrational modes close to zero for  $\text{XeFe}_3\text{O}_6$  stem from the relatively large internal volume for Xe atom that leads to the concomitant longer bond lengths and weak interaction between Xe atoms and O atoms. The maximum distance between Xe and O atom is 2.52 Å in  $\text{XeFe}_3\text{O}_6$  at 150 GPa, which is much longer than that of Xe oxides (e.g. ~2.37 Å in  $\text{Xe}_2\text{O}_5$ ) and  $\text{Xe}_2\text{FeO}_2$  with CN=3 of Xe (2.42 Å) at the same pressure. As a result, Xe-O bonds of  $\text{Xe}_2\text{FeO}_2$  are much stronger than that of  $\text{XeFe}_3\text{O}_6$ . To explore the possible dynamical instabilities, we have move one Xe atom along the channels of the Fe-O framework (the vibration eigenvector of the mode for the lowest-frequency branch at F) while fixing the other atoms. The calculated static energy shows that the original structure is located at an energy minimum on the energy surface, signifying its dynamical stability. The curve is smooth near the equilibrium position (e.g., < 0.2 Å), making it easier for the Xe atoms to move about along the eigenvector of the low-frequency phonon mode, in agreement with the theoretical phonon spectrum. Meanwhile, the curve has a rather high energy cost at large displacements, and the phase transition is impeded by kinetic barrier of ~26.8 meV/atom at 150 GPa and zero temperature, indicating that it is difficult for the Xe atoms to escape from the lattice. With the consideration of temperature effect, our AIMD calculations also reveal that Xe atoms can only vibrate near the balanced positions below melting points.



**Supplementary Figure 5. Enthalpies of formation of various Oxide-Xe (Oxide = FeO, SiO<sub>2</sub>, MgO, CaO or Al<sub>2</sub>O<sub>3</sub>) compounds at 200 GPa.** All the Oxide-Xe compounds which have positive formation enthalpies are not stable at 200 GPa. (Correlation effects among the Fe 3d electrons were treated in the GGA + *U* approach, adopting the recently proposed on-site Coulomb interaction *U* = 5.0 eV and a Hund's coupling *J* = 0.8 eV and the spin-polarized and magnetic states are considered to calculate the formation enthalpies.)



**Supplementary Figure 6. Enthalpies of formation of various  $FeO_2$ -NG (NG=Ne, Ar, Kr) compounds at 200 GPa.** All the  $FeO_2$ -NG compounds which have positive formation enthalpies are not stable at even 200 GPa.

**Supplementary Table 1. Calculated structural parameters of  $\text{XeFe}_3\text{O}_6$  and  $\text{Xe}_2\text{FeO}_2$ .**

Space group		Lattice Parameters	Atomic coordinates (fractional)			
		(Å, °)	Atoms	x	y	
$\text{XeFe}_3\text{O}_6$ (150 GPa)	$P-1$	$a = 5.043$	Fe1(2i)	0.7501	0.0025	0.5003
		$b = 5.702$	Fe2(2i)	0.2503	0.4999	0.0014
		$c = 5.780$	Fe3(1d)	0.5000	0.0000	0.0000
		$\alpha = 119.475$	Fe4(1a)	0.0000	0.0000	0.0000
		$\beta = 95.276$	O1(2i)	0.7114	0.7456	0.9008
		$\gamma = 96.930$	O2(2i)	0.7866	0.2544	0.0979
			O3(2i)	0.9452	0.3337	0.7559
			O4(2i)	0.4869	0.0716	0.3269
			O5(2i)	0.5565	0.6692	0.2431
			O6(2i)	0.0113	0.9333	0.6761
			Xe(2i)	0.2500	0.4979	0.5014
$\text{Xe}_2\text{FeO}_2$ (150 GPa)	$P2_1/c$	$a = 11.100$	Fe1(4e)	0.0003	0.5086	0.7496
		$b = 5.584$	Fe2(4e)	0.0001	0.7501	0.4994
		$c = 9.544$	O1(4e)	0.8919	0.2600	1.0763
		$\alpha = 90.000$	O2(4e)	0.1085	0.2590	0.5776
		$\beta = 136.089$	O3(4e)	0.8928	0.0025	1.3271
		$\gamma = 90.000$	O4(4e)	0.1070	0.4958	0.3271
			Xe1(4e)	0.6567	0.5036	0.7971
			Xe2(4e)	0.3420	0.7476	0.0480
			Xe3(4e)	0.3438	0.2477	0.0468
			Xe4(4e)	0.6571	0.0033	0.7974
$\text{XeFeO}_2$ (150 GPa)	$R-3m$	$a = b = 2.676$	Fe (3a)	0.0000	0.0000	0.0000
		$c = 16.629$	O (6c)	0.0000	0.0000	0.2794
		$\alpha = \beta = 90.000$	Xe (3b)	0.0000	0.0000	0.5000
		$\gamma = 12.000$				

## REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This difference between expected and actual abundance of xenon in the Earth's atmosphere is known as the "missing xenon paradox", which has left scientists stumped for decades. Attempt to explain of the paradox, many hypotheses have been proposed, e.g., Xe might be located within the Earth's as stable compounds. However, the pursuit of Xe-bearing compounds in the environment of the Earth's mantle has all failed. To explore possible capture and stabilization of Xe by suitable minerals in Earth's mantle will provide critical implications for the origin and evolution of the Earth and even the universe.

