

REVIEW ARTICLE



High-pressure and high-temperature behaviour of α -FeOOH and ϵ -FeOOH: a geological perspective

Shun-Feng Yan^{a,b}, Lin Li^{a,b}, Mao-Wen Yuan^{a,c}, M. Santosh^{c,d} and Sheng-Rong Li^{a,c}

^aState Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing, People's Republic of China; ^bInstitute of Earth Sciences, China University of Geosciences, Beijing, People's Republic of China; ^cSchool of Earth Science and Resources, China University of Geosciences, Beijing, People's Republic of China; ^dDepartment of Earth Sciences, University of Adelaide, Adelaide, SA, Australia

ABSTRACT

α -FeOOH exhibits high thermodynamic stability and is the most abundant iron hydroxide in soils and sediments, commonly found as a weathering product in various rocks. Under high pressure, it undergoes a phase transition to the high-pressure phase ϵ -FeOOH. This review discusses the structural, thermal, physical, and spectroscopic properties of α -FeOOH and ϵ -FeOOH. Through a combination of experimental observations and theoretical models, it has been demonstrated that ϵ -FeOOH can form stable solid solutions with δ -AlOOH and MgSiO_4H_2 , thereby extending the stability range of these phases into the lower mantle. The key effects of phase transitions of α -FeOOH and ϵ -FeOOH, including hydrogen bond symmetrization and spin state changes, directly influence the physical properties of these minerals, such as bulk modulus, electrical conductivity, and elasticity. The ultrahigh-pressure phase Py-FeOOH_x may decompose in rising mantle plumes, contributing sporadic oxygen sources for the Great Oxidation Event. The Great Oxidation Event, lasting from approximately 2.4 to 2.06 billion years ago, may have been triggered by a prolonged period of instability. Whether other hydrous minerals exhibit similar behaviours, potentially leading to an underestimation of sporadic deep sources, remains an open question for future research.

ARTICLE HISTORY

Received 29 August 2024
Accepted 16 February 2025

KEYWORDS

HTHP; FeOOH; phase transition; physical properties; CaCl_2 -type solid solution

Contents

	PAGE
1. Introduction	2
2. Structure, phase transition and thermal behaviour of α -FeOOH and ϵ -FeOOH	4
2.1. Crystal structures and phase transitions of α -FeOOH and ϵ -FeOOH	4
2.2. Quenching of ϵ -FeOOH and temperature effects	5
2.3. Thermal dehydroxylation and decomposition behaviour of α -FeOOH and ϵ -FeOOH under high-temperature and high-pressure conditions	5
2.4. Hydrogen bond symmetrization and spin transition of ϵ -FeOOH under high pressure	7

2.5. Phase transition of ϵ -FeOOH under extreme pressure and temperature conditions	9
3. Physical properties of α-FeOOH and ϵ-FeOOH	9
3.1. Bulk modulus of α -FeOOH and ϵ -FeOOH under high-temperature and high-pressure conditions	9
3.2. Electrical conductivity of α -FeOOH and ϵ -FeOOH under high-temperature and high-pressure conditions	11
3.3. Elastic properties of α -FeOOH and ϵ -FeOOH under high-temperature and high-pressure conditions	14
3.4. Electronic structure of α -FeOOH and ϵ -FeOOH under high-temperature and high-pressure conditions	16
4. Vibrational spectroscopic properties of α-FeOOH and ϵ-FeOOH	17
4.1. Infrared spectra	17
4.2. Raman spectra	21
5. CaCl_2-type (ϵ-FeOOH – δ-AlOOH – MgSiO_4H_2) solid solution	23
6. Conclusions and outlook	25
Disclosure statement	27
Funding	27
References	28

1. Introduction

The major iron oxides and iron hydroxides in terrestrial environments comprise include goethite (α -FeOOH), hematite (α -Fe₂O₃), magnetite (γ -Fe₂O₃), akaganéite (β -FeOOH) and lepidocrocite (γ -FeOOH), etc. Among these, α -FeOOH is the most abundant iron hydroxide in soils and sediments due to its high thermodynamic stability [1,2]. The oxidation of iron sulfides invariably results in the formation of α -FeOOH, both in close association with the sulfides and as distal precipitates [3]. Other oxyhydroxide minerals identified as secondary precipitates are β -FeOOH and γ -FeOOH, but occurrences are generally insignificant relative to the abundance and distribution of α -FeOOH [3]. α -FeOOH is a crucial soil mineral and a significant contaminant in bauxite deposits. It is present in large quantities in soils and occurs in mineralized zones, iron ore deposits, and hydrothermal ore formations [4–6]. Additionally, it is a common weathering product in various types of rocks [6–8]. The structures of iron hydroxides, including α -FeOOH (Figure 1a), β -FeOOH (Figure 1b), and γ -FeOOH (Figure 1c), are illustrated in the corresponding figures.

The occurrence, abundance, distribution, and influence of volatile components in the Earth's interior on the physical properties of mantle minerals have been one of the focal themes in experimental mineral physics over the past two decades [9–12]. The accommodation, distribution, and circulation of hydrogen in the deep Earth are crucial to understanding the evolution of the Earth's interior [13,14]. Geophysical observations indicate that the Earth's mantle and transition zone contain significant amount of hydrogen, at least in localized regions [15–19]. Additionally, evidence from seismic imaging supports the hypothesis that subducting lithospheric plates cross the transition zone, potentially

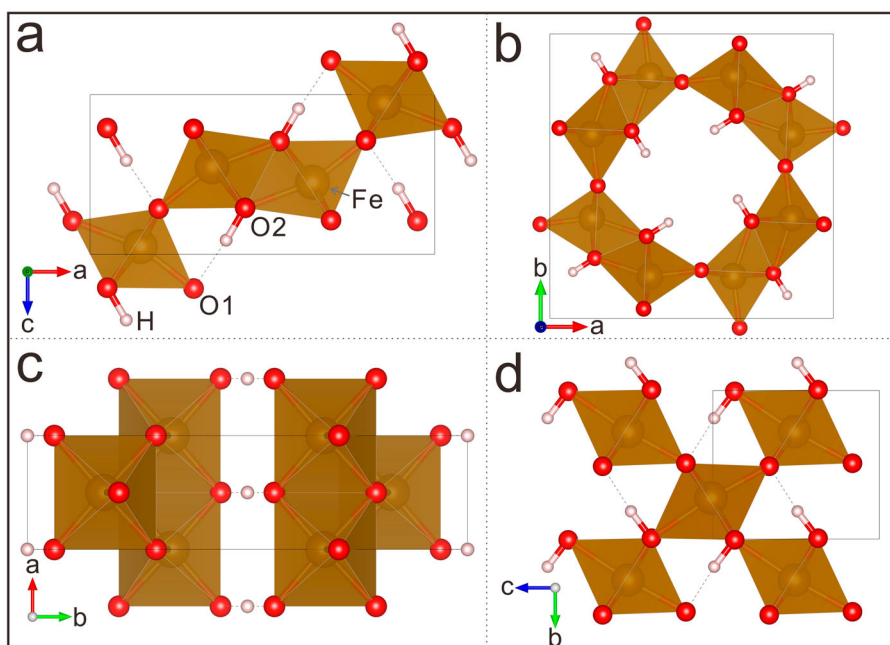


Figure 1. Structure of iron hydroxides (CIF from American Mineralogist Crystal Structure Database, drawing by VESTA software).

introducing water into the Earth's lower mantle [20]. Hydrous minerals (phases) are widely regarded as potential water reservoirs in the Earth's interior, serving as carriers of hydrogen and oxygen. Under high-temperature and high-pressure conditions, these minerals (phases) undergo dehydration / deoxygenation / dehydrogenation reactions, influencing the key physicochemical properties of mantle minerals [21–31].

Several studies have investigated the stability domains of various hydrous phases. The end-member model is the MSH ternary system of $\text{MgO-SiO}_2\text{-H}_2\text{O}$, which forms a series of dense hydrous magnesium silicate phases (DHMSs), including Phase A [32], Phase B [32–34], Superhydrous Phase B = Phase C [32,35,36], Phase D = Phase F = Phase G [37–43], and Phase H [44], etc.; The sediment layer and oceanic crust in the upper part of the subducting plate are richer in Al and Si than the lithospheric mantle, forming an ASH ternary system composed of $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. Hydrous minerals (phases) that can be formed include $\alpha\text{-AlOOH}$ [45], Phase δ [46], Phase Pi [47,48], Topaz-OH [49,50], Phase egg [51,52], and Al-phase D [53], etc.; Solid solution phases and other hydrous minerals (phases) formed between the MSH and ASH systems include lawsonite [54], Phengite [55], Phase H- δ solid solution [56], Mg-Phase egg [57], $\epsilon\text{-FeOOH}$ [58], HH Phase [59] and Py- FeOOH_x [60,61], etc.

The high-pressure phase ($\epsilon\text{-FeOOH}$, Figure 1d) is a significant hydrous phase in subducted slabs of the Earth's mantle, containing ~ 19.13 wt.% of water [58,60,61]. The presence of water in $\epsilon\text{-FeOOH}$ can substantially influence the physical and chemical properties of the Earth's deep interior, affecting its structure and dynamics [62–64]. The discovery of Py- FeOOH_x has sparked interest in the study of simple hydroxy oxides in recent years [60,61,65–67]. Understanding the stability and properties of simple hydroxy

oxides under high-pressure and high-temperature conditions provides an important first step in quantifying the more complex hydroxy oxides relevant to the Earth's interior [68]. However, the stability and phase transition effects of hydroxyl and hydrogen bonding within minerals under these conditions remain unresolved. Fe is a major chemical component of the Earth's deep interior, and its valence state is influenced by pressure and oxygen fugacity. Furthermore, α -FeOOH and α -Fe₂O₃ have been discovered on the surface of Mars [69]. The properties of iron oxides and iron hydroxides are important to geochemistry, mineralogy, and planetary science. The ϵ -FeOOH is of particular interest due to its potential to form hydrogen-bearing solid solutions with Phase δ and Phase H, which may facilitate water transport into the lower mantle. The potential dehydration of Py-FeOOHx is related to various phenomena, including the incorporation of hydrogen into the outer core [60], the formation of ultra-low velocity zones [67], and the occurrence of the Great Oxidation Event (GOE) [61].

2. Structure, phase transition and thermal behaviour of α -FeOOH and ϵ -FeOOH

2.1. Crystal structures and phase transitions of α -FeOOH and ϵ -FeOOH

The structure of α -FeOOH was first determined by Goldshtaub [70] and Hoppe [71] through X-ray diffraction. It was not until 2006 that Yang et al. [72] conducted a detailed structural analysis of natural α -FeOOH crystals, including anisotropic atomic displacement parameters. α -FeOOH belongs to the orthorhombic system, and its space group was revised from *Pbnm* to *Pnma* according to the International Tables for Crystallography [73].

In the structure of α -FeOOH, the oxygen (O) atoms are arranged in slightly distorted hexagonal close packing. The iron (Fe) atoms occupy half of the octahedral sites, forming edge-sharing Fe³⁺ O₆ octahedra chains parallel to the b-axis. These chains are further connected through shared vertices, forming a three-dimensional structure. The edge-sharing Fe³⁺ O₆ octahedra form so-called double chain of rutile parallel to the b-axis. The channels between the chains are parallel to the c-axis, and hydrogen bonding (O-H...O) spans across the channels. Two distinct positions exist for the O atoms in the structure. O1 atoms are surrounded by Fe atoms, forming an almost planar triangle, while O2 atoms are hydrogenated and coordinated by three Fe atoms and one hydrogen (H) atom, forming a distorted tetrahedral coordination. Hydrogen bonds are connected to the O1 atoms (Figure 1a), with the hydrogen bond vectors having a significant component parallel to the a-axis. The compressibility of the α -FeOOH crystal axes is anisotropic, with the compressibility of the a-axis being twice that of the other axes [74]. Forsyth et al. [75] experimentally demonstrated through neutron diffraction that the hydrogen bonds in α -FeOOH are nonlinear under ambient pressure, primarily due to the repulsion between hydrogen ions and adjacent Fe ions. These nonlinear hydrogen bonds in α -FeOOH are of moderate strength and are the most common type of hydrogen bond [76].

