I. Introduction

Fe/O is an important planetary mineral and a significant component of the Earth’s mantle, and it may also be important within the Earth’s core. Seismological studies have shown that the density of the Earth’s solid inner core is 2–3% too low to be plausibly explained by pure Fe, leading to the suggestion that light elements must also be present [1, 11–14]. The identities and concentrations of light elements present in the core have yet to be established, although various arguments favour O, Si, C, S and H as the most likely candidates [2].

In an earlier paper we investigated the formation of iron carbides at high pressures [3], and here we study iron oxides. O has been suggested as an important light element for explaining both the density jump at the Earth’s inner core boundary and the observed seismic wave velocities [4]. The possible presence of O within the core has stimulated a range of experimental [4–7] and theoretical [8, 9] investigations of the Fe/O system, albeit only for a handful of stoichiometries. In this paper we present a broader investigation spanning 12 different stoichiometries at three different pressures. We search for stable structures at each stoichiometry and pressure, and construct convex hull diagrams to determine which
phases are stable against decomposition. We also present results for transitions between solid phases up to pressures of 500 GPa.

Temperatures within the Earth extend to above 6000 K [10]. Atoms such as O could be present in the Earth’s core as isolated impurities, as in a solid solution or, alternatively, Fe/O compounds could be formed. A solid solution has a much higher configurational entropy than an ordered Fe/O compound plus crystalline Fe, but the formation of crystalline Fe/O compounds could lead to more favorable bonding arrangements than are obtained in a solid solution. To help understand the conditions under which solid solutions and ordered compounds might be stable it is necessary to determine which compounds are energetically favorable, taking into account a wide range of stoichiometries. This is a formidable task in its own right, although it should be augmented by calculating finite temperature effects arising from the vibrational motion of the atoms, the configurational entropy of the solid solution, and the electronic entropy. We leave the estimation of finite temperature effects to subsequent work.

We have performed searches at 100, 350 and 500 GPa. The pressure at the bottom of the Earth’s mantle is about 136 GPa, and our data at 100 GPa correspond to a pressure within the lower mantle. The pressures within the solid core are believed to be in the range 330–360 GPa [11–14], and our results at 350 GPa are therefore representative of inner core pressures. The highest pressure at which we have performed searches of 500 GPa is above that found within the Earth, although such pressures occur in other planets, including exoplanets.

II. Computational details

Determining the most stable structure of a material corresponds to finding the global minimum energy state within a high-dimensional space. A number of methods have been developed to tackle this problem, which have met with varying degrees of success. The method we use, which has been shown to be successful in determining structures that have subsequently been verified by experiments [15–18], is called ab initio random structure searching (AIRSS) [19]. AIRSS has been applied to many systems at high pressures, including iron [20] and oxygen [21]. Within AIRSS the energy landscape is sampled by generating random structures. The structures are then relaxed to the local enthalpy minimum for some chosen pressure using the CASTEP plane-wave density functional theory (DFT) code [22]. This process is repeated until the lowest enthalpy structure is found several times or the available computational resources have been exhausted.

To improve the efficiency of the searches we can impose a number of biases. One bias we use is to reject initial structures in which the smallest inter-atomic separation is less than some chosen value. Structures which contain atoms that are very close together are extremely high in enthalpy and may even cause the geometry optimization procedure to fail. Since the number of local minima is known to increase exponentially with the system size [23], an additional bias may be required for searches over larger unit cells. We use a bias that exploits the fact that low enthalpy structures tend to possess symmetry. We can create an initial structure with a particular symmetry by first selecting a ‘structural unit’ containing A formula units (fu). This structural unit is chosen to be the lowest enthalpy structure found in an A fu search. A random space group containing B symmetry operations is then chosen and applied to the structural unit. This generates a larger initial structure containing $A \times B$ fu. In this investigation A and B range from 1–3 and 2–4, respectively.

Structures found to be metastable at one pressure may become stable at another. Expanding the enthalpy around the pressure $p_0$ at which a search is performed gives

\[ H(p) = H(p_0) + (p - p_0) \frac{dH}{dp}_{p_0} + \frac{1}{2}(p - p_0)^2 \frac{d^2H}{dp^2}_{p_0} + \ldots \]  

(1)

The second-order derivative in equation (1) is related to the bulk modulus and is computationally expensive to evaluate. A useful approximation can, however, often be obtained by neglecting the second-order term and using the fact that the first derivative of $H$ with respect to pressure $p$ at $p_0$ is equal to the volume $v_0$, so that

\[ H(p) \approx H(p_0) + v_0 (p - p_0). \]  

(2)

Since $H(p_0)$ and $v_0$ are evaluated within the structure searching, equation (2) may be used to estimate the enthalpies of the phases at any pressure $p$. This allows us to determine approximate pressures at which phase transitions may occur, which we then refine by performing higher accuracy DFT calculations.