In the current manuscript, the authors carried out a comprehensive structure search of stable structures of Xe with common mantle minerals. The results show that FeO<sub>2</sub> and Xe can form thermodynamically stable compounds of Xe<sub>2</sub>FeO<sub>2</sub> and XeFe<sub>3</sub>O<sub>6</sub> with intriguing chemical bonding pattern in a wide range of pressure-temperature conditions of the Earth's mantle environment that support their viability in vast lower mantle region. In sharp contrast, the other noble gases do not react with major mantle oxides. The results offer new insights into robust materials basis, formation mechanism, and geological viability for elucidating the longstanding "missing xenon paradox". The study has been done professionally, clearly presented, and well written. I recommend its publication in Nature Communications after minor revisions, as suggest below.

1. The authors have provided substantive analyses on phonon dispersions to check for the dynamic stability of these proposed xenon-iron oxides. However, the detailed information for the supercell size and convergence criteria for the calculated dynamical dispersions are missing, which may be useful to the readers.
2. As shown in Fig. 1d, the crystal structure of Xe<sub>2</sub>FeO<sub>2</sub> appears to have a pseudo-layered bonding pattern. Although the Van der Waals (vdW) interaction may have little contribution to the energy and transition pressure at high-pressure conditions for these heavy elements, the authors still need to examine the contribution or give proper discussion to the lattice energy arising from vdW interaction.

Reviewer #3 (Remarks to the Author):

### Manuscript Review

Robust Xenon-Iron Oxides Predicted in Earth's Lower Mantle  
Peng, F. et al.

### General Comments

This paper proposes yet another phase for storing the xenon that is "missing" from Earth's atmosphere based on comparisons between solar or primordial noble gas abundances and present-day atmospheric noble gas concentrations. In this case, it is suggested that iron (II) peroxide (FeO<sub>2</sub>) will react with elemental xenon in Earth's mantle to produce two possible candidate ternary phases, Xe<sub>2</sub>FeO<sub>2</sub> and XeFe<sub>3</sub>O<sub>6</sub>. These could presumably provide an explanation and mineral repository for Earth's "missing" xenon.

This is a very important question that has been addressed numerous times over the past several decades, and the present work is potentially an interesting contribution to this discussion from a mineral physics perspective. Evolutionary structure-searching methods are used to generate the two candidate compositions and structures, and analysis of the structures and properties of these two candidate phases at P-T conditions appropriate to Earth's mantle by first principles electronic structure and molecular dynamics simulations show that indeed the two phases could be stable at these conditions if formed. The two candidate phases are also adequately shown to be stable with respect to decomposition with respect to a number of different phase combinations. Density and sound velocity calculations are used to compare to currently accepted deep Earth models to show that the presence of these phases in the deep Earth are moderately consistent with observation. The methods are sound and conclusions justified with respect to the stability of the phases at the P-T conditions examined. On balance, the methods used are well-established and not particularly novel at this point in their development. The geochemical/geophysical context is not well developed or supported. The results, however, do potentially constitute an interesting contribution to the literature of high pressure chemistry.

In the opinion of this reviewer, however, work in this area has passed the stage at which simply stating that xenon is present in the Earth and showing by experiment or theoretical modeling that xenon may form stable phases upon combination with existing mineral phases in Earth's interior can provide a useful approach to this problem. At this point, from the geochemical perspective, that the "missing" xenon is present somewhere in the Earth is clear enough. It is now important for authors proposing this type of mineral physics solution to the "missing xenon" problem to establish that in fact free xenon should be present at the depth where, and P-T conditions at which, these existing mantle mineral phases are proposed to react with it. In the case of the present manuscript, this is particularly important, since the presence of FeO<sub>2</sub>, whose actual presence in the mantle is highly suspect on geophysical and geochemical grounds anyway, is required for the formation of the candidate phases discussed by the authors. In that respect, it should be clearly established by the authors that free xenon should be available at the specific mantle P-T conditions they propose for reaction with FeO<sub>2</sub> (i.e., the P-T conditions at which goethite presumably transforms to FeO<sub>2</sub>). If that information is not available presently in the literature, then the geophysical speculations provided by the authors are out of place and the manuscript should be reformulated as a relevant contribution to xenon chemistry. Indeed, with the first-principles methods employed in this work, there is certainly enough in the way of discussion of redox chemistry with xenon and ferric iron to make a very interesting study.

#### Specific Comments

1. It seems that over the years, the missing xenon "problem" has become the missing xenon "paradox." Perhaps this makes attempts at solving the problem more pressing or relevant, but this is not a paradox, but rather simply an unsolved problem—perhaps a puzzling problem without a clear answer yet, but still just a scientific problem nonetheless. A paradox exists when the available evidence logically suggests one outcome, when something opposite is actually observed. That is not the case here. The reason why the xenon is missing is understood, we just don't yet know where it is in the Earth.

2. The second to last statement in the abstract, if true, would appear to have solved the missing xenon problem already. In fact, this is clearly not the case, even given the results of the present work. Xe does not react with major mantle oxides either, according to the authors later in the manuscript at line 158, and therefore the fact that other noble gases do not react with major mantle oxides is not a reason for the selective depletion of xenon observed in Earth's atmosphere. This statement should be removed because it is obviously false as well as contradictory.

3. The authors use the Caldwell, et al. (1997) paper to reference work that proposed that Xe is stored in stable compounds within the Earth. In fact, this 1997 paper suggests quite clearly that

the answer to the missing Xe problem lies most likely not in deep mantle or core phases.

4. XeFeO<sub>2</sub> would appear to have the simplest structure and might be predicted over the other two at deep mantle conditions, as minerals tend to become structurally simpler with increasing pressure and temperature. Structurally speaking, why is this composition so unstable compared to the other two? This question should be addressed explicitly.