Nagai et al. [74] conducted a study on α -FeOOH using synchrotron X-ray diffraction and found no significant structural changes until reaching an experimental pressure of 24.5 GPa, it is believed that the small peaks observed on the compression curves of each axis $\sim$ 11 GPa are due to non-hydrostatic stability caused by the solidification of a 4:1 mixture of methanol and ethanol as a pressure medium [77]. Gleason et al. [78] also proposed that the

observed discontinuities in lattice parameters during high-pressure experiments supported this notion, with isothermal compression smoothly passing through the discontinuity at 9 GPa at ambient temperature. The glass transition of the methanol–ethanol mixture leads to non-hydrostatic stability, explaining the lack of continuity in high-pressure data [79]. Mao et al. [80] also found similar features when studying Phase δ . The experimental $K_0 V_0$ values of α -FeOOH are nearly the same as those of Phase δ . It is generally believed that the $K_0 V_0$ values of the same structure are constant [81]. Bendeliani et al. [82] conducted a study on the Fe_2O_3 - H_2O system under conditions of 9 GPa and 673 K, synthesizing a high-pressure iron hydroxides polycrystalline phase and reporting the discovery of this new phase (ϵ -FeOOH). The calculations and experimental results jointly demonstrate that at pressures greater than 6–7 GPa, α -FeOOH transform into the high-pressure phase (ϵ -FeOOH) (Figure 1d), the closely-packed, edge-shared Fe^{3+}O_6 units form the structure along the c-axis, with hydrogen atoms occupying the channels between these closely-packed octahedra [1,46,58,83–87]. Gleason et al. [78] used the G vs. g method to obtain a zero-pressure volume of $66.3(\pm 0.5) \text{ \AA}^3$ for ϵ -FeOOH, which is consistent with the experimental value of the ambient-pressure single crystal [88,89].

2.2. Quenching of ϵ -FeOOH and temperature effects

There is still controversy regarding whether ϵ -FeOOH can be quenched. Gleason et al. [78] obtained the non-quenchable phase of ϵ -FeOOH within a pressure range of 6–29.4 GPa and a temperature range of 296–573 K; Suzuki et al. [89] synthesized the quenched phase of ϵ -FeOOH using a Kawai-type Multi-Anvil Apparatus (MAA) at 11 GPa and 800 K for 10 minutes; Thompson et al. [62] also achieved the quenched phase of ϵ -FeOOH using the same method as Suzuki; Xu et al. [90] observed the reversible behaviour of ϵ -FeOOH upon decompression at 54 GPa; Kawazoe et al. [91] synthesized the quenched phase of δ -(Al, Fe)OOH using a Kawai-type MAA at 21 GPa and 1470 K for 4 hours; Liu et al. [87] observed the reversible behaviour of ϵ -FeOOH upon decompression after being pressurized to 35.2 GPa during diamond anvil cell (DAC) experiments conducted at ambient temperature; Ikeda et al. [92] synthesized the quenched phase of ϵ -FeOOH using a Kawai-type MAA at 8 GPa and 753 K for 60 minutes; Xu et al. [93] obtained the quenched phase of ϵ -(Fe, Al)OOH using a MAA under conditions of 15–25 GPa and 973–1373 K for 40–90 minutes; Tang et al. [94] observed the reversible behaviour of the ϵ -FeOOH when compressed to 32 GPa at ambient temperature using DAC during Raman experiments. Based on these experimental data, it can be concluded that the obtainability of quenched high-pressure phases is significantly influenced by the experimental temperature (Figure 2).

2.3. Thermal dehydroxylation and decomposition behaviour of α -FeOOH and ϵ -FeOOH under high-temperature and high-pressure conditions

Under ambient pressure, α -FeOOH undergoes thermal dehydroxylation between 460–620 K, transforming into α - Fe_2O_3 [95–99]. The thermodynamic properties and particle size effects of the α -FeOOH – α - Fe_2O_3 reaction have been extensively studied [100–102]. Upon heating, α -FeOOH transforms into α - Fe_2O_3 by removing hydroxyl layers and forming water from some oxygen atoms in the bands parallel to the c-axis. During this transformation, the (100), (010), and (001) directions of α -FeOOH become the (001), (110), and

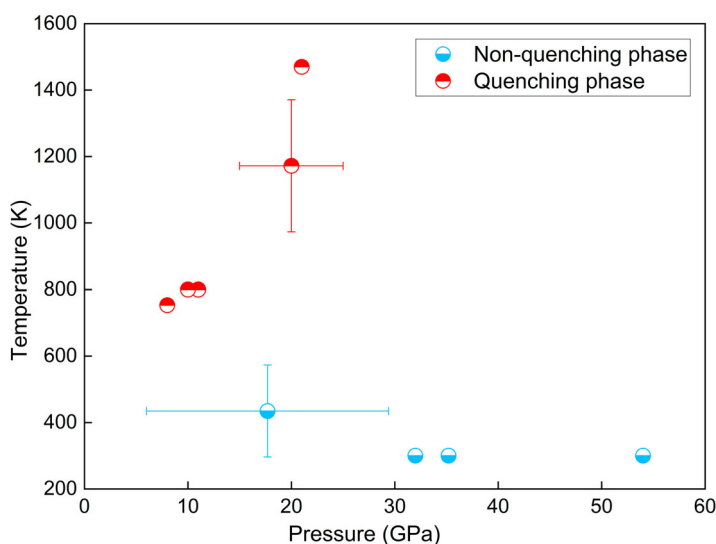


Figure 2. Diagram of high-pressure phase quenching and temperature-pressure relationship [62,78,87,89,90,92–94].

(1 $\bar{1}$ 1) directions of the α -Fe₂O₃ unit cell [7,98,103]. Although the thermal decomposition products are entirely α -Fe₂O₃, they maintain the original morphological characteristics of α -FeOOH. Additionally, the specific surface area and pore structure of the products exhibit significant differences with changes in calcination temperature. During the dehydroxylation process, residual hydroxyl units in α -FeOOH are transferred to the resulting α -Fe₂O₃, forming what is known as hydrous α -Fe₂O₃ [99,104,105]. During calcination at 500 K, the α -FeOOH pseudoparticles undergo dehydroxylation, resulting in the formation of pores ranging from 1–5 μ m within their internal structure, possessing the maximum specific surface area. As the calcination temperature increases, the growth of α -Fe₂O₃ crystals leads to the enlargement of the interstitial gaps between the crystals, causing the specific surface area to gradually decrease. When the calcination temperature exceeds 973 K, particle sintering occurs due to the growth of α -Fe₂O₃ crystals, further reducing the internal and external porosity of the α -FeOOH pseudoparticles. At 1173 K, the needle-shaped morphology transforms into a shorter, thicker cylindrical shape [106].

Yoshino et al. [107] studied the dehydration behaviour of ϵ -FeOOH under pressures up to 20 GPa and found that the dehydration temperature increases with pressure. Gan et al. [65] discovered through shock recovery experiments that ϵ -FeOOH partially decomposes into Fe₂O₃ and Fe₃O₄ within the pressure and temperature range of 35–70 GPa and 1150–2750 K, starting from 35 GPa, more than 90% of ϵ -FeOOH undergoes decomposition, releasing H₂O and O₂ (2FeOOH $\rightarrow$ Fe₂O₃ + H₂O, 12FeOOH $\rightarrow$ 4Fe₃O₄ + 6H₂O + O₂, and 6Fe₂O₃ $\rightarrow$ 4Fe₃O₄ + O₂). Experiments utilizing DAC and laser heating apparatus also indicate that ϵ -FeOOH partially dehydrates and decomposes to form η -Fe₁₂O₁₉H₂ within the pressure and temperature range of 60–70 GPa and 1400–1950 K [108]. η -Fe₁₂O₁₉H₂ can be represented as 6Fe₂O₃·H₂O, indicating that the dehydration process of ϵ -FeOOH may involve the formation of intermediate phases, resulting in the indirect formation of Fe₂O₃ and H₂O [95,104,109]. At pressures exceeding

60 GPa and temperatures of 2000 K, the oxidation–reduction reaction of Fe_2O_3 has been observed, formation of a Fe_5O_7 phase and the release of oxygen ($10\text{Fe}_2\text{O}_3 \rightarrow 4\text{Fe}_5\text{O}_7 + \text{O}_2$) [110]. Studies suggest that the subduction of ϵ - FeOOH might have significantly contributed to the oxygen content in the early Earth's mantle, crust, and atmosphere [65,111]. Under high-pressure and temperature conditions of 35–80 GPa and 1150–2750 K, ϵ - FeOOH partially decomposes to form various forms of iron oxide (Fe_2O_3 , Fe_3O_4 , Fe_5O_7 , Fe_7O_{10} , $\text{Fe}_{6.32}\text{O}_9$), H_2O , and either oxygen or oxygen-rich fluids. This process is believed to consume around 90% of ϵ - FeOOH [65,111]. At relatively lower temperatures and higher pressures, the decomposition ratio of ϵ - FeOOH is low. Under conditions of 1150 K and 35 GPa, the decomposition rate is only 5%, suggesting that ϵ - FeOOH may persist in cold slabs [65]. Koemets et al. [111] suggested that ϵ - FeOOH has poor thermal stability and can only be preserved in fast-subducting cold slabs.

2.4. Hydrogen bond symmetrization and spin transition of ϵ - FeOOH under high pressure

Gleason et al. [78] conducted high-temperature and high-pressure experiments on α - FeOOH ($T = 296$ – 523 K, $P = 0$ – 29.4 GPa). The thermal expansion coefficient of α - FeOOH at ambient pressure was determined to be $\alpha_0 = 2.3 (\pm 0.6) \times 10^{-5} \cdot \text{K}^{-1}$, with a Debye temperature of $740 (\pm 5)$ K. Pressure mainly affects the channels within the α - FeOOH crystal structure, where the $\text{O}-\text{H}\cdots\text{O}$ are located. The distance between $\text{O}\cdots\text{O}$ decreases with increasing pressure at a rate of approximately $-0.023 \text{ \AA/GPa}$. At 9 GPa, the bond length is $2.60 \text{ \AA}$ [112]. The octahedral volume decreases by $\sim 3\%$ in the pressure range of 0.5–9.0 GPa, with a corresponding decrease in the unit cell by 7%. This result supports the conclusion that channel compression controls the cell volume [74]. Tunega et al. [113] also confirmed through theoretical calculations that compression occurs primarily through the compression of channel of hydrogen bond. Compression of the $\text{O}\cdots\text{O}$ distance may alter the properties of hydrogen bonds, as the shorter $\text{O}\cdots\text{O}$ distance leads to increased importance of quantum mechanical effects on hydrogen bond energies, generally, when the bond length of the $\text{O}\cdots\text{O}$ hydrogen bond is less than $2.5 \text{ \AA}$, the proton tunnelling effect between the donor and acceptor oxygen atoms is enhanced [112].

Hydrogen bond symmetrization refers to the process in which, with the increase of pressure, longer and softer hydrogen bonds compress faster than shorter and harder ones. This process occurs in asymmetric hydrogen bond units, where the hydrogen atom between two oxygen atoms gradually becomes more centred [114]. Once hydrogen bonds become symmetrical, the distances between the donor O and acceptor O relative to the H become equal (Figure 3). The charge balance associated with this symmetry can lead to subtle structural changes. Nagai et al. [74] predicted that when the pressure reaches 40 GPa, the distance between $\text{O}\cdots\text{O}$ will be less than $2.4 \text{ \AA}$, indicating a potential occurrence of symmetric hydrogen bonding. Additionally, the $\text{Fe}-\text{O}1$ and $\text{Fe}-\text{O}2$ bond lengths will converge linearly, and the bond strengths between $\text{O}1$ and $\text{O}2$ will become equal.