We used ultrasoft pseudopotentials [24] to represent the cores of the Fe and O atoms. For the structure searching we used a fairly soft Fe pseudopotential in which only the 4s and 3d electrons were treated explicitly, while for O we treated the 2s and 2p electrons explicitly. For the higher quality calculations we used a harder Fe pseudopotential in which the 3s, 3p, 4s, and 3d electrons were treated explicitly. Both the harder Fe pseudopotential and the O pseudopotential have been successfully tested up to terapascal pressures [20, 21, 25].

The final structures were obtained using a two-step procedure. We first used AIRSS in medium-quality calculations which were optimized for computational speed. The medium quality settings consisted of a k-point sampling grid of spacing of $2\pi \times 0.07$ Å$^{-1}$ and a plane-wave cut-off energy of 490 eV. The lowest enthalpy structures for each stoichiometry were then further relaxed in a higher-quality calculation using a finer k-point sampling grid of spacing $2\pi \times 0.03$ Å$^{-1}$ and a plane-wave cut-off energy of 1000 eV. In all of our searches we used the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) exchange correlation functional [26].

The Fe/O system is known to be problematic for DFT-based methods because of magnetic and strong correlation effects. The presence of magnetism in FeO at high pressures has been documented, although there are some conflicting reports. Mössbauer spectroscopy has shown that a continuous transition from high-spin to low-spin states [27] occurs at
90–120 GPa, leading to an eventual collapse at 140 GPa and 300 K. This is in contrast to experiments performed using x-ray emission spectroscopy for FeO at 300 K, which have suggested that a magnetic state exists up to at least 143 GPa [28], while a magnetic collapse in Fe₂O₃ has been observed at 50 GPa [29]. In addition, zero-temperature static lattice GGA DFT calculations have predicted a magnetic collapse of FeO at around 200 GPa [30].

The existence of magnetic order under core conditions can be safely ruled out, as it would be destroyed by the high temperatures. We have not performed searches with spin-polarization because they are very costly, but to investigate the effects of magnetism on the enthalpies, we have re-relaxed our structures with high quality settings starting from a high spin state. If a relaxation did not achieve convergence we reduced the initial spin state and re-relaxed until convergence was achieved. We found that the small magnetic moments have a negligible effect on the enthalpies at the high pressures considered here (~0.002 eV per atom at 100 GPa in the worst case). For these reasons we do not believe magnetism plays a significant role at the pressures we have investigated and hence we have not considered it further.

Similar arguments can be made about the effects of strong Coulomb correlations which arise in iron oxides from interactions involving the localized Fe d electrons. The strength of such correlations is conventionally measured by the parameter U/W, where U is the Hubbard U energy and W is the d band width. Electrons tend to delocalize at high pressures, which has the effect of increasing W and reducing U [30]. Under these conditions, where the correlations are less strong, GGA DFT is likely to be reasonably accurate [31].

III. Convex hulls

We have plotted our energy data on convex hull diagrams to assess the stability of the phases with respect to decomposition. To construct the hulls we also need the enthalpies of the end members, pure Fe and pure O. Fe is predicted to adopt the hexagonal close packed (hcp) structure over the pressure range of interest here, while for oxygen at 500 GPa we use the P63/mmc phase predicted by Sun et al [21]. At pressures below 500 GPa we use the ζ phase [32].

The enthalpy of formation per atom of a compound with respect to its elements is

$$\Delta H = \frac{H_x - (N_x H_{Fe} + N_{O} H_{O})}{N_{O} + N_{Fe}},$$

(3)

where N_x and H_x are the number of atoms and enthalpy per atom of element x, respectively, and H is the enthalpy of the structure. A negative \( \Delta H \) indicates that the structure is stable with respect to decomposition into its elements, although it may be unstable with respect to decomposition into compounds of other stoichiometries. Structures lying above the convex hull are unstable with respect to decomposition into other compounds and are therefore less likely to form. Structures lying on the convex hull are thermodynamically stable and are therefore more likely to form.

