Metallized ε-FeOOH and the heterogeneous electrical conductivity structure in the lower mantle

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Article

Keywords: electrical conductivity, ε-FeOOH, lower mantle, insulator-metal transition

DOI: https://doi.org/10.21203/rs.3.rs-55843/v1

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Abstract

Electrical heterogeneity at the depth of 900-1400 km in Earth's interior is a key factor to constrain the minor phase composition of the lower mantle. However, prevailing mineralogical models including Fe- or Al-enriched silicates or ferropericlase are insufficient to explain the ultra-high electrical conductivity in local areas of subduction slabs. Here, we measure the electrical conductivity of ε-FeOOH up to 61 GPa. A 3-order abrupt jump of electrical conductivity is observed in 45-50 GPa, reaching $1.24\pm0.19 \times 10^3$ S/m at 61 GPa. Density mean field theory simulations suggest that ε-FeOOH undergoes a Mott-type electronic transition, which leads the conduction mechanism to switch from small polaron conduction to free electron conduction. Compared with bridgmanite, ferropericlase and conventional mantle compositional models, the electrical conductivity of the metallic ε-FeOOH is 1-3 orders of magnitude higher. Minor or moderate incorporation of metallic ε-FeOOH into the ambient lower mantle could reproduce the observed electrical heterogeneity derived from geomagnetic data at 900-1400 km depth.

Introduction

The lower mantle occupies more than half of the solid Earth by volume. Its mineral composition has attracted enormous research interests as it holds key to understand the Earth's bulk structure, dynamics and physicochemical properties$^1$. Based on mineral physics experiments, the lower mantle is dominated by bridgmanite (Brg) and ferropericlase (Fp) with a small amount of Ca-perovskite$^2, 3$. However, recent seismological measurement$^4$, electromagnetic tomography$^5$ and deep diamond inclusion$^6$ suggest the lower mantle can be locally heterogeneous and thus not fully covered by popular mineralogical models$^2, 7$.

Using a combination of global three-dimensional (3D) and one-dimensional (1D) induction studies$^5, 8, 9, 10, 11, 12$, pioneers have mapped out the electrical conductivity (EC) profiles and have located a couple of areas with very high EC. For example, Constable and Constable constructed a 1-D conductivity model by Occam smooth inversion and showed the EC values surge to $10^2$ S/m at around 1300 km depth in the lower mantle$^{11}$. Those high conductivity regions are observed at depths of 900–1400 km beneath Eastern Africa, South-East Asia and Eurasia in stark contrast to the large low conductivity areas under Australian region, Western Africa, near Japan, North and Central America$^5, 12$. The high conductivity number, which is almost two orders of magnitude greater than the mean value, agreed with the 1D conductivity profile obtained with the global earth response and a synthetic 3D model$^5$. However, conductivity measurements of Brg or Fp at high pressures indicate that neither Brg nor Fp can reach such high EC values$^{13, 14, 15, 16}$, even considering temperature effects$^{17}$.

As a transport property, EC is mainly controlled by pressure, temperature, oxygen fugacity$^{18}$, phase transitions$^{14, 19, 20}$ and is also sensitive to factors like water solubility$^{21}$ and partial melting$^{22}$. The large variations of EC in the lower mantle indicate that multiple conductivity mechanisms may co-exist at similar depth. For example, applying high pressure and hydration effect promote the EC of nominal
anhydrous olivine by orders of magnitude due to the onset of proton conduction. Wüstite (FeO) enters an exotic metallic state when pressure increases above 70 GPa and temperature is higher than 1900 K. Those observations provide potential mechanisms to explain the electrical conductivity profiles in the transition zone and the lower mantle.