5. The authors should be more specific about the meaning of "favorable temperature effects" at line 112.

6. Figure 1: Crystal structure representations are inadequate to observe the important details of the structure. What are the coordination geometries around Xe with its coordination numbers of 3 or 6? How does the Xe with CN = 6 in the channel of the XeFe<sub>3</sub>O<sub>6</sub> structure result in a soft phonon mode? A better resolution on the phonon dispersion curve would illustrate that soft mode more effectively.

7. The statement at line 163 suggesting that the current results explain the selective depletion of Xe from Earth's atmosphere is not supported by the current work and should be eliminated or heavily qualified. The results provide one plausible explanation for how the missing Xe is sequestered within the Earth, but an explanation for the depletion of Xe from the atmosphere must include a mechanism for how the Xe has been brought from the atmosphere into the mantle to a depth where reaction with FeO<sub>2</sub> is feasible. Likewise, the closing statements at lines 172-178 should be qualified as well.

8. There are numerous errors in usage and grammar throughout the manuscript. It should be carefully proofread by a native English speaker.

In its present form, the manuscript is not suitable for publication in Nature Communications, but may be suitable after major revision and a refocusing of the discussion away from the geochemical perspective if support for the existence of Xe at deep mantle conditions cannot be explicitly documented.

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## Response to reviewer #1

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### Reviewer #1 (Remarks to the Author):

*This difference between expected and actual abundance of xenon in the Earth's atmosphere is known as the "missing xenon paradox", which has left scientists stumped for decades. Attempt to explain of the paradox, many hypotheses have been proposed, e.g., Xe might be located within the Earth's as stable compounds. However, the pursuit of Xe-bearing compounds in the environment of the Earth's mantle has all failed. To explore possible capture and stabilization of Xe by suitable minerals in Earth's mantle will provide critical implications for the origin and evolution of the Earth and even the universe.*

*In the current manuscript, the authors carried out a comprehensive structure search of stable structures of Xe with common mantle minerals. The results show that FeO<sub>2</sub> and Xe can form thermodynamically stable compounds of Xe<sub>2</sub>FeO<sub>2</sub> and XeFe<sub>3</sub>O<sub>6</sub> with intriguing chemical bonding pattern in a wide range of pressure-temperature conditions of the Earth's mantle environment that support their viability in vast lower mantle region. In sharp contrast, the other noble gases do not react with major mantle oxides. The results offer new insights into robust materials basis, formation mechanism, and geological viability for elucidating the longstanding "missing xenon paradox". The study has been done professionally, clearly presented, and well written.*

*I recommend its publication in Nature Communications after minor revisions, as suggest below:*

**Reply:** We are grateful to the reviewer for the positive assessment of our work, and we appreciate the recommendation for publishing our paper in Nature Communications.

**1. The authors have provided substantive analyses on phonon dispersions to check for the dynamic stability of these proposed xenon-iron oxides. However, the detailed information for the supercell size and convergence criteria for the calculated dynamical dispersions are missing, which may be useful to the readers.**

**Reply:** We thank the reviewer for the constructive suggestion. We have now included the following theoretical details starting on line 11 in **Methods** section in the revised manuscript: "To determine the dynamical stability, we performed phonon calculations by the direct supercell method using the Hellmann-Feynman theorem, as implemented

in Phonopy code. The harmonic interatomic force constants are calculated by  $3 \times 3 \times 3$  and  $3 \times 2 \times 2$  supercells for  $P2_1/c$ - $Xe_2FeO_2$  and  $P-1$ - $XeFe_3O_6$ , respectively. Forces were calculated for atomic displacements of  $0.01 \text{ \AA}$ , with a convergence threshold of  $1 \times 10^{-5} \text{ eV}/\text{\AA}$ .

*2. As shown in Fig. 1d, the crystal structure of  $Xe_2FeO_2$  appears to have a pseudo-layered bonding pattern. Although the Van der Waals (vdW) interaction may have little contribution to the energy and transition pressure at high-pressure conditions for these heavy elements, the authors still need to examine the contribution or give proper discussion to the lattice energy arising from vdW interaction.*

**Reply:** We thank the reviewer for raising this issue. To examine the contribution of vdW interaction to the lattice energy, we have calculated the enthalpy of formation of  $Xe_2FeO_2$  at high pressures using the vdW-DF2 density functional. Our results show that the enthalpy of formation is less sensitive to the contribution of vdW correction at high-pressure conditions for Xe-FeO<sub>2</sub> compounds, e.g., at 0.6 meV/atom for  $P2_1/c$   $Xe_2FeO_2$  at 135 GPa, thus vdW interaction is not considered in the calculations of lattice energy, as pointed by the reviewer.

We have added the above discussion to line 15 in the **Methods** section in the revised manuscript.

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## Response to the third reviewer

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### Reviewer #3 (Remarks to the Author):

#### General Comments

*This paper proposes yet another phase for storing the xenon that is “missing” from Earth’s atmosphere based on comparisons between solar or primordial noble gas abundances and present-day atmospheric noble gas concentrations. In this case, it is suggested that iron (II) peroxide ( $FeO_2$ ) will react with elemental xenon in Earth’s mantle to produce two possible candidate ternary phases,  $Xe_2FeO_2$  and  $XeFe_3O_6$ . These could presumably provide an explanation and mineral repository for Earth’s “missing” xenon.*