Figure 1. Convex hull diagrams for Fe/O at 100, 350 and 500 GPa.

The convex hull diagrams at 100, 350 and 500 GPa shown in figure 1 exhibit fairly smooth variations with composition. Figure 1(a) shows that the only stoichiometries that lie on the hull at 100 GPa are Fe₂O₃ and FeO₂. At 350 GPa, Fe₇O, Fe₅O, Fe₄O₂, Fe₂O, FeO, Fe₂O₃ and FeO₂ are found to lie on, or very close to, the hull, and similar results are found at 500 GPa. Perhaps the most notable difference at 500 GPa is that FeO₄ is found to lie on the hull. FeO₂ and Fe₂O₃ are predicted to be stable with respect to decomposition at all pressures investigated. Fe₂O₄, which is believed to be an important phase in the Earth’s lower mantle [34], is found to be marginally unstable.
Table 1. The lowest enthalpy structures found from searching at 100, 350 and 500 GPa.

| X    | N   | S_{100} | S_{350} | S_{500} |
|------|-----|---------|---------|---------|
| FeO  | 0.10| 3 [Ann2 (1)] | [Ann2 (1)] | [Ann2 (1)] |
| Fe2O | 0.25| 4 [P6m2 (1)] | [P6m2 (1)] | [P4/mnmm (2)] |
| Fe3O | 0.33| 6 P6/mnm (2) | I4/mnm (1) | I4/mmm (1) |
| FeO2 | 0.40| 4 Pm (3) | C2/m (1) | Pm (2) |
| Fe   | 0.50| 8 P32121 (3) | R3m (1) | R3m (1) |
| Fe3O5| 0.56| 2 P4/n (2) | P3m1 (1) | P3m1 (1) |
| Fe2O3| 0.57| 4 Pca21 (4) | P21/c (4) | P21/c (4) |
| FeO  | 0.70| 3 P21/m (1) | I43d (2) | I43d (2) |
| Fe2O | 0.74| 4 P41 (4) | P41 (4) | Cmcm (2) |
| FeO  | 0.80| 4 Fdd2 (2) | P21/c (2) | P21/c (2) |

Note: X is the fraction of oxygen atoms. Entries which show space groups within square brackets indicate mixtures of structures of phases with other stoichiometries, see text. N is the maximum number of formula units used in the searches. S is the space group of the lowest enthalpy structure found at pressure P. In each case, the number of formula units in the primitive cell is given in round brackets.

with respect to decomposition at the pressures considered here.

Increasing pressure appears to stabilize Fe rich phases, an effect that is most noticeable between 100 and 350 GPa. There is also a stabilization of O rich phases with increasing pressure. For example, FeO and FeO2 can be seen to move considerably closer to the hull between 100 GPa and 500 GPa. The former also coincides with a transition from a low symmetry P1 phase to a phase of Cmcm symmetry.

It is possible that structures that lie just above the convex hull correspond to metastable mixtures of phases rather than single phases. This is particularly likely for large unit cells. We have found several such cases in our results, and the fact that they lie just above the hull suggests that the interfacial energies between the different structures present are small. The P6m2 structure of Fe3O is found to be a mixture of phases consisting of Fe and Fe2O while the P4/mnm structure is found to consist of Fe2O and FeO phases. Finally, Fe2O (Ann2) is found to consist of Fe and FeO phases and the PM phase of Fe2O2 (at 500 GPa) is found to consist of Fe2O and FeO phases. These mixtures of phases are indicated by square brackets in table 1.

IV. Phase transitions

We predict pressure-driven phase transitions for all of the stoichiometries considered in this study, with the exception of Fe3O. We have obtained accurate transition pressures by performing additional calculations at pressures around the values predicted using equation (1). Plots of relative the enthalpies as a function of pressure are shown in figure 4. Three of the stoichiometries considered, Fe2O3, FeO and Fe3O4, have already been investigated extensively and their properties, particularly at ambient pressure, are well known. However, most of the stoichiometries that we discuss here have not been studied before and hence little is known about their high pressure behaviour. Unless stated otherwise, all of the lowest enthalpy phases were found by searching and, to the best of our knowledge, have not been discovered before.

FeO. The most stable structure of FeO found has Ann2 symmetry, but it turns out to be a mixture of phases.