The discontinuous variation of the axial compression ratio has been used as an indicator for second-order phase transitions in materials [115–117]. As the pressure continues to increase to 20 GPa, a noticeable discontinuity in the $\text{O}1\cdots\text{O}2$ bond length, indicating a second-order phase transition [90]. Thompson et al. [62] confirmed the pressure-induced hydrogen bond symmetrization in ϵ - FeOOH at 18 ± 1 GPa through the ratio of a/b and

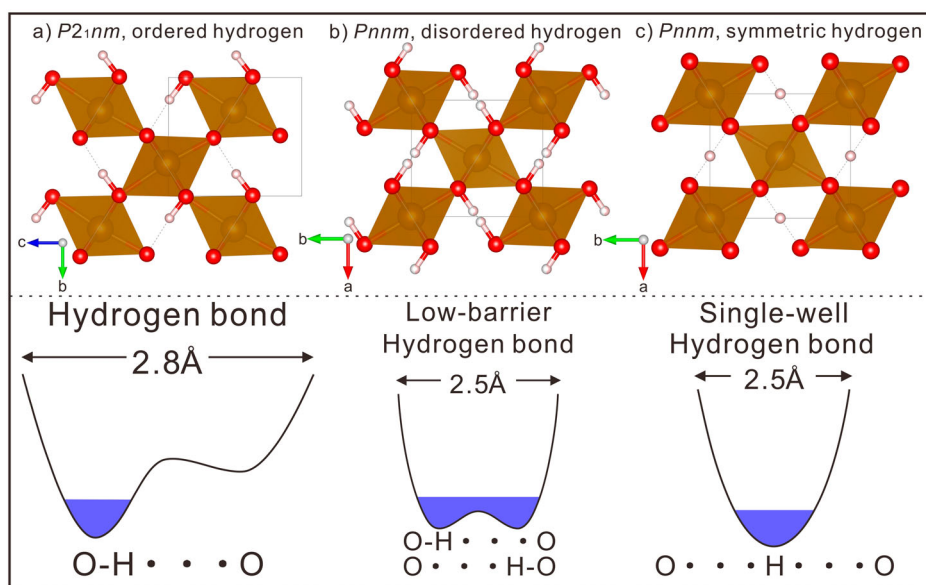


Figure 3. Schema of structural transformations of ϵ -FeOOH and changes in hydrogen bonding, modified from [62].

b/c lattice parameters. This second-order phase transition transforms the structure from $P2_1nm$ to $Pnnm$. This finding is consistent with previous density functional theory calculations as well as recent experimental predictions [63,92]. Theoretical calculations have shown that hydrogen bond symmetrization in minerals occurs only in pure phases and not in solid solutions; hydrogen bonds in solid solutions remain asymmetric under high pressure [118]. There is ongoing debate regarding the pressure-induced symmetrization of hydrogen bonds and its effect on space group changes [63,90,92,119]. In ϵ -FeOOH and other isostructural MOOH phases, the MO_6 octahedra transition from a slightly offset position to a position along the twofold axis centre, resulting in an increase in symmetry from $P2_1nm$ to $Pnnm$ [116,117]. Additionally, in a state of proton disorder, both H and Fe atoms exhibit disorder along the twofold axis, which can lead to FeOOH with $Pnnm$ symmetry. The diffraction patterns of these structures are nearly indistinguishable from those with symmetric hydrogen bonding [84,120]. A recent neutron diffraction study revealed that proton disorder is a precursor to hydrogen bond symmetrization [121]. Xu's study found that the compressibility of ϵ -FeOOH decreases at ~ 16 GPa, however, however, the study did not establish a connection between this property change and the pressure-induced symmetrization of hydrogen bonds or the onset of proton disorder [90]. Due to the occurrence of pressure-induced hydrogen bond symmetrization or proton disorder, other hydrous phases also show a similar increase in bulk modulus [122–124].

Additionally, ϵ -FeOOH undergoes a spin transition. During the transition from high spin to low spin, the Fe^{3+} radius contracts, which has been shown to significantly reduce the volume of other Fe-containing minerals [125]. Otte et al. [1] proposed through first-principles calculations that this transition occurs at a pressure of 7.7 GPa, much lower than in other Fe-containing minerals. Experimental results from Gleason indicate that the spin transition occurs at ~ 40 GPa and is completed at ~ 60 GPa [119]. Xu et al. [90]

combined Mössbauer spectroscopy and single-crystal diffraction to accurately determine the pressure of this electronic transition to be ~ 45 GPa. Thompson et al. [62] found that ϵ -FeOOH undergoes a second structural transition at ~ 45 GPa. In Thompson's study, it was observed that the transition occurred within a pressure range of ~ 3 GPa, significantly smaller than the previously reported pressure range of 20 GPa for the spin transition [62,90]. This difference may be attributed to the lack of a pressure-transmitting medium in the earlier study, which could have resulted in pressure gradients. Gleason et al. [119] proposes that hydrogen-bonding symmetry induces the spin transition, while Xu et al. [90] suggests that the spin transition leads to hydrogen-bonding symmetry. However, the studies unanimously agree that the transition from high spin to low spin leads to a significant volume reduction. First-principles calculations predicted that the intermediate structure *Pbca* is stable between the *Pnnm* and *Pa3* phases of δ -AlOOH [126]. Thompson et al. [62] attempted to index the high-pressure (> 45 GPa) XRD data with the proposed *Pbca* space group. The volume reduction during the phase transition was found to be 26%, resulting in a decrease in the quality of the fit. They also attempted to fit the CaCl_2 -type (*Pnnm*) oxide with the α - PbO_2 structure (*Pbcn*), but this did not yield a reasonable fit to the data. Therefore, Thompson et al. [62] interpreted the transition at 45 ± 2 GPa as an isostructural volume collapse (i.e. *Pnnm* $\rightarrow$ *Pnnm*). The spin transition corresponds to an approximate 11% change in volume and represents an isostructural phase transition [1,62,90,119], accompanied by a transformation from proton disorder to hydrogen-bonding symmetry.

2.5. Phase transition of ϵ -FeOOH under extreme pressure and temperature conditions

Recent studies have shown that ϵ -FeOOH containing a small amount of Ti remains stable within the temperature and pressure range of 12–19 GPa and 1300 K in the presence of water in MORB compositions [127,128]. Hu and Nishi employed DAC combined with laser heating apparatus to investigate the stability of ϵ -FeOOH under lower mantle P-T conditions [60,61,129]. They reported that ϵ -FeOOH can remain stable in the lower mantle to a depth of approximately 1800 km (~ 80 GPa), after which it transforms into Py-FeOOH_X ($X \leq 1$, space group: *Pa3*). This Py-FeOOH_X phase remains stable under conditions of 129 GPa and 1500 K, as well as 111 GPa and 2400 K [60] (Figure 4). Completely dehydrogenated Py-FeOOH_X may decompose in rising plumes, providing sporadic oxygen source for the GOE [61]. The calculation of ϵ -FeOOH and Py-FeOOH_X indicates a significantly large pressure interval with very small energy changes near the transition pressure, which explains the extensive coexistence of these two phases from 54 GPa to 87 GPa [130]. First-principles calculations also support the stability of ϵ -FeOOH before its transformation into Py-FeOOH_X [60,130].

3. Physical properties of α -FeOOH and ϵ -FeOOH

3.1. Bulk modulus of α -FeOOH and ϵ -FeOOH under high-temperature and high-pressure conditions

Under high-temperature and high-pressure conditions, the lattice parameters of minerals typically undergo significant changes. The *P-V-T* equation of state of a mineral reflects properties such as density, elasticity, and thermal expansion under high-temperature and

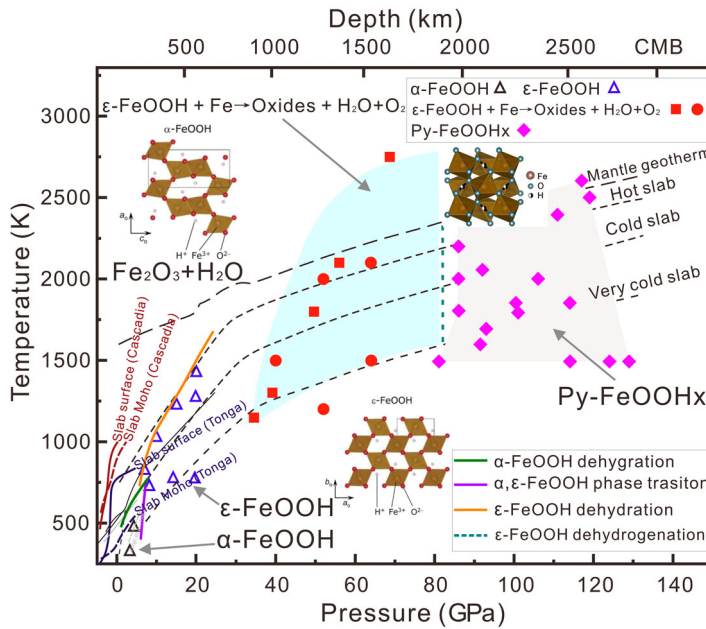


Figure 4. Phase diagram of FeOOH, modified from [60, 61, 65, 78, 85, 86, 107, 111].

pressure conditions, providing essential data for further theoretical calculations. At the same time, the results of the equation of state can be compared with seismic wave inversion results, providing crucial constraints on the structural state, composition, and geological processes of materials in the deep Earth [131].

Previous studies have extensively investigated the bulk modulus of α -FeOOH and ϵ -FeOOH under various pressure ranges, as shown in Table 1. Kim et al. [132] were the first to determine the bulk modulus of α -FeOOH, using DAC and energy-dispersive X-ray diffraction (ED-XRD) to fit the pressure-volume data of 0–27.8 GPa, obtaining $K_0 = 147.9$ GPa. Nagai et al. [74] observed a discontinuity in the pressure-volume data, attributing it to non-hydrostatic stability caused by the solidification of a 4:1 mixture of methanol and ethanol as the pressure medium. They fitted the pressure-volume data of 0–24.5 GPa, obtaining $K_0 = 111(2)$ GPa, and 0–11 GPa, obtaining $K_0 = 108.5$ GPa. Kim et al. [133] employed a DIA-type large-volume press (LVP) combined with ED-XRD to fit the pressure-volume data of 0–19.54 GPa, obtaining $K_0 = 131.1$ GPa, attributing the observed discrepancies to factors such as sample volume, assembly orientation, pressure calibration methods, and the solidification of a 4:1 mixture of methanol and ethanol. Gleason et al. [78] fitted the pressure-volume data of 0–29.4 GPa, obtaining $K_0 = 140.3(3.7)$ GPa, proposing that α -FeOOH transitions to ϵ -FeOOH above 5 GPa, and obtained $K_0 = 158(5)$ GPa by fitting the data of 4–20 GPa. Otte et al. [1] used density functional theory (DFT) with the GGA + U method to calculate the bulk modulus of α -FeOOH and spin-state-dependent bulk modulus of ϵ -FeOOH, showing that when an on-site Coulomb repulsion parameter (U) is considered, the calculated values align more closely with experimental data. Tunega et al. [113] used a similar approach, fitting pressure-volume data of 0–80 GPa for α -FeOOH and obtaining a K_0 value close to that of Otte's results. Xu et al. [90] fitted pressure-volume data

across various pressure ranges to obtain bulk modulus values for α -FeOOH, ϵ -FeOOH, and low-spin ϵ -FeOOH, while Ohira et al. [136,137] studied the effect of Al content on the bulk modulus by fitting pressure-volume data of δ -(Al, Fe)OOH.

In these experiments, some researchers did not observe significant discontinuities in the unit cell parameters with pressure and therefore fitted both α -FeOOH and ϵ -FeOOH data to calculate the bulk modulus. Other studies focused on a single phase or observed discontinuities in unit cell volume, performing segmented fitting to calculate the bulk modulus for individual phases. Theoretical calculations for iron hydroxides typically use unit cell data for a single phase, resulting in bulk modulus values for that phase. The results from these studies suggest that the substitution of aluminum reduces the bulk modulus of high-pressure phases. Pressure-induced disorder or symmetrization of hydrogen bonds, along with spin transitions, lead to a decrease in unit cell volume, resulting in an increase in the bulk modulus.

3.2. Electrical conductivity of α -FeOOH and ϵ -FeOOH under high-temperature and high-pressure conditions

Electrical conductivity (EC) experimental studies aim to determine the conductivity of minerals, rocks, melts, and fluids by effectively controlling variables such as temperature, pressure, and oxygen fugacity. Compared to other geophysical parameters – such as thermal conductivity, gravity, density, and wave velocity – EC is highly specific and sensitive to variations in temperature, trace elements in minerals (e.g. Fe, Na, water, F), and highly conductive substances with connectivity (e.g. melts, aqueous fluids at particle boundaries, graphite, metals). By combining geophysical data (e.g. geomagnetic bathymetry) and experimental EC data of minerals and rocks, researchers can obtain better constraints on the physical and chemical conditions (e.g. temperature, pressure, oxygen fugacity), material composition, and spatial distribution in the deep Earth at both macroscopic and microscopic scales. Extensive research has been conducted on the factors influencing the EC of minerals and rocks, such as temperature, pressure, oxygen fugacity, iron content, grain size, and iron spin state [12,138–144].