*This is a very important question that has been addressed numerous times over the past several decades, and the present work is potentially an interesting contribution to this discussion from a mineral physics perspective. Evolutionary structure-searching methods are used to generate the two candidate compositions and structures, and analysis of the structures and properties of these two candidate phases at P-T conditions appropriate to Earth’s mantle by first principles electronic structure and molecular dynamics simulations show that indeed the two phases could be stable at these conditions if formed. The two candidate phases are also adequately shown to be stable with respect to decomposition with respect to a number of different phase combinations. Density and sound velocity calculations are used to compare to currently accepted deep Earth models to show that the presence of these phases in the deep Earth are moderately consistent with observation. The methods are sound and conclusions justified with respect to the stability of the phases at the P-T conditions examined. On balance, the methods used are well-established and not particularly novel at this point in their development. The geochemical/geophysical context is not well developed or supported. The results, however, do potentially constitute an interesting contribution to the literature of high pressure chemistry.*

**Reply:** We appreciate the reviewer’s overall positive assessment on our reported work.

*In the opinion of this reviewer, however, work in this area has passed the stage at which simply stating that xenon is present in the Earth and showing by experiment or theoretical modeling that xenon may form stable phases upon combination with*

*existing mineral phases in Earth’s interior can provide a useful approach to this problem. At this point, from the geochemical perspective, that the “missing” xenon is present somewhere in the Earth is clear enough. It is now important for authors proposing this type of mineral physics solution to the “missing xenon” problem to establish that in fact free xenon should be present at the depth where, and P-T conditions at which, these existing mantle mineral phases are proposed to react with it. In the case of the present manuscript, this is particularly important, since the presence of  $\text{FeO}_2$ , whose actual presence in the mantle is highly suspect on geophysical and geochemical grounds anyway, is required for the formation of the candidate phases discussed by the authors. In that respect, it should be clearly established by the authors that free xenon should be available at the specific mantle P-T conditions they propose for reaction with  $\text{FeO}_2$  (i.e., the P-T conditions at which goethite presumably transforms to  $\text{FeO}_2$ ). If that information is not available presently in the literature, then the geophysical speculations provided by the authors are out of place and the manuscript should be reformulated as a relevant contribution to xenon chemistry. Indeed, with the first-principles methods employed in this work, there is certainly enough in the way of discussion of redox chemistry with xenon and ferric iron to make a very interesting study.*

**Reply:** We thank the reviewer for the positive evaluation of our work and constructive suggestions for improving the manuscript. We have carefully considered the reviewer’s comments and revised the manuscript accordingly, improving both the physics and the presentation. We have strengthened the description of xenon chemistry at the beginning of the revised manuscript, adding the following discussions.

“The chemical reaction of inert xenon (Xe), a quintessential full-shell element, was earliest predicted by Pauling in 1933 and the first xenon compound was experimentally produced in 1962<sup>1</sup>. Then, more xenon compounds were experimentally synthesized at ambient pressure, containing some most electronegative atoms like fluorine<sup>2-5</sup> or oxygen<sup>6-9</sup>. Subsequently, scientists found that pressure can effectively improve the chemical reactivity of Xe<sup>10-17</sup>. At moderate pressures, solid xenon forms weakly bonded compounds with other species, e.g., with  $\text{H}_2\text{O}$ <sup>10</sup> and  $\text{O}_2$ <sup>11,12</sup> at 1 and 3 GPa, respectively. Strikingly, several novel Xe compounds with unusual stoichiometries have been found to be thermodynamically stable at high pressures, e.g., Xe oxides<sup>13,14</sup>, Xe nitrides<sup>15</sup>, xenon-hydrogen<sup>16</sup>, and Xe-Mg compounds<sup>17</sup>.”

1. Bartlett, N. Xenon Hexafluoroplatinate(v)  $\text{Xe}^+[\text{PtF}_6]$ . *Proc. Chem. Soc.* **1**, 218 (1962).
2. Chernick, C. L. et al. Fluorine Compounds of Xenon and Radon. *Science* **138**, 136 (1962).

3. Claassen, H. H., Selig, H. & Malm, J. G. Xenon Tetrafluoride. *J. Am. Chem. Soc.* **84**, 3593 (1962).
4. Gavin JR, R. M. & Bartell, L. S. Molecular Structure of  $\text{XeF}_6$ . I. Analysis of Electron-Diffraction Intensities, *J. Chem. Phys.* **48**, 2460 (1968).
5. Hoppe, R., Daehne, W., Mattauch, H. & Roedder, K. Fluorination of Xenon. *Angew. Chem. Int. Ed. Engl.* **1**, 599 (1962).
6. Smith, D. F. Xenon Trioxide. *J. Am. Chem. Soc.* **85**, 816 (1963).
7. Templeton, D. H., Zalkin, A., Forrester, J. D. & Williamson, S. M. Crystal and Molecular Structure of Xenon Trioxide. *J. Am. Chem. Soc.* **85**, 817 (1963).
8. Huston, J. L., Studier, M. H. & Sloth, E. N. Xenon Tetroxide: Mass Spectrum. *Science* **143**, 1161 (1964).
9. Selig, H., Claassen, H. H., Chernick, C. L., Malm, J. G. & Huston, J. L. Xenon Tetroxide: Preparation and Some Properties. *Science* **143**, 1322 (1964).
10. Sanloup, C., Mao, H.-K. & Hemley, R. J. High-pressure transformations in xenon hydrates. *Proc. Natl. Acad. Sci. USA* **99**, 25 (2002).
11. Dewaele, A., Loubeyre, P., Dumas, P. & Mezouar, M. Oxygen impurities reduce the metallization pressure of xenon. *Phys. Rev. B* **86**, 014103 (2012).
12. Weck, G., Dewaele, A. & Loubeyre, P. Oxygen/noble gas binary phase diagrams at 296 K and high pressures. *Phys. Rev. B* **82**, 014112 (2010).
13. Zhu, Q., Jung, D. Y., Oganov, A. R., Glass, C. W., Gattiand, C. & Lyakhov, A. O. Stability of Xenon Oxides at High Pressures. *Nat. Chem.* **5**, 61 (2012).
14. Hermann, A. & Schwerdtfeger, P. Xenon Suboxides Stable under Pressure. *J. Phys. Chem. Lett.* **5**, 4336 (2014).
15. Peng, F., Wang, Y., Wang, H., Zhang, Y. & Ma, Y. Stable Xenon Nitride at High Pressures. *Phys. Rev. B* **92**, 094104 (2015).
16. Somayazulu, M. et al. Pressure-induced bonding and compound formation in xenon–hydrogen solids. *Nat. Chem.* **2**, 50 (2010).
17. Miao, M. S. et al. Anionic Chemistry of Noble Gases: Formation of Mg–NG (NG = Xe, Kr, Ar) Compounds under Pressure. *J. Am. Chem. Soc.* **137**, 14122 (2015).