Fe2O. See figure 4(a). Between 100 and 350 GPa, the most stable structure of FeO of P6m2 symmetry turns out to correspond to a mixture of phases rather than a single phase. At about 350 GPa we find a phase of P4/mnm symmetry to be the most stable, but it also turns out to be a mixture of phases. We also relaxed Fe3O between 100 and 500 GPa in the BiI3 structure, which has previously been suggested as a low enthalpy phase [8]. However, we found this structure to be between 0.3 eV and 2 eV per fu higher in enthalpy than our best structures found from searching.

Fe2O. See figure 4(b). We predict that FeO forms a structure of P63/mnm symmetry at 100 GPa. At about 180 GPa we find a transformation to a phase of P3 m1 symmetry, which is stable up to about 288 GPa, at which point we predict it to transform into a phase of I4/mmm symmetry.

FeO. See figure 4(c). At 100 GPa we predict that Fe2O will adopt a structure of C2/m symmetry at about 127 GPa, we predict a phase transition to a structure of C2/m symmetry followed by a further transition to a phase of Pm symmtery at about 486 GPa.

FeO. See figure 4(d). Previous DFT calculations for FeO have shown the stability of a phase of P321 symmetry [35] between 65 GPa and 190 GPa. We also find this structure from searching and our results shown in figure 4(d) agree well with those previously reported. However, Oganov et al [35] predict that this phase will transform to the distorted NaCl structure at 190 GPa. We instead find that the P321 structure transforms to a new phase of Pnma symmetry at about 195 GPa, which then undergoes a transformation to another new phase of R3m symmetry at about 285 GPa. In addition to this, figure 4(d) shows another new phase of Cmcm symmetry, which we predict to be stable at pressures above 500 GPa. Our results suggest a somewhat different picture from that obtained from compression experiments up to 324 GPa [4] and at temperatures up to 4880 K. These differences may arise for a number of reasons. Firstly, experiments on FeO normally use a non-stoichiometric compound, Fe1-xO, where x is typically about 0.05, whereas our calculations assume stoichiometric FeO. Secondly, we have performed static lattice calculations in contrast to real-world experiments which may yield phases stabilized by nuclear vibrational motion. Thirdly, kinetic barriers between structures could also influence the structures that are observed in experiments. Finally, the use of an approximate density functional will lead to further uncertainties in our results. It is worth remarking, however, that the PBE density functional, which obeys the uniform limit and gives a good account of the linear response of the electron gas to an external potential, [26] is likely to become more accurate as the pressure is increased.

A notable example of where our predictions for FeO differ from observations is at relatively low pressures where experiments (extrapolated to 0 K) have shown that FeO adopts
Figure 2. Structures found from searching that lie on the convex hull. The O atoms are shown in red and the Fe atoms are in blue. (a) Fe$_2$O ($I4/mmm$) (350 GPa). (b) FeO ($R3m$) (350 GPa). (c) Fe$_2$O$_3$ ($P2_12_2_1$) (350 GPa). (d) FeO$_2$ ($Pa3$) (100 GPa). (e) FeO$_2$ ($R3m$) (500 GPa). (f) FeO$_4$ ($P2_1/c$) (500 GPa).
Figure 3. Electronic densities of states for structures lying on the convex hull. Each plot shows the total density of states and its decomposition into contributions from Fe and O. The Fermi energies are at 0 eV. (a) Fe$_2$O$_3$ (Pbcn) at 100 GPa. (b) Fe$_2$O (I4/mmm) at 350 GPa. (c) FeO (R$ar{3}$m) at 350 GPa. (d) Fe$_2$O$_3$ (P2$_1$2$_1$2$_1$) at 350 GPa. (e) FeO$_2$ (Pa$ar{3}$) at 350 GPa. (f) FeO$_2$ (R$ar{3}$m) at 500 GPa. (g) FeO$_4$ (P2$_1$/c) at 500 GPa.
the rhombohedrally distorted NaCl (rB1) structure, which is predicted to be stable up to about 100 GPa [4]. Above 100 GPa a phase transition to the NiAs (B8) structure is predicted. We find the inverse-B8 (iB8) structure to be more stable than B8 between about 100 GPa and 165 GPa. The stability of the iB8 structure has been predicted theoretically before [31, 36], although it has yet to be verified by experiment. Although our results correctly predict the B8 phase to be more stable than the rB1 phase at high pressures, our best structures obtained from searching are lower in enthalpy than the previously known phases across the entire pressure range considered. We are not aware of any experimental evidence suggesting that a $P\bar{3}22_1$ phase of FeO is stable at 100 GPa, but we believe that this discrepancy may be explained by our arguments in the previous paragraph, and we note that earlier work suggested that the predicted stability of the $P\bar{3}22_1$ phase may simply be an artefact of the PBE density functional [35].