Previous studies on the EC of α -FeOOH were primarily conducted under ambient and high-pressure conditions. Liu [87], Shen [145], Tang [94] used DAC to investigate the EC properties of α -FeOOH under ambient-temperature and high-pressure conditions. Zhuang [64] and Wang [146] conducted experimental research on the conductivity of ϵ -FeOOH under high-temperature and high-pressure conditions (Figure 5).

Due to differences in high-pressure experimental apparatus and electrode installation, variations in EC measurements have been observed across different experiments. In high-pressure EC experiments of α -FeOOH, three distinct transition intervals are observed: 5–10 GPa, 15–21 GPa, and 44–50 GPa. The broader pressure ranges in the first two intervals may be attributed to the absence of a pressure-transmitting medium in some high-pressure EC experiments, resulting in pressure gradients. The third interval may be related to spin crossover phenomena. The EC of α -FeOOH is positively correlated with pressure. When pressurized to 5–10 GPa, the EC slope changes, indicating a first-order phase transition from α -FeOOH to ϵ -FeOOH. When the pressure reaches 15–21 GPa, the EC slope undergoes another abrupt change, and in some studies, a negative value for the EC slope was observed, which may be attributed to the transition of ϵ -FeOOH from the

Table 1. Values of the experimental and theoretically calculated of the bulk modulus of α -FeOOH, ϵ -FeOOH and δ -(Al, Fe)OOH.

Phase	K_0 (GPa)	K_0'	Method	Pressure Medium	Pressure Range (GPa)	Note	References
α -FeOOH, ϵ -FeOOH	147.9	4	DAC	ME (4:1)	0–27.8	$Pnma \rightarrow P2_1nm$	[132]
α -FeOOH, ϵ -FeOOH	111.0(2)	4	DAC	ME (4:1)	0–24.5	$Pnma \rightarrow P2_1nm$	[74]
α -FeOOH	108.5(6)				0–11	$Pnma$ (in doubt)	
α -FeOOH, ϵ -FeOOH	131.1(58)	4	LVP	ME (4:1)	0–9.54	$Pnma \rightarrow P2_1nm$	[133]
α -FeOOH, ϵ -FeOOH	140.3(3.7)	4.6 ± 0.4	DAC	ME (4:1)	0–29.4	$Pnma \rightarrow P2_1nm$	[78]
ϵ -FeOOH	158.0(5)	4 (fixed)			4–20	$P2_1nm$ (in doubt)	
α -FeOOH	90.6	5.8	GGA	–	–	$Pnma$	[1]
	108.8	5.9	GGA + U				
ϵ -FeOOH	104.0	5.6	GGA			$P2_1nm$, high spin (AFM)	
	123.2	5.7	GGA + U				
	152.7	4.6		$P2_1nm$, high spin (AFM)			
	124.3	5.9		$P2_1nm$, low spin (AFM)			
	187.0	6.0	GGA	$P2_1nm$, high spin (FM)			
	135.1	5.9	GGA + U	$P2_1nm$, low spin (FM)			
α -FeOOH	126(3)	10(1)	LVP	NaCl	0–8.6	$Pnma$	[89]
α -FeOOH	93.5	–	GGA	–	0–80	$Pnma$	[113]
	114.3(118.7)	4.1(4.0)	GGA + U				
α -FeOOH	120(3)	4	DAC	He, Ne	0–16	$Pnma$ (in doubt)	[90]
ϵ -FeOOH	140(5)				17–44	$P2_1nm$	
	224(13)	45–52				$Pnnm$, low spin	
ϵ -FeOOH	135(3)	6.1(9)	–	–	8–11	$P2_1nm$	[134]
α -FeOOH	85.9(15)	12.6(8)	LVP	NaCl	0–7.55	$Pnma$	[135]
α -FeOOH	112.26(2.6)	4 (fixed)	LVP	Vaseline	0–7.1	$Pnma$	[86]
ϵ -FeOOH	142.8(15.1)				7.1–7.5	$P2_1nm$	
ϵ -FeOOH	188(4)	5.19(12)	GGA + U	–	0–20	$P2_1nm$ low spin	[63]
	223(2)	4.07(3)			30–140	$Pnnm$ low spin	
α -FeOOH	126(5)	–	DAC	Ne	0–32	$Pnma$ (in doubt)	[94]
α -FeOOH, ϵ -FeOOH	152(4)	4.9 (2)	DAC	Ne, KBr	0–45	$Pnma \rightarrow P2_1nm \rightarrow Pnnm$	[62]
	170(1)	4 (fixed)					
ϵ -FeOOH	176(3)		18–45			$P2_1nm \rightarrow Pnnm$	
δ -(Al _{0.832} (5) ⁵⁷ Fe _{0.117} (1))OOH _{1.15} (3)	241(14)	4 (fixed)	DAC	Ne	1.1–64.8	$P2_1nm \rightarrow Pnnm$	[136]
δ -(Al _{0.908} (9) ⁵⁷ Fe _{0.045} (1))OOH _{1.14} (3)	223(11)				0–55.6		
δ -(Al _{0.877} ⁵⁷ Fe _{0.123})OOH	147(1)	4	DAC	Ne	–	$P2_1nm$	[137]
	155(22)	8(2)				$Pnnm$, high spin	
	241(14)	4				$Pnnm$, low spin	

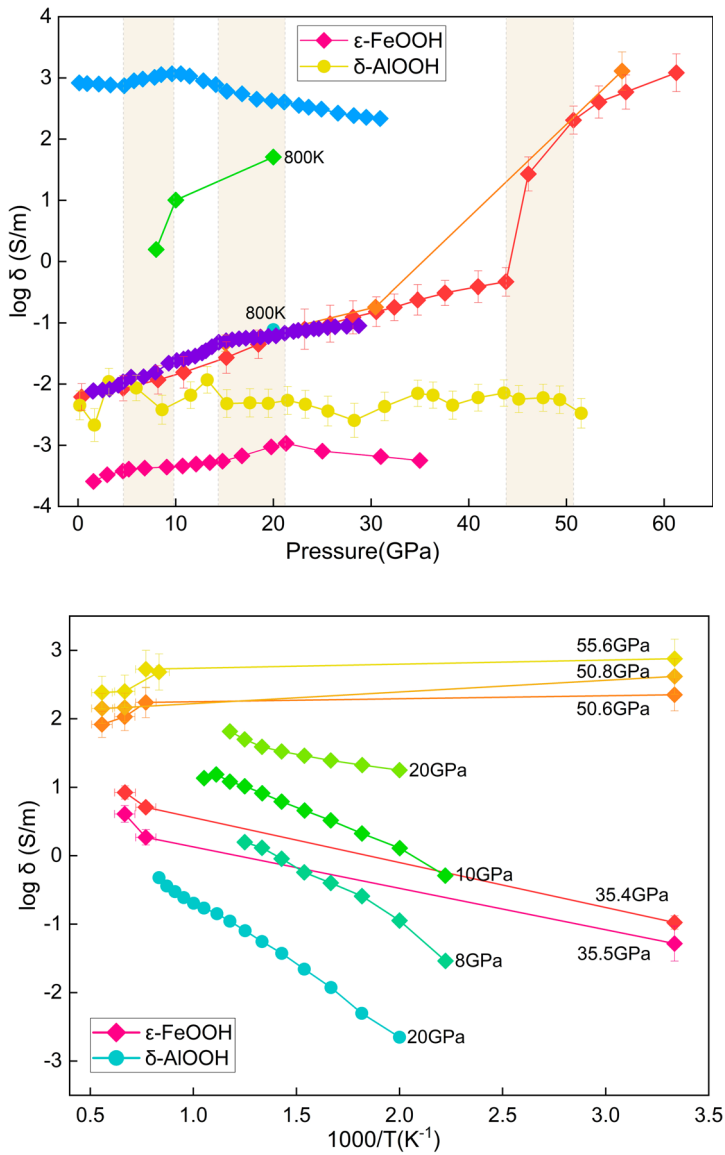


Figure 5. The figures show the electrical conductivity (EC) of α -FeOOH, ϵ -FeOOH, and δ -AlOOH at high temperature and pressure. The first panel displays the log of conductivity ($\log \delta$) as a function of pressure, with the x-axis ranging from 0 to 60 GPa. The data is represented with diamond symbols for ϵ -FeOOH and circle symbols for δ -AlOOH. This panel illustrates how the conductivity changes with pressure for these phases. The second panel shows the conductivity as a function of $1000/T$ at different pressures, with the x-axis ranging from 0.5 to 3.5 K⁻¹. This panel demonstrates how the conductivity varies with temperature under high pressure, using the same symbols as the first panel to represent the different phases [64, 87, 94, 146, 147].

$P2_1nm$ phase to the $Pnmm$ hydrogen-disordered phase. Upon further compression to 44 GPa, the EC value exhibits a sharp increase, reaching $1.24(12) \times 10^{-3}$ S/m at 61.2 GPa, with such high EC values comparable to those of metallic compounds [147,148]. In contrast, for

the structurally similar δ -AlOOH under high pressure, its EC shows little correlation with pressure, and there is no sharp increase in EC for the Al end-member above 40 GPa. Therefore, the sharp increase in EC in ϵ -FeOOH may be attributed to the presence of Fe ions, as well as electron spin transitions or hydrogen bond symmetrization from $P2_1nm$ to $Pnnm$ phase.

Researchers have also investigated the influence of high temperatures on the EC of ϵ -FeOOH. At pressures below 35.5 GPa, despite differences in the slope of various studies, the EC of ϵ -FeOOH shows a negative correlation with temperature, a typical characteristic of a semiconductor. However, at pressures above 50 GPa, there is a positive correlation between EC and temperature, providing clear evidence of a semiconductor-to-metal transition in ϵ -FeOOH. The conductivity mechanism of ϵ -FeOOH is attributed to small polaron hopping, similar to other hydroxides or hydrous minerals [149]. This study also provides key information on the phase transition process of ϵ -FeOOH. At 53.5 GPa, a second semi-circular arc appears in the low-frequency region next to the main circle in the Nyquist plot [64]. The onset of the second arc is attributed to grain boundary resistance [150], and it was previously regarded as a symbol of charge carrier transport anisotropy in the crystallites [151]. The second arc likely originates from spin pairing of Fe^{3+} , which may give rise to mixed spin states.

3.3. Elastic properties of α -FeOOH and ϵ -FeOOH under high-temperature and high-pressure conditions

The anisotropy of the α -FeOOH single crystal structure was demonstrated by the elastic constants calculated from inelastic neutron scattering data [152]; Thompson et al. [63] utilized first principle calculations to investigate the elastic properties of ϵ -FeOOH under low-spin hydrogen symmetrical conditions in the pressure range of 30–140 GPa. Among the 9 independent elastic constants of ϵ -FeOOH, 7 exhibited positive slopes and smooth trends, indicating an increase in stiffness with increasing pressure, C55 showed insensitivity to the elastic constants, while C44 decreased with increasing pressure, suggesting the eventual occurrence of instability in C44 at sufficiently high pressures. Compared to phase δ [153] and MgSiO_4H_2 [154], ϵ -FeOOH exhibits smaller diagonal elastic constants and larger off-diagonal elastic constants, resulting in a greater anisotropy in wave velocities. The bulk modulus (K) of ϵ -FeOOH steadily increases with pressure, while the shear modulus (μ) shows little dependence on pressure. This may be related to the low-spin configuration assumed in the calculations for ϵ -FeOOH [63]. The compressional wave velocity (V_p) is positively correlated with pressure, while the shear wave velocity (V_s) is negatively correlated with pressure. Ikeda et al. [92] conducted measurements of the sound velocities and density of ϵ -FeOOH at room temperature using an ultrasonic pulse-echo-overlap method and a Kawai-type MAA, the highest pressure reached was 24 GPa. Within the experimental pressure range, the compressional (V_p) and shear (V_s) wave velocities of ϵ -FeOOH were approximately 15% lower than those of the isostructural δ -AlOOH. The fluctuation in V_p around 16–18 GPa is believed to be associated with the transition from a proton-ordered state to a disordered state [62]. The experiment did not observe the pressure-dependent decrease in V_s as predicted in the calculations [62], which suggests the influence of spin transitions on the elastic properties. Ohira et al. [137] conducted tests on the elastic properties of δ -(Al, Fe)OOH under pressures range of 0–79 GPa using DAC and synchrotron