Below we clarify the technical issues raised by the reviewer.

#### *Specific Comments:*

*1. It seems that over the years, the missing xenon “problem” has become the missing xenon “paradox.” Perhaps this makes attempts at solving the problem more pressing or relevant, but this is not a paradox, but rather simply an unsolved problem —perhaps a puzzling problem without a clear answer yet, but still just a scientific problem nonetheless. A paradox exists when the available evidence logically suggests one outcome, when something opposite is actually observed. That is not the case here. The reason why the xenon is missing is understood, we just don’t yet know where it is in the Earth.*

**Reply:** We thank the reviewer for clarifying the issue. We have changed the “missing xenon paradox” into the “missing xenon problem” in our revised manuscript.

*2. The second to last statement in the abstract, if true, would appear to have solved the missing xenon problem already. In fact, this is clearly not the case, even given the results of the present work. Xe does not react with major mantle oxides either, according to the authors later in the manuscript at line 158, and therefore the fact that other noble gases do not react with major mantle oxides is not a reason for the selective depletion of xenon observed in Earth’s atmosphere. This statement should be removed because it is obviously false as well as contradictory.*

**Reply:** We are thankful for the reviewer’s constructive suggestion. In the revised abstract, we have appropriately rewritten the sentence of

“Meanwhile, major mantle oxides do not react with Kr, Ar, and Ne, explaining the selective depletion of Xe in Earth’s atmosphere”

to

“Meanwhile, Fe oxides do not react with Kr, Ar, and Ne, suggesting the distinct possibility that Xe could be captured in Earth’s lower mantle.”

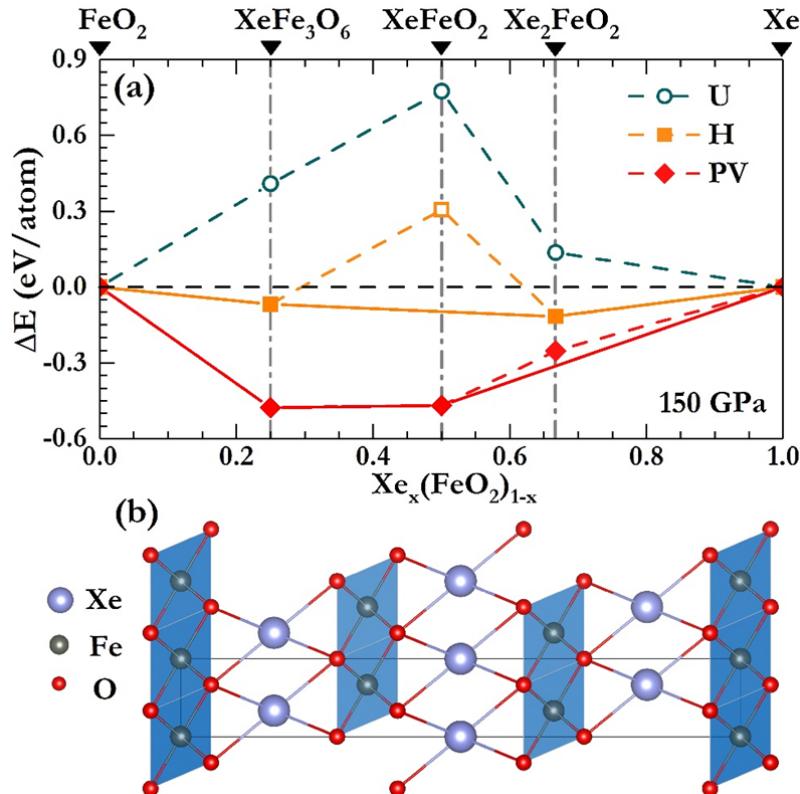
*3. The authors use the Caldwell, et al. (1997) paper to reference work that proposed that Xe is stored in stable compounds within the Earth. In fact, this 1997 paper suggests quite clearly that the answer to the missing Xe problem lies most likely not in deep mantle or core phases.*

**Reply:** We thank the reviewer for a careful reading and correction. We have made the adjustment and cited this reference as Ref. [22] in line 5, paragraph 2, in the section of **Introduction**.

*4.  $XeFeO_2$  would appear to have the simplest structure and might be predicted over the other two at deep mantle conditions, as minerals tend to become structurally simpler with increasing pressure and temperature. Structurally speaking, why is this composition so unstable compared to the other two? This question should be addressed explicitly.*

**Reply:** We thank the reviewer for making this suggestion. In response, we now present in **Supplementary Figure 1** the relative enthalpies  $\Delta H$ , internal energies  $\Delta U$ , and pressure-volume terms  $\Delta(PV)$  to examine the mechanism of thermodynamic stability for these  $FeO_2$ -Xe compounds. Our results show that the pressure-volume terms, associated with packing efficiency, make similar contributions to lowering the enthalpy for  $XeFe_3O_6$  and  $XeFeO_2$ , while the unfavorable internal energy, associated with bonding enhancement, leads to a positive formation enthalpy for  $XeFeO_2$ .