Figure 4. Plots of relative enthalpy against pressure for various stoichiometries. The reference structures appear as a horizontal line at 0 eV. Dashed lines represent structures known prior to this work. (a) Fe$_3$O. (b) Fe$_2$O. (c) Fe$_3$O$_2$. (d) FeO. (e) Fe$_2$O$_3$. (f) Fe$_3$O$_4$. (g) Fe$_2$O$_3$. (h) FeO$_2$. (i) Fe$_2$O$_5$. (j) FeO$_3$. (k) FeO$_4$. 
*Fe₃O₅.* See figure 4(c). Compression experiments have identified a phase of Fe₃O₅ with *Cmcm* symmetry to be the most stable between 5 and 30 GPa [33]. Our results show this phase to be unstable at 100 and 500 GPa with respect to the new structures found in our searches. At 100 GPa we predict Fe₃O₅ to adopt a structure with *P4₂/n* symmetry prior to a transition to a structure of *P₃m₁* symmetry at about 231 GPa, which we predict to be stable to at least 500 GPa.

*Fe₂O₄.* See figure 4(f). Under ambient conditions Fe₂O₄ adopts an inverse spinel structure of *Fd₃m* symmetry [37]. Between ~20–60 GPa, Fe₂O₄ is observed to make a slow transformation to a new phase (sometimes denoted by h-Fe₂O₄) with orthorhombic symmetry [34, 37]. The exact structure of h-Fe₂O₄ has, however, been difficult to resolve [34]. In light of this, a number of candidate structures have been proposed. Fei et al proposed a structure of *Pbcm* symmetry [38] which, although it agreed well with the available x-ray diffraction data, was later found to be inconsistent with Mössbauer spectroscopy data [34]. It was later suggested that a structure of *Cmcm* symmetry (sometimes referred to using the non-standard *Bmmn* setting) is also consistent with the x-ray diffraction data and it currently seems to be favoured as the high pressure phase of Fe₂O₄ [39].

First principles calculations have shown the *Cmcm* phase to be more stable than the *Pbcm* phase at pressures >65 GPa [37]. Our searches at 100 GPa found a new phase with *Pca₂₁* symmetry to be the lowest in enthalpy up to ~340 GPa, above which a phase transition is found to occur to another new phase of *P₂₁/c* symmetry. Figure 4(f) shows that the *Cmcm* phase is energetically unfavourable at the pressures considered. The *Pca₂₁* structure is found to be much more stable than the *Cmcm* phase, being ~1.4 eV per fu lower in enthalpy at 100 GPa. The fact that the *Pca₂₁* phase is also of orthorhombic symmetry does not preclude it from being a candidate for h-Fe₂O₄. Ascertaining whether the *Pca₂₁* phase is indeed h-Fe₂O₄ would require a more detailed investigation, which we leave to subsequent work.

*Fe₂O₃.* See figure 4(g). At ambient pressures the stable phase of Fe₂O₃ is hematite, which is a corundum-type structure of *R₃c* symmetry [40]. The high pressure phase of Fe₂O₃ has been proposed to be either a Rh₂O₃(II)-type structure of *Pbcm* symmetry or a GaFeO₃ orthorhombic perovskite structure [40]. Room temperature compression experiments have shown that hematite transforms to the Rh₂O₃(II)-type structure at about 50 GPa [41]. However, compression experiments at higher temperatures (800–2500 K) predict a phase transition to occur between hematite and the high pressure phase at a much lower pressure of ~26 GPa [42]. Ono et al have suggested that the observed transition at room temperature is between hematite and metastable Rh₂O₃(II) [40, 42]. The perovskite-type phase is suggested to be kinetically inhibited and therefore only obtainable at high temperatures [40, 42]. This view is supported by hybrid-DFT calculations, which show that the Rh₂O₃(II) phase is metastable with respect to the perovskite phase at 50 GPa [40]. At about 60 GPa and temperatures >1200 K the high pressure phase is observed to transform into a CaFe₂O₄-type (post-perovskite) structure [40, 43]. Hybrid-DFT calculations have predicted the anti-ferromagnetically ordered CaFe₂O₄ type structure to be the most stable between about 46 and 90 GPa with the low-spin Rh₂O₃(II) phase gradually becoming stable as the pressure approaches 90 GPa [40]. It appears likely that this phase will become stable at around 100 GPa and hence become consistent with our results shown in figure 4(g). We found the (non-magnetic) Rh₂O₃(II) structure of space group *Pbcm* in our searches at 100 GPa. Our calculations find this structure to be more stable than both the CaIrO₃ and GaFeO₃ (non-magnetic) structures between 100 and about 233 GPa. We predict that the Rh₂O₃(II) phase transforms into a new phase of *P₂₁₂₀* symmetry at 233 GPa.