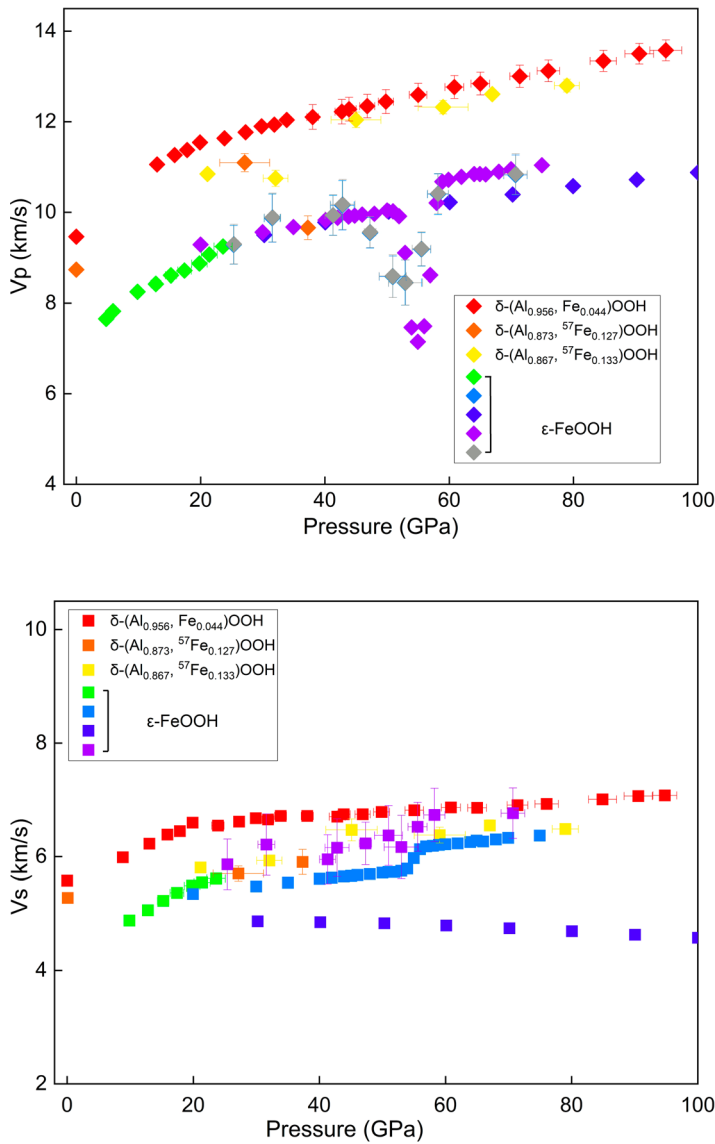


Figure 6. Velocity of α -FeOOH and ϵ -FeOOH, modified from [63, 64, 92, 138, 157].

radiation. The inclusion of Al resulted in an earlier spin transition in iron and an increase in V_p and V_s . Zhuang et al. [64] investigated the elastic properties of ϵ -FeOOH in the pressure range of 20–75 GPa through experiments and first-principles calculations. Gan et al. [155] studied the spin transition behaviour and thermal elastic properties of ϵ -FeOOH using shock recovery experiments and first-principles simulations. The results indicate that the spin transition in ϵ -FeOOH leads to a softening of V_p and bulk modulus (K), while V_s and shear modulus (μ) exhibit a slight increase. The elastic properties of α -FeOOH and ϵ -FeOOH are shown in the Figures 6 and 7.

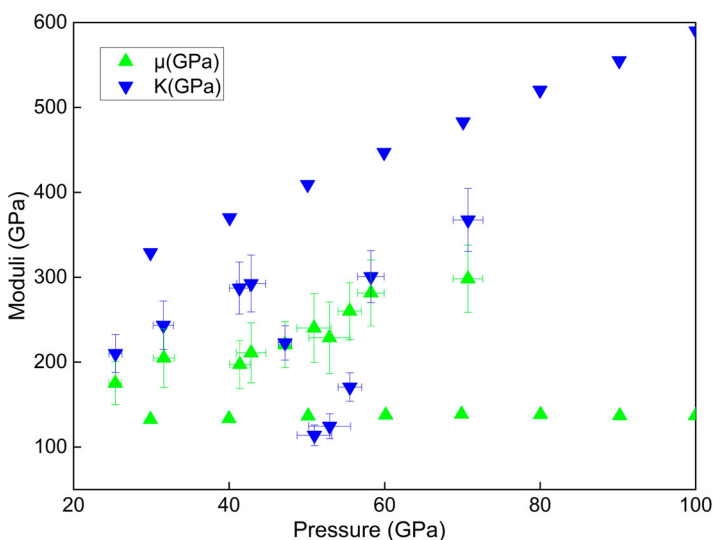


Figure 7. Moduli of ϵ -FeOOH, modified from [63,155].

3.4. Electronic structure of α -FeOOH and ϵ -FeOOH under high-temperature and high-pressure conditions

Metal oxide electronic structure simulation calculations show that the conduction band (CB) bottom and valence band (VB) top are primarily composed of hybridization between the metal element's 3d, 4s, or 4p orbitals and the oxygen element's 2p orbitals. Lu et al. [130] calculated the density of states (DOS) of α -FeOOH at zero pressure, the band gap of α -FeOOH is 1.96 eV, slightly lower than the experimental values (2.1–2.5 eV) [6,156]. Due to the underestimation of band gap by GGA + U, the calculated result is slightly lower than the experimental values, hybrid functionals can provide reasonable band gaps, but the calculation time will increase significantly. Ding et al. [157] calculated the DOS of pure α -FeOOH and found that it has a band gap width of 2.64 eV. Fuente et al. [158] calculated the band gap of 25 mol% Al α -FeOOH to be 2.0 eV (Table 2). Ding et al. [157] further calculated that the band gap width decreases to 2.55 eV for 25 mol% Al α -FeOOH, indicating that the addition of Al can reduce the band gap width of α -FeOOH. The partial density of states (PDOS) of α -FeOOH shows that the VB bottom is composed of O 1s orbitals, and the peak shape is very sharp, indicating strong electron localization and limited participation in bonding [130,157]. At the top of the VB, there is an overlap between the O 2p and Fe 3d electronic states, indicating hybridized bonding between them. The CB bottom is mainly contributed by the Fe 3d electronic states, with some contribution from the O 2p electronic states. The Al 2p orbitals only participate in the composition of the VB bottom, mainly forming bonding with a portion of the O 2p orbitals. This indicates that the reduction in band gap width in Al-doped α -FeOOH is primarily due to the participation of Al in the composition of the VB, causing an upward shift in the VB and resulting in an overall decrease in the band gap width (Figure 8) [157].

Under a pressure of 5 GPa, the band gap of ϵ -FeOOH is 1.94 eV [130]. In the DOS's structure at pressures above 20 GPa, there is a pressure evolution independent of hydrogen

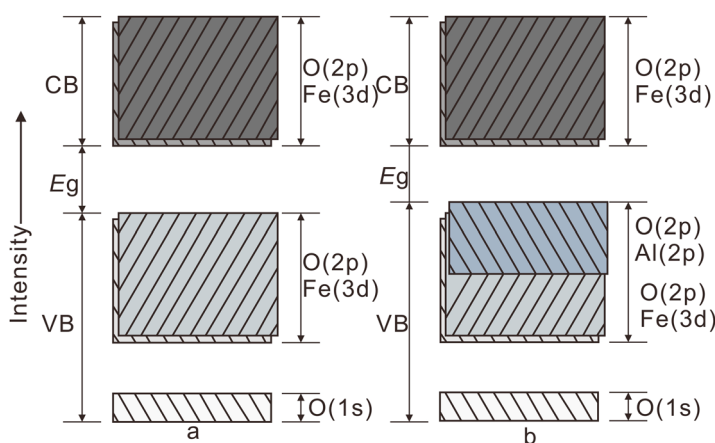


Figure 8. Schematic energy band structures of pure and Al-doped α -FeOOH (a) and (b), modified from [157].

Table 2. The relative conduction band energy and band gap width of α -FeOOH and ϵ -FeOOH.

Sample	Relative energy/eV		E_g /eV	Methods	Reference
	VB	CB			
Natural α -FeOOH	527.46	539.46	2.30	Exp.	[157]
Standard α -FeOOH	536.83	529.40	2.57	Exp.	
α -FeOOH			2.64	Cal.	
25mol% Al- α -FeOOH			2.55	Cal.	
α -FeOOH	527.5	530.0	2.5	Exp.	[159]
γ -FeOOH	527.5	529.9	2.4	Exp.	
25mol% Al- α -FeOOH			2.0	Cal.	[158]
α -FeOOH			2.1–2.5	Exp.	[6]
α -FeOOH			1.96	Cal.	[130]
ϵ -FeOOH			1.94	Cal.	

bonding symmetry. Under pressures of 40–50 GPa, a pressure-induced reduction in the band gap of ϵ -FeOOH has been observed. At 60 GPa, the DOS and band gap width exhibit similarities to the structure of low-spin ϵ -FeOOH calculated by Otte [1] under similar pressures. With reference to the Fermi level and DOS indicates a significant sudden change in the electronic orbital structure before and after hydrogen bonding symmetry [63]. Above 70 GPa, a pressure-induced transition from a semiconductor to a conductor is observed. Both Py-FeOOH at 70 GPa and M-FeOOH at 200 GPa exhibit clear metallic characteristics in the DOS near the Fermi level [130]. The total DOS near the Fermi level is mainly contributed by Fe 3d orbitals, while the contribution of H 1s orbitals is negligible, indicating a transfer of valence electrons from H atoms to nearby O atoms in the structure.

4. Vibrational spectroscopic properties of α -FeOOH and ϵ -FeOOH

4.1. Infrared spectra

Numerous experiments were conducted on the infrared absorption spectra and micro-infrared analysis of synthesized α -FeOOH and natural α -FeOOH. The assignment of

infrared spectroscopic peaks for natural, synthetic samples, and computational results is shown in Table 3.

Two strong spectral bands are observed in the hydroxyl stretching vibration region of α -FeOOH. The computational results predict the presence of four hydroxyl stretching vibrations in α -FeOOH within the range of $3027 \sim 3000 \text{ cm}^{-1}$. These vibrations occur in different coupled or uncoupled modes [158]. Cambier et al. [168] suggested that the stretching of the hydroxyl groups corresponds to the range of $3170\text{--}3085 \text{ cm}^{-1}$. This peak is sensitive to temperature and is one of the important spectral bands used to characterize the degree of dehydroxylation in α -FeOOH. Experimental results demonstrate that the position and intensity of this peak exhibit a linear relationship with the temperature of dehydroxylation. As the temperature increases, the peak shifts to higher wavenumbers, indicating a decrease in bond strength. Conversely, a shift towards lower wavenumbers indicates an increase in bond strength [99]. The range of $3483\text{--}3470 \text{ cm}^{-1}$ corresponds to the stretching vibration of H-O-H, which represents a typical mode of non-stoichiometric hydroxyl units (excess water) in the α -FeOOH structure. These types of hydroxyl units can be incorporated into the α -FeOOH structure and adsorbed onto the crystal surface during synthesis. An increase in the substitution of Al leads to a relative increase in intensity, indicating an increase in the content of non-stoichiometric hydroxyls. With increasing temperature, the relative intensity of this peak gradually decreases. The relative intensity of this spectral band exhibits a linear relationship with temperature [98,169–171]; The bending vibrations of hydroxyl groups in the a-b plane appear at $1129\text{--}863 \text{ cm}^{-1}$ (δ) and 1153 cm^{-1} (Al-OH), while the bending vibrations of hydroxyl groups out of the a-b plane occur at $1014\text{--}784 \text{ cm}^{-1}$ (γ) and 1068 cm^{-1} (Al-OH). The first overtones of the bending vibrations are observed at $1693\text{--}1675 \text{ cm}^{-1}$ (δ') and $1645\text{--}1613 \text{ cm}^{-1}$ (γ'), a shoulder peak associated with the bending vibration of water is observed at $1713\text{--}1707 \text{ cm}^{-1}$, attributed to the $\delta''(\text{OH})$ mode, these vibrations can be attributed to the in-plane and out-of-plane vibrations of non-stoichiometric hydroxyl units [98,172]. Within the range of $640\text{--}533 \text{ cm}^{-1}$, there is a peak corresponding to the symmetric stretching vibration of Fe-O bonds, the stretching vibration of Al-O occurs at 659 cm^{-1} . The range of $497\text{--}461 \text{ cm}^{-1}$ corresponds to the asymmetric stretching vibration of Fe-O bonds. The range of $450\text{--}400 \text{ cm}^{-1}$ corresponds to the symmetric stretching vibration of Fe-OH bond; The range of $368\text{--}270 \text{ cm}^{-1}$ corresponds to the asymmetric stretching vibration of Fe-OH bonds. The splitting of deformation and bending bands of hydroxyl groups, as well as the splitting of stretching bands, is caused by strong coupling between different hydroxyl vibration modes [172]. Previous studies on the infrared spectra of α -FeOOH have shown that although all hydroxyl units are in the same environment, the hydrogen bonds point in two different directions, resulting in the splitting of the hydroxyl stretching bands. This characteristic can be observed through the asymmetric nature of the peaks in α -FeOOH's hydroxyl vibrations [98,172]. In-plane bending vibrations and out-of-plane bending vibrations are considered characteristic vibrations of α -FeOOH [99]. In-plane bending vibrations involve orientation vibrations within the inclined plane, which change the angle between hydroxyl groups and the triangular arrangement of iron atoms and hydrogen bonds. Out-of-plane vibrations are oriented parallel to the c-axis and do not involve significant tilting of hydroxyl units with respect to adjacent iron atoms or hydrogen bonds [160].