Although the value of pressure-volume term of  $\text{Xe}_2\text{FeO}_2$  is much lower than those of  $\text{XeFe}_3\text{O}_6$  and  $\text{XeFeO}_2$ , it still offsets the relatively weak negative effect of internal energy to enthalpy, thus yielding its thermodynamical stability with formation enthalpy lying on the convex hull. To address this question, we added a figure [Supplementary Figure 1] in the Supplementary Information and give the above discussion in the figure caption.



[New Supplementary Figure 1 in revised Supplementary Information]. **Calculated energetic terms of  $\text{FeO}_2$ -Xe compounds and the  $\text{XeFeO}_2$  structure at 150 GPa.** (a) The enthalpies  $\Delta H$ , the internal energies  $\Delta U$ , and the pressure-volume term  $\Delta(PV)$  for the Xe-Fe oxides. (b) The polyhedral views of theoretically predicted  $\text{XeFeO}_2$  structure. We discuss the energetic terms to examine the mechanism of thermodynamic stability for these  $\text{FeO}_2$ -Xe compounds. The pressure-volume terms, associated with packing efficiency, make similar contributions to lowering the enthalpy for  $\text{XeFe}_3\text{O}_6$  and  $\text{XeFeO}_2$ , while the unfavorable internal energy, associated with bonding enhancement, leads to a positive formation enthalpy for  $\text{XeFeO}_2$ . Although the value of pressure-volume term of  $\text{Xe}_2\text{FeO}_2$  is much lower than those of  $\text{XeFe}_3\text{O}_6$  and  $\text{XeFeO}_2$ , it still offsets the relatively weak negative effect of internal energy to enthalpy, thus yielding its thermodynamic stability with formation enthalpy lying on the convex hull.

*5. The authors should be more specific about the meaning of “favorable temperature effects” at line 112.*

**Reply:** To avoid ambiguity, we have changed the sentence

“Favorable temperature effects reduce Gibbs free energy of the Xe-Fe oxides even more relative to their separate constituents, …”

into

“The temperature effect (i.e., thermal vibration of atomic positions) are favorable to reduce Gibbs free energy of the Xe-Fe oxides even more relative to their separate constituents,”

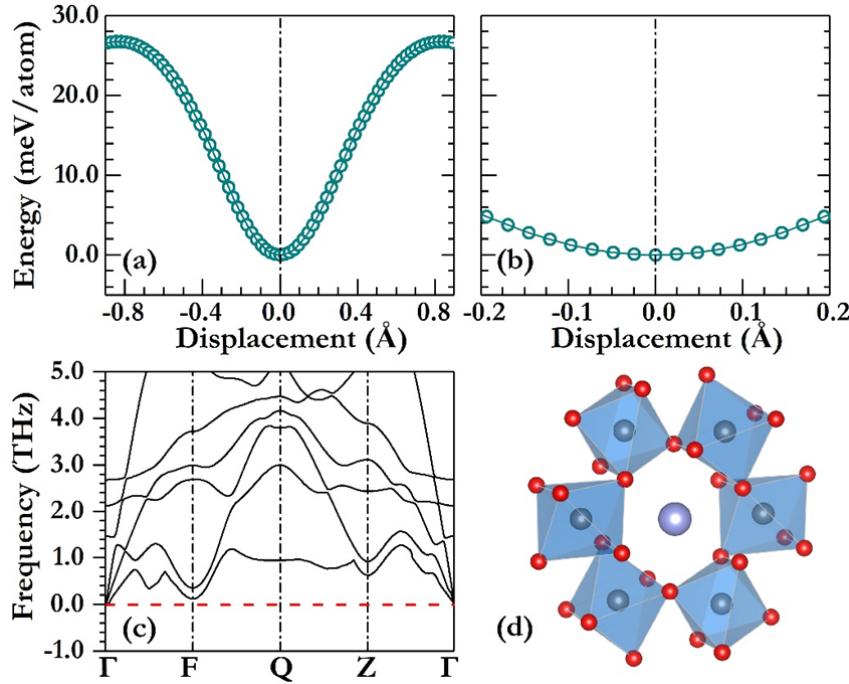
in our revised manuscript.

*6. Figure 1: Crystal structure representations are inadequate to observe the important details of the structure. What are the coordination geometries around Xe with its coordination numbers of 3 or 6? How does the Xe with CN = 6 in the channel of the  $\text{XeFe}_3\text{O}_6$  structure result in a soft phonon mode? A better resolution on the phonon dispersion curve would illustrate that soft mode more effectively.*

**Reply:** We thank the reviewer for making this constructive suggestion. To present clearly the coordination numbers of Xe, the units of Xe-O for  $\text{Xe}_2\text{FeO}_2$  and  $\text{XeFe}_3\text{O}_6$  are shown in Fig. 1(d) and 1(e) in the revised manuscript. The coordination geometries around Xe with the coordination numbers of  $\text{Xe}_2\text{FeO}_2$  and  $\text{XeFe}_3\text{O}_6$  are 3 and 6, respectively.