*FeO₂.* See figure 4(h). At 100 GPa FeO₂ we predict a structure of *Pa₃* symmetry, see figure 2(d), which is stable across a wide pressure range of about 100–465 GPa. In this structure the Fe atoms form a face centred cubic (fcc) arrangement. At 465 GPa the *Pa₃* phase is predicted to transform into a phase of *R₅m* symmetry.

*FeO₄.* See figure 4(i). Between about 100 and 160 GPa we predict a structure of *P₂₁m* symmetry, and above 160 GPa we expect it to transform into a phase of *I₄̅3d* symmetry.

*Fe₂O₇.* See figure 4(j). We find a structure of *P1* symmetry to be the most stable above 100 GPa, and we predict that it will transform into a different structure of *P1* symmetry above 162 GPa. At about 395 GPa this structure is predicted to transform into a phase of *Cmcn* symmetry.

*FeO₄.* See figure 4(k). We find a structure of *Fdd₂* symmetry to be the most stable at 100 GPa, which is predicted to transform into a structure of *P₂₁c* symmetry at about 108 GPa.

A summary of the structures found is given in table 1, and the details of the structures are reported in the supplemental material at (stacks.iop.org/JPhysCM/27/455501/mmedia) for details of the structures obtained in this study.

V. Density of electronic states

An analysis of the electronic densities of states of the phases was performed with the Lindos code [44] which uses a linear extrapolation method [45, 46]. A Gaussian smearing of width 0.3 eV was applied to the density of states in all cases. Figure 3 shows the density of states for all of the structures found to lie on the convex hull. In all cases, with the exception of FeO₄ at 500 GPa, a significant density of states is observed at the Fermi energy, indicating that these structures are metallic.

The Fe 3s and Fe 3p states lie at, respectively, ~−87 and ~54 eV below the Fermi energy in all Fe–O phases. We found the O 2s states to lie at ~20 eV below the Fermi energy and almost all of the occupied electronic density of states around the Fermi energy arises from the Fe d bands, except in the O-rich structures.

VI. Conclusion

We have used DFT methods and the AIRSS technique to identify high pressure structures in the Fe/O system at zero temperature across a wide range of stoichiometries. This is a crucial preparatory stage for modelling the Fe/O system at finite temperatures. By constructing the convex hull at different pressures we have determined energetically favourable...
stoichiometries, some of which have not been considered before. Our results broaden the range of possible stable stoichiometries considerably from those studied previously.

We have found new structures of FeO and Fe₂O₃ which are calculated to be stable against decomposition at 350 and 500 GPa. Structures with stoichiometries Fe₂O₃ and FeO₂ are found to be stable against decomposition at each of the three pressures studied. Fe₂O₃, FeO₂, Fe₃O, FeO, Fe₂O₃ and FeO₂ are found to lie on, or very close to the hull at both 350 GPa and 500 GPa, although some of these structures are mixtures of phases, see table 1. At 500 GPa FeO₂ is also found to lie on the hull.

We have found structures of Fe₃O₄ and Fe₄O₅ at high pressures that are more stable than those predicted previously, although they are unstable to decomposition at the pressures studied here.

Increasing pressure tends to stabilize Fe/O compounds with respect to the separated elements over the range 100–500 GPa. Increasing pressure stabilizes Fe rich phases, an effect that is most noticeable between 100 and 350 GPa. There is also a stabilization of O rich phases with increasing pressure.

The energy reduction from compound formation in Fe/O at high pressures is much larger than in Fe/C. For example, at 350 GPa, the DFT results reported in [3] show that the minimum in the convex hull occurs at Fe₂C with an enthalpy of about 1.76 eV per atom for FeO₂. Our results show that Fe/O compounds are stable (or nearly stable) over a wider range of stoichiometries at 350 GPa than Fe/C compounds.

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