In theory, any peak position or peak width variation is related to the single lattice mode, polyhedral distortion, crystal ordering, lattice parameters, and local heterogeneity within

Table 3. The assignment of the IR peaks of α -FeOOH /cm⁻¹.

Minerals	Method	Source	ν_1 (H-O-H stretching)	ν_2 (O-H stretching)	First overtones bend	ν (O-H in a-b plane bend)	ν (O-H out a-b plane bend)	ν (Fe-O stretch)	ν (Fe-O asymmetric stretching)	ν (Fe-OH stretching)	ν (Fe-OH asymmetric stretching)	ν (Fe-O symmetric stretching)	Reference
α -FeOOH	Exp.	Synthesis	3195	3080	-	890	795	610, 670	-	-	410, 395	-	[160]
	Exp.	-	-	-	-	680	-	630	495	450	401	368, 270	[161]
	Exp.	Synthesis	-	-	-	670.3	-	633.3	497.0	450.7	409.4, 395.8	360.9, 290.3, 268.3	[162]
	Exp.	Synthesis	3483–3450	3236–3206	δ' –1693–1675, γ' –1645–1613, γ'' –1713–1707	δ –890–863	γ –799–783	~ 533	~ 461	-	-	-	[98,99,104,163,164]
	Exp.	-	-	3170–3085	-	890	795	640–620	-	-	-	-	[160,165,166]
	Exp.	-	-	-	-	-	-	630	-	400	-	-	[167]
	Cal.	-	-	3027	-	1099–1023	1001–998	635	-	-	-	-	[158]
	Cal.	25 mol%	-	2980–2953 (Al-Fe) 2977–2895 (Fe-Fe2) 3227	-	1153 (Al-OH)	1068 (Al-OH)	659 (Al-OH)	-	-	-	-	[158]
	Cal.	-	-	-	-	1129 (Fe-OH)	1014 (Fe-OH)	629 (Fe-OH)	-	-	-	-	
	Exp.	Synthesis (10 mol%)	3434	3227	-	-	-	540	-	-	-	-	[99]
Al- α -FeOOH	Exp.	Synthesis (20 mol%)	3448	3239	-	-	-	543	-	-	-	-	
	Exp.	Synthesis (30 mol%)	3453	3240	-	-	-	545	-	-	-	-	

the structure [162,168]. According to the research conducted by Williams, the shift of the hydroxyl bending band is caused by the increase in repulsive force between the hydrogen ion and the adjacent cation due to the shorter distance of the nonlinear hydrogen bond Fe-O-H...O-Fe [160]. When α -FeOOH is doped with Al, the cell parameters decrease, resulting in changes in bond lengths and angles, leading to frequency variations. Additionally, the symmetry of the unit cell is disrupted, resulting in the appearance of more distinct features in the spectrum, particularly in the stretching and bending vibrations of hydroxyl groups connected to Fe and Al. Stiers and Schwertmann reported that with increasing substitution of Mn^{3+} and Al^{3+} in α -FeOOH, the stretching and bending vibrations of O-H shift to higher frequencies, and the spectra also broaden with increasing Al content [162,173], as shown in the Table 3.

Attempts were also made at high-temperature and pressure infrared experiments on α -FeOOH (Figure 9). Williams was the first to use DAC to study the infrared spectroscopic properties of α -FeOOH under ambient temperature, with a maximum pressure of 24 GPa [160]. It was found that the bending vibration of the hydroxyl group merged into two peaks when the pressure exceeded 13 GPa, suggesting that significant changes of hydrogen ions occurred at this pressure. The out-of-plane bending of the O-H bond is parallel to the c-axis and involves almost no angular tilt of the hydroxyl group relative to the neighbouring iron atoms or hydrogen bonds. In contrast, the in-plane bending occurs in a vibrational mode oriented within a tilted plane, thereby altering the angle between the hydroxyl group and both the iron atoms and hydrogen bonds [160,161,174]. Therefore, the frequencies of the two O-H bending vibrations merge around 13 GPa and remain constant with further increase in pressure. This provides direct evidence that the in-plane and out-of-plane vibrations become energetically indistinguishable. This observation can be explained by the movement of hydrogen towards equidistant positions with its three neighbouring iron atoms within this pressure range [160].

Thompson et al. [62] collected infrared absorption spectra of FeOOH under ambient temperature and 2–50 GPa. Under ambient pressure conditions, the O-H stretching region appeared as a broad feature ($2600 \sim 3100 \text{ cm}^{-1}$), which is consistent with the previously reported spectra of α -FeOOH [160,175]. As the pressure increases, the O-H stretching region further broadens and shifts to lower wavenumbers [62]. Under ambient pressure, the infrared spectrum of α -FeOOH exhibits three distinct absorption bands at 965, 1145, and 1175 cm^{-1} . Based on comparisons with similar structures, these bands have been determined to correspond to O-H bending vibrations [62,160,176,177]. Similarly to the stretching region, these peaks also broaden with increasing pressure, beyond $\sim 17.5 \pm 1$ GPa, the two high-frequency bands become difficult to distinguish [62]. The lowest frequency band still undergoes changes with increasing pressure, and above $\sim 17.5 \pm 1$ GPa, there is a noticeable shift in the pressure dependence of this region. The sudden change in the pressure dependence of this region suggests a reorientation of the O-H bonds, indicating that pressure induces hydrogen bond symmetrization or the onset of proton disorder. Kagi observed a similar change in the pressure dependence of the O-H absorption band in δ -AlOOH, a structurally similar compound, at ~ 10 GPa [178]. This is consistent with the onset of proton disorder at this stage [121].

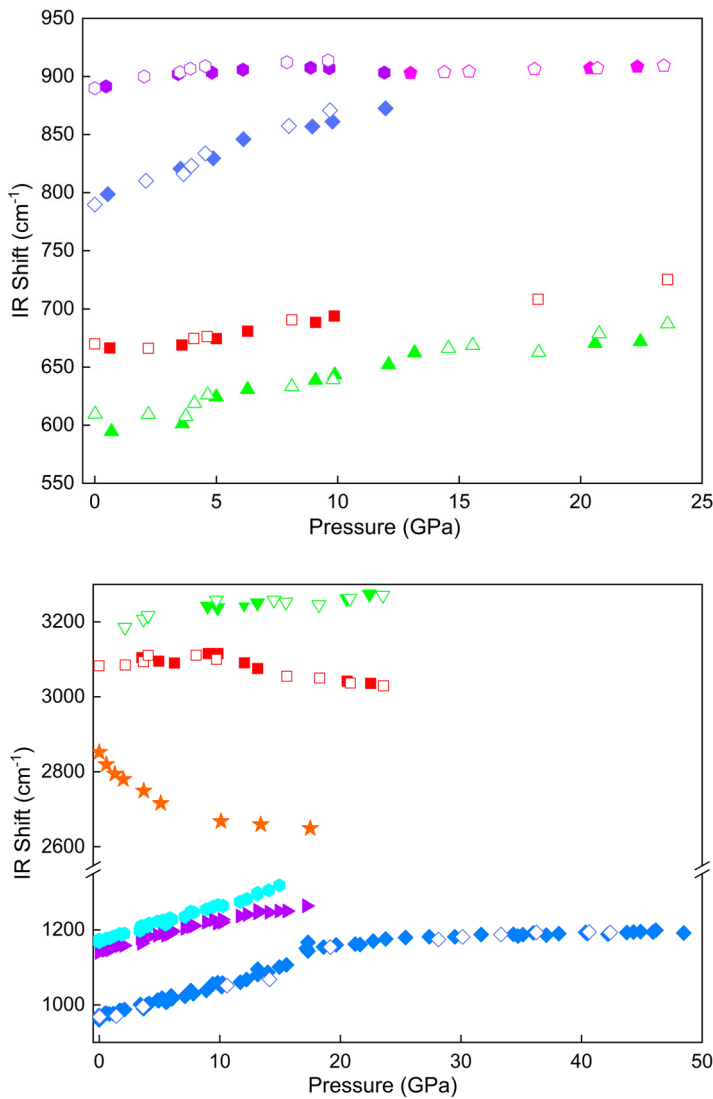


Figure 9. Trends of IR peaks with pressure (Solid: Compression; Hollow: Decompression), modified from [62,160].

4.2. Raman spectra

Raman spectra is a probe for monitoring mineral phase transitions under high-temperature and pressure conditions [179]. In the α -FeOOH, there are six typical Raman peaks. The peaks at 250 and 687 cm^{-1} correspond to Fe-O stretching vibrations; The peak at 302 cm^{-1} corresponds to the symmetric bending vibration of Fe-OH; The peak at 388 cm^{-1} corresponds to the symmetric stretching vibration of Fe-O-Fe/OH; The peaks at 486 and 556 cm^{-1} correspond to the antisymmetric stretching vibration of Fe-OH (Table 4). Some Raman experiments also observed some unassigned peaks at 209, 399, 420, 887, 1020, and 1117 cm^{-1} [87,90,183]. Raman peaks above 800 cm^{-1} are associated

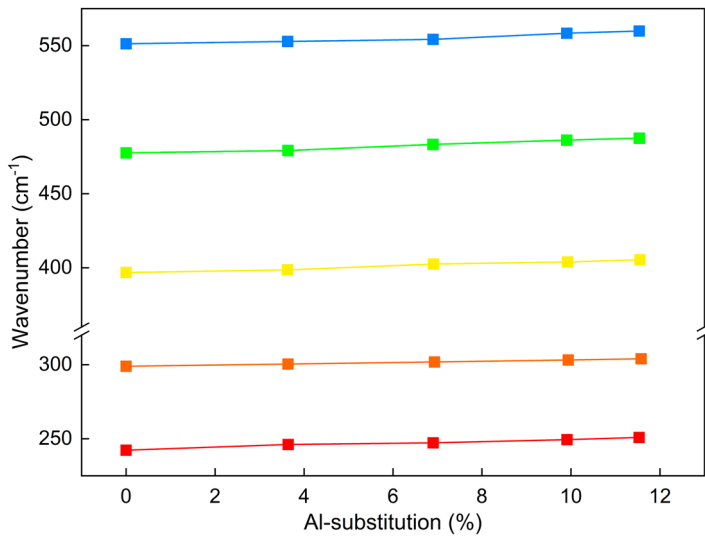


Figure 10. The Raman peaks shift diagram of Al substitution, modified from [184].

Table 4. The assignment of the Raman peaks of α -FeOOH and ϵ -FeOOH /cm⁻¹ [94,180–182].

Label	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Wavenumber	250	302	391	486	556	687
Assignment	Fe-O symmetric stretching vibration	Fe-OH symmetric bending vibration	Fe-O-Fe/-OH symmetric stretching vibration	Fe-OH antisymmetric stretching vibration	Fe-OH antisymmetric stretching vibration	Fe-O symmetric stretching vibration

with the OH bonding, making them difficult to observe in some Raman experiments [94]. The substitution of Al will cause a high wavenumber shift in the characteristic peak of α -FeOOH, and the magnitude of the shift is consistent with the content of Al substitution [184] (Figure 10).

Several workers addressed the high-temperature and pressure Raman features of α -FeOOH. Liu [87] investigated the Raman features of α -FeOOH $\sim$ 35 GPa under room temperature in the range of 150–900 cm⁻¹. Tang studied the Raman peak features of α -FeOOH under room temperature compression up to 32 GPa in the range of 150–1300 cm⁻¹ [94].