Indeed, the vibrational modes close to zero for  $\text{XeFe}_3\text{O}_6$  stem from the relatively large internal volume for Xe atom that leads to the concomitant longer bond lengths and weak interaction between Xe atoms and O atoms. The maximum distance between Xe and O atom is 2.52 Å in  $\text{XeFe}_3\text{O}_6$  at 150 GPa, which is much longer than that in Xe oxides (e.g. ~2.37 Å in  $\text{Xe}_2\text{O}_5$ ) and  $\text{Xe}_2\text{FeO}_2$  with CN=3 of Xe (2.42 Å) at the same pressure. As a result, Xe-O bonds of  $\text{Xe}_2\text{FeO}_2$  are much stronger than that of  $\text{XeFe}_3\text{O}_6$ . To explore possible dynamical instabilities, we have moved one Xe atom along the channels of the Fe-O framework (the vibration eigenvector of the soft phonon mode) while fixing all other atoms. The calculated static energy presented in **Supplementary Figure 4** shows that the original structure is located at an energy minimum on the energy surface, signifying its dynamical stability. The curve is smooth near the equilibrium position (e.g., < 0.2 Å), making it easier for the Xe atoms to move about along the eigenvector of the low-frequency phonon mode, in agreement with the theoretical phonon spectrum. Meanwhile, the curve has a rather high energy cost at large displacements and the phase transition is impeded by a

kinetic barrier of  $\sim$ 26.8 meV/atom at 150 GPa and zero temperature, indicating that it is difficult for the Xe atoms to escape from the lattice. With the consideration of temperature effect, our AIMD calculations also reveal that Xe atoms can only vibrate near the balanced positions below melting points. To address this question, we have appropriately modified **Supplementary Figure 4** in the Supplementary Information and give the above discussion in the figure caption.



**[New Supplementary Figure 4 in revised Supplementary Information]. The vibrational analyses for  $\text{XeFe}_3\text{O}_6$ .** (a) The internal energy difference at various Xe positions along the channels (the vibration eigenvector of the soft phonon mode) of the Fe-O framework at 150 GPa and zero temperature. The original structure is located at an energy minimum on the energy surface, signifying its dynamical stability. (b) The internal energy difference of  $\text{XeFe}_3\text{O}_6$  at various Xe positions along the channels near the equilibrium position. (c) The theoretical phonon spectrum at the low-frequency region. (d) The snapshot for the Fe-O framework with Xe atom in the channel. The vibrational modes close to zero for  $\text{XeFe}_3\text{O}_6$  stem from the relatively large internal volume for Xe atom that leads to the concomitant longer bond lengths and weak interaction between Xe atoms and O atoms. The maximum distance between Xe and O atom is 2.52 Å in  $\text{XeFe}_3\text{O}_6$  at 150 GPa, which is much longer than that of Xe oxides (e.g.  $\sim$ 2.37 Å in  $\text{Xe}_2\text{O}_5$ ) and  $\text{Xe}_2\text{FeO}_2$  with CN=3 of Xe (2.42 Å) at the same pressure. As a result, Xe-O bonds of  $\text{Xe}_2\text{FeO}_2$  are much stronger than that of  $\text{XeFe}_3\text{O}_6$ . To explore the possible dynamical instabilities, we have move one Xe atom along the channels of the Fe-O framework (the vibration eigenvector of the soft phonon mode) while fixing the other atoms. The calculated static energy in **Supplementary Figure 4** shows that the original structure is located at an energy minimum on the energy surface, signifying its dynamical stability. The curve is

smooth near the equilibrium position (e.g.,  $< 0.2 \text{ \AA}$ ), making it easier for the Xe atoms to move about along the eigenvector of the low-frequency phonon mode, in agreement with the theoretical phonon spectrum. Meanwhile, the curve has a rather high energy cost at large displacements, and the phase transition is impeded by kinetic barrier of  $\sim 26.8 \text{ meV/atom}$  at 150 GPa and zero temperature, indicating that it is difficult for the Xe atoms to escape from the lattice. With the consideration of temperature effect, our AIMD calculations also reveal that Xe atoms can only vibrate near the balanced positions below melting points.

**7. The statement at line 163 suggesting that the current results explain the selective depletion of Xe from Earth's atmosphere is not supported by the current work and should be eliminated or heavily qualified. The results provide one plausible explanation for how the missing Xe is sequestered within the Earth, but an explanation for the depletion of Xe from the atmosphere must include a mechanism for how the Xe has been brought from the atmosphere into the mantle to a depth where reaction with  $\text{FeO}_2$  is feasible. Likewise, the closing statements at lines 172-178 should be qualified as well.**

**Reply:** We thank the reviewer for this constructive suggestion and agree with the reviewers' viewpoints. We have changed the statements in line 163 in our previous version of manuscript:

“This result explains the selective depletion of Xe from Earth's atmosphere.”.

to

“These results provide the possibility that Xe could be the sole inert element for reacting with deep-Earth constituents under mantle conditions.”

We have also deleted a sentence to weaken the statement in line 175-176 in our previous version of manuscript:

“These findings offer new insights into key material composition and physics mechanism for elucidating the longstanding “missing xenon paradox”.”

**8. There are numerous errors in usage and grammar throughout the manuscript. It should be carefully proofread by a native English speaker.**

**Reply:** In response to the reviewer's suggestion, we have polished our manuscript carefully.

In its present form, the manuscript is not suitable for publication in Nature Communications, but may be suitable after major revision and a refocusing of the discussion away from the geochemical perspective if support for the existence of Xe at deep mantle conditions cannot be explicitly documented.

**Reply:** We thank the reviewer for a careful reading of our manuscript and for making numerous constructive suggestions for its improvement. Following these suggestions, we have made extensive revisions accordingly, and we hope that these revisions are satisfactory and that the revised manuscript is now acceptable for publication in Nature Communications.

## REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

This revision has improved the quality substantially, addressing the most concerns raised by the referees. Clearly, the paper presents interesting new results that may have some implications for the experimental studies of Xenon-Iron Oxides. Thus, I would recommend the manuscript for publication based on the results providing a valuable understanding of the phase diagram in Xenon-Iron Oxides.

Reviewer #3 (Remarks to the Author):

Overall, the points raised in the original review have been adequately addressed, with the exception of specific point #7:

As stated in the initial review, if the proposed compounds are to be invoked as a potential solution to the "missing Xe problem" then the presence of Xe in the lower mantle must be established from the existing geochemical literature and clearly stated, if it in fact exists. Otherwise the authors have not done their homework and the paper is not appropriate as a contribution to the solution of the missing Xe problem. If this evidence from the geochemical literature does not exist, then this must be clearly stated in the text. In this paper, no evidence from the literature has been provided for Xe existing in the lower mantle from 24 GPa / 1900 K - 145 GPa / 3500 K. Therefore, the most that can be said here is that \*\*\* IF \*\*\* Xe exists in the lower mantle at the same pressures as FeO<sub>2</sub>, then the potential exists for these compounds to form, and these could provide the repository for the atmosphere's missing Xe. This should be explicitly stated in the abstract and in the text. It should be further pointed out that the P-T stability range of FeO<sub>2</sub> has not been established, and so it should be clearly stated that this is the case. Otherwise, the authors are taking what is actually a very thorough contribution to xenon chemistry and evading the real issue that is necessary for it to be considered as a solution to the missing Xe problem. The authors should not be permitted to discuss their results as though these two key requirements for their proposed compounds are actually confirmed. This would be a matter for the editor to decide.

The paper is suitable for publication after this minor revision.

Given the preceding comments, I would also suggest that the title be changed to something like "Xenon Iron Oxides Predicted as Potential Xe Hosts in Earth's Lower Mantle"

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## **Response to reviewer #1**

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### ***Reviewer #1 (Remarks to the Author):***

*This revision has improved the quality substantially, addressing the most concerns raised by the referees. Clearly, the paper presents interesting new results that may have some implications for the experimental studies of Xenon-Iron Oxides. Thus, I would recommend the manuscript for publication based on the results providing a valuable understanding of the phase diagram in Xenon-Iron Oxides.*

**Reply:** We appreciate the reviewer's positive assessments of our reported work and the recommendation for publishing our paper in *Nature Communications*.

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## **Response to reviewer #3**

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### ***Reviewer #3 (Remarks to the Author):***

*Overall, the points raised in the original review have been adequately addressed, with the exception of specific point #7:*

*As stated in the initial review, if the proposed compounds are to be invoked as a potential solution to the “missing Xe problem” then the presence of Xe in the lower mantle must be established from the existing geochemical literature and clearly stated, if it in fact exists. Otherwise the authors have not done their homework and the paper is not appropriate as a contribution to the solution of the missing Xe problem. If this evidence from the geochemical literature does not exist, then this must be clearly stated in the text. In this paper, no evidence from the literature has been provided for Xe existing in the lower mantle from 24 GPa / 1900 K - 145 GPa / 3500 K. Therefore, the most that can be said here is that \*\*\* IF \*\*\* Xe exists in the lower mantle at the same pressures as FeO<sub>2</sub>, then the potential exists for these compounds to form, and these could provide the repository for the atmosphere’s missing Xe. This should be explicitly stated in the abstract and in the text. It should be further pointed out that the P-T stability range of FeO<sub>2</sub> has not been established, and so it should be clearly stated that this is the case. Otherwise, the authors are taking what is actually a very thorough contribution to xenon chemistry and evading the real issue that is necessary for it to be considered as a solution to the missing Xe problem. The authors should not be permitted to discuss their results as though these two key requirements for their*

*proposed compounds are actually confirmed. This would be a matter for the editor to decide.*

**Reply:** We appreciate the reviewer's professional considerations and constructive suggestions for improving our manuscripts. We have carefully considered the reviewer's comments and revised the manuscript accordingly. In the revised manuscript, we have added the following sentence

*"It means that if Xe exists in the lower mantle at the same pressures as FeO<sub>2</sub>, xenon iron oxides are predicted as a potential Xe hosts in Earth's lower mantle and could provide the repository for the atmosphere's missing Xe."*

at line 9 in the section of **Abstract**.

We have also rewritten the sentence

*"Recently discovered FeO<sub>2</sub> synthesized at lower mantle conditions<sup>35</sup> offers an intriguing new possibility."*

to

*"Recently discovered FeO<sub>2</sub> synthesized at lower mantle conditions<sup>35</sup> and stabilized above 74 GPa in theoretical calculation<sup>36</sup>, offer an intriguing new possibility."*

at line 2, paragraph 3 in **Introduction**

and supplemented the sentence

*"(actually P-T stability range of FeO<sub>2</sub> has still not been completely established in experiments)"*

at line 5, paragraph 3, in the section of **Introduction**.

*The paper is suitable for publication after this minor revision.*

**Reply:** We are grateful to the reviewer's recommendation for publishing our paper in *Nature Communications* after this minor revision.

*Given the preceding comments, I would also suggest that the title be changed to something like "Xenon Iron Oxides Predicted as Potential Xe Hosts in Earth's Lower Mantle".*

**Reply:** We thank the reviewer for the constructive suggestion. In response, we have changed the title to "Xenon Iron Oxides Predicted as Potential Xe Hosts in Earth's Lower Mantle".