In this work, we focus on the $EC$ of $\varepsilon$-FeOOH, a high-pressure phase found to form solid solution with $\delta$-AlOOH and phase H under the CaCl$_2$-type hydroxide. FeOOH is also a major component of band iron formations, which were largely subducted with deep ocean during the Archaean era by plate tectonic process. It is reported that $\varepsilon$-FeOOH is a potential water carrier into the deep mantle in the recycled subduction slabs. For its possible minor presence in the lower mantle, we first measured the $EC$ of $\varepsilon$-FeOOH up to 61 GPa, which is then compared against those of $\gamma$-AlOOH (boehmite) and $\delta$-AlOOH to provide a holistic view on the effect of iron. Our in-situ measurements indicate that Fe$^{3+}$ in $\varepsilon$-FeOOH metalizes at 45–50 GPa and the electronic transition pushes $EC$ above $10^3$ S/m. This is approximately 2 to 2.5 orders of magnitude higher than that of pyrolite or Mid-Ocean Ridge Basalt (MORB) composition and may significantly contribute to the high conductivity observed at the corresponding 900–1400 km depth.

**Results**

The high-pressure phases of $\varepsilon$-FeOOH and $\delta$-AlOOH are synthesized using a large volume multi-anvil press (MAP, see Materials and Methods for details). The pressure-temperature ($P-T$) conditions for MAP experiments are summarized in Table 1. We conducted a set of MAP experiments to synthesize high-pressure samples as well as to constrain the phase stability fields of FeOOH, as shown in Fig. 1. At low pressure (< 7 GPa), FeOOH dehydrates along a steep $P/T$ curve. At higher pressure, our results generally agree with previous MAP results by Yoshino, et al. Also plotted in Fig. 1 are four different subduction slab geotherms from Kirby et al. Although the high-pressure $\varepsilon$-FeOOH dehydrates at the conditions of mantle geotherm and not considered as a superior stable phase to survive all categories of subducting slabs, it bears the $P-T$ conditions of subducting slabs with relatively older age and faster sinking conditions. Once $\varepsilon$-FeOOH descends to deeper mantle, it benefits from improved thermal stability (Fig. 1) such that it is capable to carry hydrous and ferric iron enriched fragments deeper. On the other hand, partially dehydrated $\varepsilon$-FeOOH may possibly rehydrate in wet local regions of the mantle transition zone. Therefore, $\varepsilon$-FeOOH is a potential minor phase transporting water down to the lower mantle through cold subducting slabs.
Table 1
Starting samples and products of MAP synthesis.

| Run #          | Sample   | $T$ (°C) | $P$ (GPa) | Time (minute) | Product   |
|---------------|----------|----------|-----------|---------------|-----------|
| 160314G1127   | Goethite | 600      | 12        | 240           | ε-FeOOH   |
| 160317G1128   | Goethite | 700      | 12        | 240           | ε-FeOOH   |
| 160320G1129   | Goethite | 800      | 12        | 240           | ε-FeOOH   |
| 160411G1135   | Goethite | 900      | 12        | 120           | Hematite  |
| 160414G1136   | Goethite | 900      | 14        | 120           | ε-FeOOH   |
| 160417G1137   | Goethite | 1000     | 14        | 120           | Hematite  |

We perform our high-pressure $EC$ experiments using impedance spectroscopy at ambient temperature and up to 61 GPa for ε-FeOOH (Fig. 2, Table 2). Parallel experiments of δ-AlOOH and γ-AlOOH are performed up to 53 GPa to study the effects of Fe$^{3+}$. Throughout the experiments, the errors of resistances in the Nyquist plot fitting are less than 1% (Table 2). The high-pressure in situ $EC$ numbers are calculated by the van der Pauw method$^{34}$ (Details in Methods). In Fig. 2, the $EC$ of γ-AlOOH is almost invariently correlated with pressure, while those of γ-AlOOH and ε-FeOOH climb with pressure. Specifically, the $EC$ of ε-FeOOH exhibits an abrupt jump at ~ 45 GPa and reaches $1.24 \pm 0.19 \times 10^3$ S/m at 61.2 GPa. We note that a similar trend of change is also observed in goethite α-FeOOH within similar pressure range$^{35,36}$. In contrast, the $EC$ of γ-AlOOH shows a small kink between 30 and 40 GPa but the increment of $EC$ is less than one order of magnitude.
Table 2

EC numbers of ε-FeOOH at ambient temperature.