In the study by Liu, the Raman peaks during compression and decompression were divided into several stages: below 7 GPa, between 7–20 GPa, and above 20 GPa [87]. There are two noticeable discontinuities in the Raman peaks at 7 and 20 GPa. At 7 GPa, two Raman peaks at 243 and 299 cm⁻¹ exhibit significant splitting, resulting in the appearance of four new split peaks at 257 cm⁻¹ (M1), 263, 302 cm⁻¹ (M2), and 316 cm⁻¹. The 257 cm⁻¹ (M1) peak disappears beyond 20 GPa, while the 302 cm⁻¹ (M2) peak shows a pressure-dependent negative shift. All Raman peaks shifting positively with pressure represent the compression-induced contraction of atomic distances in α -FeOOH, while the negative shift indicates an increase in bond angles during compression in α -FeOOH [180]. In the high-pressure experiments conducted by Tang, a significant splitting of the peak at 302 cm⁻¹ was observed upon compression to 5.2 GPa [94]. Additionally, at the same pressure, the main peak at 391 cm⁻¹ lost one of its two shoulder peaks on the higher

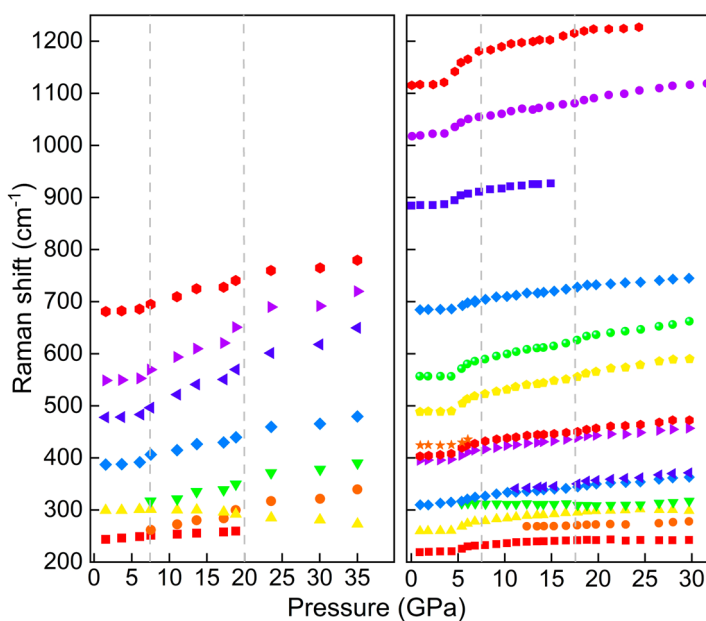


Figure 11. The Raman peaks shift of α -FeOOH and ϵ -FeOOH, modified from [87,94].

wavenumber side. These shoulder peaks were theoretically predicted by density functional theory calculations for α -FeOOH [185]. Furthermore, an additional peak appeared at 260 cm^{-1} when the pressure increased from 10.6 GPa to 11.7 GPa, and a small shoulder peak was observed again at 302 cm^{-1} . Only slight variations in the slopes of the shifts were observed. These subtle changes appear to occur in the ν_4 and ν_5 peaks below 20 GPa (Figure 11). Considering the presence of new Raman peaks and pressure-dependent Raman peaks, it is possible that a pressure-induced phase transition occurred ~ 7 GPa and ~ 20 GPa, given the observed discontinuities.

5. CaCl_2 -type (ϵ -FeOOH – δ -AlOOH – MgSiO_4H_2) solid solution

In the natural environment, iron hydroxides rarely exist in the form of single endmembers. The changes in Mössbauer spectra resulting from Al substitution in α -FeOOH were first observed 50 years ago [186]. The substitution of Al for Fe in natural α -FeOOH can reach up to $36 \pm 3\text{ wt.}\%$ [187], and 33 mol% in synthetic samples [6]. Composition constraints suggest a miscibility gap in the α -FeOOH – α -AlOOH solid solution between $\sim 33\%$ and 85% [6,188]. Under ambient conditions, the radius of Fe ions differs from that of Al ions by 17%. The unit cell volume of α -FeOOH differs from diasporite by 14%. As Al substitution increases, the lattice parameters of α -FeOOH decrease linearly along each axis, and the volume also decreases [162]. Due to the differences in atomic size, limited structural contraction occurs even at low substitution concentrations, resulting in local elastic strains within the α -FeOOH structure [6,188,189]. This may explain why Al substitution is restricted to $x < 0.36$. The diamagnetism of Al contributes to the antiferromagnetic field of α -FeOOH, also inducing weak magnetism around the originally non-magnetic O atoms

[189]. It is impossible to form an ideal solid solution through the substitution of Al for Fe as isomorphous ions.

When metallic elements are mixed and precipitated, the chemical forms and segregation patterns of metal impurities can change over time. During the transition from an amorphous to a crystalline state, the distribution of elements significantly affects the properties of the resulting crystal. For example, in Cu and Al co-precipitates (electronic paramagnets), Cu is initially evenly distributed within the amorphous Al_2O_3 . However, as time progresses and the amorphous Al_2O_3 transforms into gibbsite, Cu clusters and CuO phases form [190]. The effects of Fe substitution by Al have been the subject of numerous studies, including those by Fazey [191], Schulze [192], and Schwertmann [187]. Most researchers consider the system to be a random solid solution substitution. Scheinost [193] proposed the existence of diaspora clusters within α - FeOOH . Theoretical calculations show that the enthalpy of clustered Al substitution at low concentrations is lower than that of random substitution. As Al substitution increases, α - FeOOH becomes shorter and less multidomainic, indicating a correlation between Al substitution and a slower crystallization rate. The substitution of Al results in fewer structural defects. Additionally, Al substitution reduces the unit cell volume and increases hydroxyl units, particularly non-stoichiometric hydroxyl units, within the α - FeOOH structure [170,171,192,194,195]. Therefore, the substitution of Al in α - FeOOH is considered an important factor controlling lattice stability and influencing the thermal decomposition of the crystal, the vibration of hydroxyl units, rearrangement of oxygen packing, and migration of cations [196–198].

The substitution of Al for Fe in α - FeOOH is also believed to be associated with excess structural OH^- , either in relation to cation vacancies or due to the protonation of O atoms and disruption of hydrogen bonds in the structure [98,199]. Al substitution has been found to facilitate the incorporation of excess OH^- into the α - FeOOH structure (excess OH^- formula: $(\text{Fe}_{1-x}\text{Al}_x)_{y/3}\text{O}_{1-y}(\text{OH})_{1+y}$) [162,170,192,200], and to promote the preservation of hydroxyl units in the α - FeOOH structure at higher temperatures (543 K), indicating that Al- α - FeOOH is more thermally stable than pure α - FeOOH [98]. However, some researchers have determined the mixed enthalpy of Al- α - FeOOH and concluded that Al- α - FeOOH is relatively metastable compared to α - FeOOH and diaspora [102]. Despite this, due to the small energy difference between α - FeOOH and Al- α - FeOOH , it can persist.

Under high-temperature and pressure conditions, the decomposition temperature of ϵ - FeOOH is slightly higher than some cold subducting plate geothermal gradients. The addition of Al significantly enhances the thermal stability of ϵ -(Fe, Al)OOH and reduces the volume of the solid solution [201]. The superhydrous phase B exists stably at the top of the lower mantle; as depth increases, it decomposes into Ferropericlase, Bridgmanite, and Phase D [202]. Phase D can be stable under pressure conditions of 44 GPa (mantle depth of ~ 1250 km) [42]. The incorporation of Al greatly enhances its thermal stability, allowing it to exist as a reservoir of water under normal geothermal gradients [203]. As pressure increases, Phase D decomposes into Phase H and stishovite [204]. The stable pressure range for hydrous Phase H has been predicted to be 40–52 GPa using first-principles calculations [44]. This phase has a narrow stability field and decomposes into perovskite and water at pressures greater than 52 GPa. Al- and Fe-poor Phase H occurs in ultramafic rocks, while Al- and Fe-rich hydroxyl oxides occur in mafic rocks. Bindi et al. [205] suggests that when the structure of diaspora transforms into $Pnmm$, it forms a complete solid solution with Phase H. Previous studies have successfully synthesized

phase- δ – MgSiO_4H_2 [46,56,206], δ - AlOOH – MgSiO_4H_2 – SiO_2 [56], δ -(Al, Fe)OOH [91,93] using high-temperature and pressure apparatus. Experimental results and theoretical calculations have shown that Phase H- δ solid solution has a wide solid solution range [44,56]. It exhibits a wide stability field at the bottom of the lower mantle, and its composition can change with temperature and pressure. At 68 GPa and 2010 K, it contains 44 mol% of the MgSiO_4H_2 component end-member, while at 128 GPa and 2190 K, the content of this component decreases to 23 mol%. Additionally, this solid solution can coexist with the major mineral bridgmanite in the lower mantle and has the potential to be an important water carrier in the subducting slab, known as the subducted peridotite mantle [207]. Ohira et al. [56] conducted experiments that demonstrated the coexistence of Phase H- δ solid solution with perovskite and post-perovskite phases. The partitioning coefficient, $D(\text{Al}_2\text{O}_3) = \text{Al}_2\text{O}_3$ (mol% in Phase H- δ solid solution)/ Al_2O_3 (mol% in Bdg or pPv), was found to be in the range of 14–26 in the lower mantle of the MASH system. In mantle peridotite and MORB, Al selectively distributes into the phase δ [208]. Recently, high-pressure and temperature experiments have shown that ϵ -FeOOH can form solid solutions with Phase H- δ solid solution over a wide range of compositions (Figure 12). These solid solutions remain stable at higher temperatures, forming a hydrogen reservoir with P-T stability extending from the lower mantle environment to the core-mantle boundary [21,56,93,118,127,128,207,209,210]. They may maintain thermodynamic stability within subducting plates and transport water into the lower mantle. Nishi et al. [209] suggested that the mutual solubility between ϵ -FeOOH and δ -AlOOH in solid solution is limited; Xu et al. [93] determined the phase relations of the (Al, Fe)OOH binary system at 15–25 GPa and 700–1200 °C, finding that δ -AlOOH and ϵ -FeOOH partially form solid solutions over a wide range of pressures and temperatures. the maximum solubility of Al and Fe in the solid solution is more influenced by temperature than pressure. Thompson [63] proposed that the ϵ -FeOOH – δ -AlOOH – MgSiO_4H_2 solid solution may contribute to the seismic properties of large low-shear-wave-velocity provinces. Experiments have confirmed that Al substitution can stabilize the H-phase, but the precise influence of Fe on this system remains unclear. In the ϵ -FeOOH – δ -AlOOH – MgSiO_4H_2 system, the spin transitions and changes in the cell volume may occur at pressures lower than those of the pure Fe endmember, resulting in anomalies in seismic wave velocities at different depths [64]. The low spin $Pnnm$ structure may be stable under conditions of the Earth's deep interior [21,93]. High-temperature and high-pressure experiments in the Fe_2O_3 - MgO - Al_2O_3 - SiO_2 - H_2O system have demonstrated that the CaCl_2 -type solid solution subducted into the lower mantle can retain major elements of the Earth, including Mg, Si, Al, and Fe. This may play a crucial role in the transport of water into the Earth's lower mantle and could contribute to explaining the geophysical heterogeneity observed in the deep Earth.

6. Conclusions and outlook

In conclusion, current review highlights several critical aspects of α -FeOOH and ϵ -FeOOH in the Earth's lower mantle:

- (1) Experimental and theoretical studies indicate that ϵ -FeOOH, a simple iron hydroxide, can stably exist in the lower mantle and at the core-mantle boundary, this phase is significant as it enters the mantle through subduction zones.

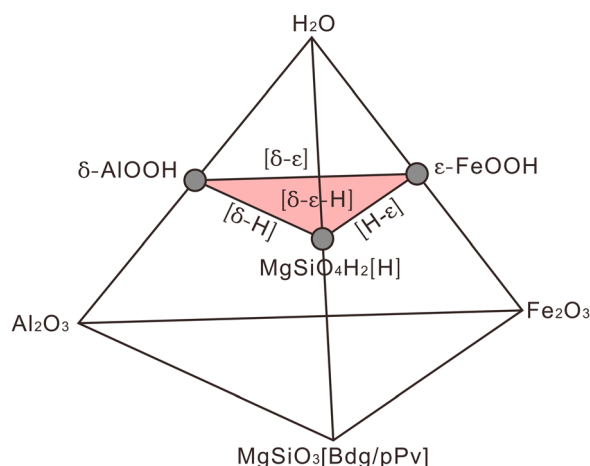


Figure 12. The MAFSH quaternary with the compositions of the hydrous phases in the DLM, modified from [207].