| Pressure (GPa) | Resistance (Ω) | Thickness (µm) | Conductivity $\sigma$ (S/m) | Conductivity Log$_{10}$[$\sigma$(S/m)] |
|---------------|----------------|----------------|----------------------------|----------------------------------------|
| 0.3(1)        | $4.7(3) \times 10^5$ | 74.1(148)      | $6.26(93) \times 10^{-3}$  | -2.20                                  |
| 4.5(5)        | $4.0(1) \times 10^5$ | 62.0(123)      | $8.67(13) \times 10^{-3}$  | -2.06                                  |
| 8.1(8)        | $3.5(2) \times 10^5$ | 52.6(105)      | $1.18(17) \times 10^{-2}$  | -1.92                                  |
| 10.7(10)      | $3.0(1) \times 10^5$ | 46.4(92)       | $1.57(23) \times 10^{-2}$  | -1.80                                  |
| 15.1(15)      | $2.1(2) \times 10^5$ | 36.9(74)       | $2.75(41) \times 10^{-2}$  | -1.56                                  |
| 18.4(18)      | $1.5(1) \times 10^5$ | 30.7(61)       | $4.54(68) \times 10^{-2}$  | -1.34                                  |
| 23.1(21)      | $1.1(1) \times 10^5$ | 23.2(46)       | $8.01(12) \times 10^{-2}$  | -1.09                                  |
| 25.7(24)      | $1.1(2) \times 10^5$ | 19.7(39)       | $9.92(14) \times 10^{-2}$  | -1.00                                  |
| 28.1(31)      | $1.0(3) \times 10^5$ | 16.9(33)       | $1.25(18) \times 10^{-1}$  | -0.90                                  |
| 30.5(33)      | $9.7(3) \times 10^4$ | 14.5(29)       | $1.55(23) \times 10^{-1}$  | -0.80                                  |
| 32.3(35)      | $9.0(2) \times 10^4$ | 13.0(26)       | $1.86(27) \times 10^{-1}$  | -0.72                                  |
| 34.7(38)      | $8.1(1) \times 10^4$ | 11.3(22)       | $2.39(35) \times 10^{-1}$  | -0.62                                  |
| 37.5(41)      | $7.2(1) \times 10^4$ | 9.84(19)       | $3.09(46) \times 10^{-1}$  | -0.50                                  |
| 40.9(44)      | $6.2(2) \times 10^4$ | 8.8(17)        | $3.96(59) \times 10^{-1}$  | -0.40                                  |
| 43.7(48)      | $5.4(3) \times 10^4$ | 8.6(17)        | $4.70(61) \times 10^{-1}$  | -0.32                                  |
| 46.1(52)      | $9.2(2) \times 10^2$ | 8.4(17)        | $2.78(41) \times 10^{1}$   | 1.44                                   |
| 50.7(55)      | $1.2(3) \times 10^2$ | 8.4(17)        | $2.08(31) \times 10^{2}$   | 2.31                                   |
| 53.3(58)      | $6.4(1) \times 10^1$  | 8.3(16)        | $4.10(63) \times 10^{2}$   | 2.61                                   |
| 56.1(61)      | $4.3(1) \times 10^1$  | 8.2(16)        | $6.03(87) \times 10^{2}$   | 2.78                                   |
| 61.2(67)      | $2.2(3) \times 10^1$  | 8.0(15)        | $1.24(19) \times 10^{3}$   | 3.09                                   |

Figure 3 showed representative Nyquist plots of ε-FeOOH up to 61.7 GPa. The plots are fitted with the Z-View software and the fitting errors are generally less than 1%. Up to 53.5 GPa, only one semi-circle exists in the high frequency region (inset in Fig. 3a). Below 45 GPa, ε-FeOOH is well defined as an
insulating phase. It has the same small polaron hopping conduction as many other insulating hydroxide or hydrous minerals\textsuperscript{38}. At 53.5 GPa, a second semi-circular arc appears in the low frequency region next to the main circle (Fig. 3b). The onset of the second arc is often attributed to grain boundary resistance\textsuperscript{39}. This is previously regarded as a symbol of anisotropy of the charge carrier transportation in the crystallites\textsuperscript{40}. While both our x-ray diffraction experiment and literature data indicate that $\varepsilon$-FeOOH is a stable phase throughout the pressure range we have investigated\textsuperscript{27,41,42}, the appearance of the second arc coincides with the spin-paring of Fe\textsuperscript{42}. The spin transition of Fe may create grain boundaries between the high-spin and low-spin domains. Above the critical pressure, the EC of $\varepsilon$-FeOOH sharply increases and is comparable to metal, for example the metallic FeO\textsuperscript{24} and FeH\textsuperscript{43}. Upon further compression, the arc at the low-frequency region becomes insignificant while the high-frequency arc dominates. Such wax and wane imply the progression of spin transition. From 53.5 to 61.7 GPa, it is possible to have two conduction mechanisms competing with each other.

In Fig. 3c, we calculate the relationship between pressure and relaxation frequency for the conduction of grain and grain boundary by fitting the impedance spectra with an equivalent-circuit method (Fig. 3a, 3b insert)\textsuperscript{44}. The characteristic relaxation frequency ($f$) can be obtained by the equivalent circuit model of a constant phase element (CPE) using the equations\textsuperscript{45}:

\[ f = \frac{1}{2\pi RC} \]

where $R$ is the resistance (intercept of the semicircle with the imaginary axis); $C$ is the capacitance, $C = (Rt)^{1/H}/R$ ($t$ is a fitting parameter that equals to the capacitance of the CPE when it behaves as an ideal capacitor and $H$ is a value between 0 and 1 depending on the suppression angle of the semi-circle). Similar to $EC$, $f$ gradually increases with the compression and spikes at $40-45$ GPa due to the electronic transition of Fe. At about 52 GPa, $f$ for grain interior significantly drops and that for grain boundary emerges. This is consistent with measured $EC$ value which soars at the same pressure range. The low-spin configuration may play a significant role in the high $EC$.

We conducted first-principles simulation to study the underlying electronic transition. For the strongly correlated system of simple iron-oxide, it is technically challenging to accurately reproduce their electronic structures\textsuperscript{46}. A previous study on the pyrite-type FeO$_2$H$_x$ indicated neither conventional density function theory (DFT) nor DFT with Hubbard correction can fully describe its electronic structure\textsuperscript{47}. Hence, we performed comprehensive DFT + density mean-field theories (DMFT) calculation for $\varepsilon$-FeOOH. This method was successfully implemented to FeO$_2$ and FeO$_2$H\textsuperscript{48,49}. We started with DFT calculations, which gave fully relaxed structures with volumes corresponding to 1 bar, 30 GPa and 50 GPa respectively. Then both Fe 3$d$ and O 2$p$ orbitals are wannierized in the energy window from $-11$ eV to 5 eV (with the Fermi level at 0 eV). We then solve the quantum impurity problem in DMFT by a continuous-time hybridization expansion solver (details in Methods).
In Fig. 4, the Fermi level comes across the valence band when unit cell volume is below 51.27 Å³, which is a clear evidence of metallization (band structures in Supplementary Fig. 1–3). The metallization is mainly associated with Fe d orbitals and the Fermi level shifts to the valence bands. This is due to the weakening of the Mott-Hubbard energy. Thermal fluctuations between the high-spin and low-spin states of Fe⁢³⁺ trigger the insulator-metal transition. The same transition mechanism is also found in BiFeO₃, which carries ferric iron⁵⁰. It is worth noting that the metallic ε-FeO₂H is in the low-spin configuration. Consequently, for low-spin ε-FeOOH, small-polaron hopping model converts to the free electron model that is often found in metal.

Discussion

The jump of EC is absent in Al endmember γ-AlOOH or δ-AlOOH up to 55 GPa. This is reasonable since Al atom has no d electrons in the valence band, thus is unlikely to metalize through a spin transition (Fig. 2). Similar to the incorporation of Mg to wüstite, adding Al to ε-FeOOH is expected to scale down the EC changes during electronic transition. Here, our results on the end members may bracket the upper and lower limits of EC.

For the large-scale electrical structure of the lower mantle, a more comprehensive mineral system should be taken into account. In Fig. 5, we compare the EC of ε-FeOOH with a variety of lower mantle components including Brg, Fp, and mineral phases in MORB compositional model. Also plotted in Fig. 5 are the high and average 1D EC profile from frequency dependent impedance response functions of the geomagnetic field by Constable and Constable¹¹ and Ohta et al.⁵¹, respectively. When pressure is below 45 GPa, EC numbers from the majority of mineral phases are varying within a modest 1–2 orders of magnitude. One exception is the semiconducting wüstite which leaves a significant gap with other compositions. The mineralogy data is generally consistent with geomagnetic models which regard the top later of the lower mantle is relatively homogeneous⁵. Crossing the transition point at 45 GPa, the EC of ε-FeOOH shoots up by 3 orders of magnitude due to metallization. Triggered by a Mott-type insulator to metal transition, the EC jump observed in ε-FeOOH at 45 GPa is distinct from other lower mantle minerals. Comparing with other ferric system, for instances the Mg⁰.⁸₃Fe⁰.₂₁Al⁰.₀₆Si⁰.₉₁O₃ Brg¹³ and Mg⁰.₆₀Fe⁰.₄₀Si⁰.₆₃Al⁰.₃₇O₃ Brg⁵² silicates, the increment of EC is only moderate and approximately monotonous with pressure without dramatic jumps. Otherwise, the high to low-spin transition of ferrous iron slows the mobility of the charge transfer carriers of low-spin Fe²⁺, thus lowers EC¹⁴. In the cases of (Mg⁰.⁷₅Fe⁰.₂₅)O¹⁴, (Mg⁰.₈₁Fe⁰.₁₉)O⁵³, and (Mg⁰.₉Fe⁰.₁)SiO₃ Brg⁵⁴, spin transition reduces total EC by ~ 0.5-1 orders across the transition point. In short, the metallization pressure in ε-FeOOH matches the pressure of significant step increase in the 1D EC profile reported by Constable and Constable¹¹ (Fig. 5). The divergence of EC in different mineral phases above 45 GPa may give rise to the lateral conductivity heterogeneity in the deep lower mantle due to their chemical (phase) heterogeneity. While the major components of the lower mantle like Brg and Fp feature low EC in their insulating phases, ε-FeOOH is
among the few phases to establish significantly higher EC. ε-FeOOH, owning to the electronic transition, would be a candidate to explain the electrically heterogenous lower mantle.

In Fig. 6, we overlay a synthetic 3D conductivity structure at 1220 km depth on a map of tectonics plates in the South China Sea region. The separation of high EC and low EC regions have an intriguing relation with the plot of tectonic plates. A large portion of the high EC regions are located at the stagnant slab beneath subduction zones, which is enriched in water and ferric iron. Mineral physics experiments also support the concentration of Fe\(^{3+}\) and water content is positively correlated. We also notice in some local regions, the EC values may surge to the level of \(10^2\) S/m, which is not fully covered by the highly conductive mid-oceanic ridge basalt (MORB) segments. Here, we assume a scenario of mixing ε-FeOOH to a MORB composition at the bottom of subduction slabs. Using the simple averaging theorem, mixing 25% of ε-FeOOH to a MORB composition yields a total EC of 18.1 ± 2.7 S/m at 50 GPa. This is 7 times higher than the average EC profile shown in Fig. 5 and in line with the higher variation of electrical heterogeneity estimated by the 3D synthetic model in the range of 1200–1400 km depth, e.g. at the Java subduction slab. In addition, when hydrous ε-FeOOH meets hotter regions in the mantle, it causes dehydration melting that would further boost the overall transport properties. We therefore suggest that those localized domains with topped \(10^2\) S/m EC may have incorporated higher concentration of ε-FeOOH, or the enrichment of other superior EC components.

To sum up, high pressure alters the electron conduction mechanism in ε-FeOOH from insulator to metal at about 45 GPa. This transition is accompanied with a nearly 3 orders of magnitude increase in EC. The metallic ε-FeOOH has much higher EC than major lower mantle compositions. Minor to moderate presence of the metallic ε-FeOOH causes the overall EC in a conventional mineral assemblage to approach the high EC profiles of the lower mantle, giving rise to a possible EC heterogeneity in the deep lower mantle. Future studies of seismology and deep diamond inclusions are on-demand to detect and constrain the availability of iron-enriched hydrous materials in the lower mantle.

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**Methods**

**Sample preparation using multianvil press**

Ambient oxy-hydroxide samples were purchased from merchant sites (α-FeOOH, purity 99%+, Alfa Aesar, CAS: 20344-49-4 and γ-AlOOH, purity 99%, Macklin CAS: 1318-23-6, natural sample). The purity of
boehmite samples were checked by electron microscope analysis. The result shows boehmite contains 0.03 wt.% of hematite (Supplementary Fig. 4). The powder samples were grounded in an agate motor with alcohol for 1 hour.

High pressure synthesis of ε-FeOOH started with grounded goethite powder. The powder was packed in a gold capsule which is rolled in a rhenium heater, and placed in a Kawai-type multi-anvil press at the Geophysical Laboratory, Carnegie Institution of Washington. Synthesis experiments were conducted at 12 or 14 GPa and in the temperature range of 600-1000 °C and kept those conditions for up to 4 hours. Since ε-FeOOH is heated to dehydrate even upon Raman laser, the recovered products were characterized by x-ray diffraction (Supplementary Fig. 5 and 6). The grain size of ε-FeOOH is around 50 μm (Supplementary Fig. 7). We varied our experimental P-T conditions to constrain the stability fields of ε-FeOOH up to 14 GPa (Fig. 1).

δ-AlOOH sample was synthesized in a Kawaii-type multi anvil press available at Jilin University. The starting composition is Al(OH)₃ and the sample was sealed in a platinum capsule during synthesis. The synthesis was performed at 18 GPa and 900 °C, and then held for 2 hours. We measured the Raman spectroscopy of the synthesized sample to confirm that the product is pure.

**In situ high-pressure EC measurements using impedance spectroscopy**

High-pressure EC experiment was performed by a Solartron-1260 AC impedance spectroscopy with frequencies between 0.1 Hz and 10 MHz incorporation with a 300-μm anvil culet symmetrical-style DAC. A T-301 steel gasket was pre-indented to a thickness of 50 μm then a hole with diameter \( d = 280 \mu m \) was drilled at the center of the indentation and filled in the mixed powder of boron nitride-epoxy. The filled hole was then compressed to ~15 GPa. Afterwards, a 100-μm hole was drilled at the center to act as the insulating sample chamber. Four Pt foils were chosen serving as the electrodes with a thickness of less than 4 μm, which can determine the resistivity of an arbitrary-shaped sample with an even thickness and minimize the resistivity effect from the contact resistance (Supplementary Fig. 8). To avoid impurities and ensure good electrode contact, no pressure medium was used for the EC measurement.

The thickness \((t)\) of the sample in Table 2 was estimated using a simple interpolation method⁶⁴. We compressed a few standard samples to different pressures \((P = 0, 10, 20, 30, 40, 50 \text{ GPa} \text{ respectively})\) and calibrated the gasket thickness by a Vernier caliper. The sampling results were fitted to a parabolic relation between pressure and gasket thickness. We calculated the thickness shrinkage rate as the slope \((\delta_t = dt/dP)\) of parabolic relation. Using the same gasket material and sample assemblage, the thickness at arbitrary pressure is interpolated by the formula:

\[
t(P) = t_{\text{min}} + P \cdot \delta_t
\]

where \(t_{\text{min}}\) is the thickness of the gasket when pressure is fully released in the experiment run. The thickness of the sample is comparable to that of the gasket. The error in thickness includes measured and systematic error, which is estimated to be about 20%.

**First principles simulation based on DFT+DMFT**
We first relaxed the crystal structure of $\varepsilon$-FeOOH using conventional DFT. The simulation was performed by Quantum Espresso version 6.3 (ref. 65). The kinetic energy cutoff is 70 Ry for wavefunctions and 600 Ry for charge density. Both lattice parameters and atomic positions were relaxed to the target pressures. We noticed the crystal structure has symmetric hydrogen bonding at 50 GPa.

To proceed with the electronic structure calculation, we used the DFT + DMFT method as was implemented in the DCore code. A noninteracting GGA Hamiltonian, which includes the Fe 3$d$ and O 2$p$ states, was constructed by the Wannier function projection$^{66}$. The quantum impurity problem was handled by a continuous-time hybridization expansion solver from TRIQS/cthyb$^{67,68}$. The calculation is performed by DCore version 2.1$^{69}$. We used the same set of Coulomb parameters ($U = 6$ eV and $J_H = 0.89$ eV) for all the structures$^{47}$. All calculations were performed at inverse temperature $\beta = 40 \text{ eV}^{-1} (~290 \text{ K})$.

**Figures**

![Figure 1](image-url)
Stability fields of FeOOH. Colors of red, blue and yellow correspond to Fe2O3+H2O, ε-FeOOH and α-FeOOH. Dot dashed curves are thermokinetic model results of four slabs representing subducting lithosphere in different trenches by Kirby et al.32. From A to D, slabs are older and faster sinking.

Figure 2

Electrical properties of ε-FeOOH, γ-AlOOH and δ-AlOOH versus pressure at ambient temperature. The EC of ε-FeOOH showed a huge jump at ~45 GPa. The errors were estimated to be ~15%.
Figure 3

Selected Nyquist plots of ε-FeOOH. The solid curves were the corresponding fitting curves with equivalent circuits showed at the corner or top of the figure. a, below 50 GPa the equivalent circuit consists of a single part of one resistor and one constant phase element (R-CPE) in parallel; b, At 53.5 GPa the equivalent circuit splits into three parts. c: Pressure dependence of relaxation frequency for the grain interior and the grain boundary of compressed ε-FeOOH.
Figure 4

Density of state (DOS) of $\varepsilon$-FeOOH at various volumes. Projected DOS of Fe t2g and eg orbitals are plotted in shaded color. At 50 GPa, $\varepsilon$-FeOOH is a correlated metal.
Figure 5

Pressure dependence of the EC in lower mantle phases compared with geomagnetic measurements. Solid asterisk: $\varepsilon$-FeOOH at 300 K by this study. Diamond: (Mg$_{0.9}$Fe$_{0.1}$)SiO$_3$, Fe-bearing Brg at 300 K54. Up-pointing triangle: (Mg$_{0.46}$Fe$_{3.0.53}$)(Si$_{0.49}$Fe$_{3.0.51}$)O$_3$, Fe-bearing Brg at 300 K55. Pentagon: Mg$_{0.83}$Fe$_{0.21}$Al$_{0.06}$Si$_{0.91}$O$_3$, Al,Fe-bearing Brg at 1800 K13. Down-pointing triangle: Mg$_{0.83}$Fe$_{0.21}$Al$_{0.06}$Si$_{0.91}$O$_3$, Al,Fe-bearing Brg at 300 K13. Circle: (Mg$_{0.75}$Fe$_{0.25}$)O at 300 K14. Square: (Mg$_{0.81}$Fe$_{0.19}$)O at 300 K53. Right-pointing triangle: FeO, wüstite at 300 K56. Cross: MORB at 1430-2100 K51. Blue and green line show geomagnetic observed high and average electrical 1D conductivity profile by Constable and Constable11 and Ohta et al.51, respectively. The gray area is 95% confidence interval.
Figure 6

The \(\varepsilon\)-FeOOH origin of heterogeneous EC layer. Left panel zoom in the Java subduction slab (JAV), whose curvature is from Goes et al.57. Right panel is an interpolated 3D EC map taken at 1220 km depth5. The green curves are the edge of tectonic plates. While the subduction zones on the right panel are: RYU-Ryukyu, IZU-Izu, HON-Honshu, KUR-Kuriles, KAM-Kamchatka, IND-India, MAR-Marianas, SUM-Sumatra.

Supplementary Files

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