- (2) ϵ -FeOOH releases H_2 at depths greater than 1800km [211]. The H_2 dissociates from the FeOOH system, leading to a net accumulation of oxygen, which, upon reaching a certain concentration, can trigger mantle plumes that release O_2 into the atmosphere, forming a deep source of atmospheric O_2 . The accumulated H_2 could also significantly impact the oxygen fugacity of the mantle.
- (3) Theoretical calculations and experiments demonstrate that ϵ -FeOOH can form solid solutions with the $CaCl_2$ -type phase δ and $MgSiO_4H_2$, remaining stable over a wide range of temperature and pressure conditions. Studying the stability of these solid solutions under lower mantle conditions is crucial for comprehending the physical properties and geological processes in the deep Earth.

It is generally believed that the GOE was a long-term event (~ 2.4 – 2.06 Ga), and its early initiation might have been a prolonged unstable period [212–216]. Whether other simple hydrous minerals exhibit similar behaviour, potentially leading to an underestimation of such sporadic, scattered deep sources remains to be investigated. Due to the challenges posed by devices and testing methods under the ultra-high-temperature and high-pressure conditions of the mantle, theoretical calculations have become crucial for studying the properties of materials in such extreme environments. The Wu-Wentzcovitch semi-analytical method (SAM) [217] and the stress-strain method at finite temperature [218] have been successfully applied to obtain the elastic tensor of minerals under high temperature and pressure conditions, even in melts. These methods have been effectively used for various minerals [219–221] and serve as important complementary tools for overcoming the challenges of testing the physical properties of minerals under deep Earth conditions.

Subject Index

α -FeOOH	3, 4, 5, 6, 7, 8, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20
ϵ -FeOOH	4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 20, 21, 22, 23

Dehydroxylation	7, 16
Hydrogen bond symmetrization	8, 9, 10
Spin transition	9,10
Bulk modulus	11, 12
Electrical conductivity	12, 13, 14
Elastic property	14, 15
Electronic structure	15, 16
Infrared radiation	16, 17, 18, 19
Raman spectra	19, 20
Solid solution	20, 21, 22, 23

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work is supported financially by the National Natural Science Foundation of China (91962101, 41603063, 41872038).

Notes on contributors



Shun-Feng Yan is a PhD candidate at the Institute of Earth Sciences, China University of Geosciences (Beijing). He holds a Bachelor's degree from Suzhou University. His current research focuses on the diffusion properties of hydrogen in minerals under high-temperature and high-pressure conditions, as well as the application of deep learning potential methods to investigate the mechanical and thermal properties of minerals under high-temperature and high-pressure conditions.



Dr. Lin Li is an Associate Professor at the Institute of Earth Sciences, China University of Geosciences (Beijing). He holds a Ph.D. in Planetary Material Science from Hokkaido University. His research focuses on mineral exploration, studying the geodynamic background and metallogenic processes of gold-dominated deposits in North China, supported by projects like the China Geological Survey and National Natural Science Foundation. His expertise in elemental, mineralogical, and geochemical techniques has advanced deep mine reserve growth and mineral searches in regions like Shanxi, Hebei, and Shandong. He has published 32 SCI papers in top journals, and received the China Gold Association Scientific and Technological Progress Award in 2021 and 2024..



Dr. Mao-Wen Yuan is currently working at the Journal Center of China University of Geosciences (Beijing). His primary research focuses on genetic mineralogy. He has published more than 20 academic papers and has participated in and completed several projects funded by the National Natural Science Foundation and the National Key Research and Development Program.



Dr. M. Santosh is a professor at China University of Geosciences (Beijing), a National Specially Appointed Expert of the Organization Department of the CPC Central Committee, an Honorary Professor at Kochi University of Technology (Japan), and a professor at the University of Adelaide (Australia). He has conducted extensive research on the formation and evolution of supercontinents, the tectonics of the North China Craton basement, and ultra-high-temperature metamorphic belts. His expertise lies in using principles and techniques from elemental, mineral, geochemistry, and isotopic geochemistry to study plate tectonics, Earth's evolutionary history, and the formation and evolution of continents and oceans.



Dr. Sheng-Rong Li is a professor at the School of Earth Science and Resources, China University of Geosciences (Beijing). He holds a Ph.D. from the same university. His research focuses on genetic mineralogy and economic geology, specializing in metallogenic processes and mineral exploration of gold, rare earth, and other metal deposits in North China and beyond. Supported by major projects like the National Natural Science Foundation of China Geological Survey, his work has advanced understanding of deposits in regions like Shandong, Shanxi, and Hebei. Dr. Li has published over 300 SCI papers in top geoscience journals and authored 10 monographs and 1 textbook. He has received prestigious awards, including the China State Teaching Achievement Prize and Land and Resources Science and Technology Prizes, and serves as Director of the Commission of Genetic Mineralogy & Prospecting Mineralogy.

References

- [1] Otte K, Pentcheva R, Schmahl WW, et al. Pressure-induced structural and electronic transitions in FeOOH from first principles. *Phys Rev B*. 2009;80(20):205116. doi:10.1103/PhysRevB.80.205116
- [2] Schwertmann U, Taylor RM. Iron oxides. *Miner Soil Environ*. 1989;1:379–438.
- [3] Blowes DW, Ptacek CJ, Jambor JL, et al. 9.05 - The geochemistry of acid mine drainage. In: HD Holland, KK Turekian, editors. *Treatise on geochemistry*. Pergamon, Oxford: Elsevier; 2003. p. 149–204.
- [4] Anthony J. *Handbook of mineralogy*. Vol. 3: halides, hydroxides and oxides. Tuscon: Mineral Data Pub; 1997.
- [5] Anand R, Gilkes R, Roach G. Geochemical and mineralogical characteristics of bauxites, Darling Range, Western Australia. *Appl Geochem*. 1991;6(3):233–248. doi:10.1016/0883-2927(91)90001-6
- [6] Cornell RM, Schwertmann U. *The iron oxides: structure, properties, reactions, occurrences, and uses*. New York: Wiley-vch Weinheim; 2003.
- [7] Özdemir O, Dunlop DJ. Intermediate magnetite formation during dehydration of goethite. *Earth Planet Sci Lett*. 2000;177(1–2):59–67. doi:10.1016/S0012-821X(00)00032-7
- [8] Stucki JW, Goodman BA, Schwertmann U. *Iron in soils and clay minerals*. Dordrecht: Springer Science & Business Media; 2012.
- [9] Ohtani E, Litasov K, Hosoya T, et al. Water transport into the deep mantle and formation of a hydrous transition zone. *Phys Earth Planet Inter*. 2004;143:255–269. doi:10.1016/j.pepi.2003.09.015
- [10] Peslier AH, Schönbachler M, Busemann H, et al. Water in the Earth's interior: distribution and origin. *Space Sci Rev*. 2017;212:743–810. doi:10.1007/s11214-017-0387-z
- [11] Xia Q-K, Liu J, Kovács I, et al. Water in the upper mantle and deep crust of eastern China: concentration, distribution and implications. *Natl Sci Rev*. 2019;6(1):125–144. doi:10.1093/nsr/nwx016
- [12] Zhang B-H, Guo X, Yoshino T, et al. Electrical conductivity of melts: implications for conductivity anomalies in the Earth's mantle. *Natl Sci Rev*. 2021;8(11):nwab064.

- [13] Karato S-i. Rheology of the deep upper mantle and its implications for the preservation of the continental roots: A review. *Tectonophysics*. 2010;481(1–4):82–98. doi:[10.1016/j.tecto.2009.04.011](https://doi.org/10.1016/j.tecto.2009.04.011)
- [14] Sarafian E, Gaetani GA, Hauri EH, et al. Experimental constraints on the damp peridotite solidus and oceanic mantle potential temperature. *Science*. 2017;355(6328):942–945. doi:[10.1126/science.aaj2165](https://doi.org/10.1126/science.aaj2165)
- [15] Van der Meijde M, Marone F, Giardini D, et al. Seismic evidence for water deep in Earth's upper mantle. *Science*. 2003;300(5625):1556–1558. doi:[10.1126/science.1083636](https://doi.org/10.1126/science.1083636)
- [16] Dixon JE, Dixon TH, Bell D, et al. Lateral variation in upper mantle viscosity: role of water. *Earth Planet Sci Lett*. 2004;222(2):451–467. doi:[10.1016/j.epsl.2004.03.022](https://doi.org/10.1016/j.epsl.2004.03.022)
- [17] Pearson D, Brenker F, Nestola F, et al. Hydrous mantle transition zone indicated by ringwoodite included within diamond. *Nature*. 2014;507(7491):221–224. doi:[10.1038/nature13080](https://doi.org/10.1038/nature13080)
- [18] Palot M, Jacobsen SD, Townsend J, et al. Evidence for H₂O-bearing fluids in the lower mantle from diamond inclusion. *Lithos*. 2016;265:237–243. doi:[10.1016/j.lithos.2016.06.023](https://doi.org/10.1016/j.lithos.2016.06.023)
- [19] Tschauner O, Huang S, Greenberg E, et al. Ice-VII inclusions in diamonds: evidence for aqueous fluid in Earth's deep mantle. *Science*. 2018;359(6380):1136–1139. doi:[10.1126/science.aao3030](https://doi.org/10.1126/science.aao3030)
- [20] Van der Hilst RD, Widiyantoro S, Engdahl E. Evidence for deep mantle circulation from global tomography. *Nature*. 1997;386(6625):578–584. doi:[10.1038/386578a0](https://doi.org/10.1038/386578a0)
- [21] Nishi M. Mantle hydration. *Nat Geosci*. 2015;8(1):9–10. doi:[10.1038/ngeo2326](https://doi.org/10.1038/ngeo2326)
- [22] Ohtani E. The role of water in Earth's mantle. *Natl Sci Rev*. 2020;7(1):224–232. doi:[10.1093/nsr/nwz071](https://doi.org/10.1093/nsr/nwz071)
- [23] Thompson AB. Water in the Earth's upper mantle. *Nature*. 1992;358(6384):295–302. doi:[10.1038/358295a0](https://doi.org/10.1038/358295a0)
- [24] Chang Y-Y, Hsieh W-P, Tan E, et al. Hydration-reduced lattice thermal conductivity of olivine in Earth's upper mantle. *Proc Natl Acad Sci USA*. 2017;114(16):4078–4081. doi:[10.1073/pnas.1616216114](https://doi.org/10.1073/pnas.1616216114)
- [25] Hou M, He Y, Jang BG, et al. Superionic iron oxide–hydroxide in Earth's deep mantle. *Nat Geosci*. 2021;14(3):174–178. doi:[10.1038/s41561-021-00696-2](https://doi.org/10.1038/s41561-021-00696-2)
- [26] Hwang H, Seoung D, Lee Y, et al. A role for subducted super-hydrated kaolinite in Earth's deep water cycle. *Nat Geosci*. 2017;10(12):947–953. doi:[10.1038/s41561-017-0008-1](https://doi.org/10.1038/s41561-017-0008-1)
- [27] Jacobsen SD, Smyth JR. Effect of water on the sound velocities of ringwoodite in the transition zone. *Earth's Deep Water Cycle*. 2006;168:131–145.
- [28] Liu H, Zhang K, Ingrin J, et al. Electrical conductivity of omphacite and garnet indicates limited deep water recycling by crust subduction. *Earth Planet Sci Lett*. 2021;559:116784. doi:[10.1016/j.epsl.2021.116784](https://doi.org/10.1016/j.epsl.2021.116784)
- [29] Mao H-K, Hu Q, Yang L, et al. When water meets iron at Earth's core–mantle boundary. *Natl Sci Rev*. 2017;4(6):870–878. doi:[10.1093/nsr/nwx109](https://doi.org/10.1093/nsr/nwx109)
- [30] Schmandt B, Jacobsen SD, Becker TW, et al. Dehydration melting at the top of the lower mantle. *Science*. 2014;344(6189):1265–1268. doi:[10.1126/science.1253358](https://doi.org/10.1126/science.1253358)
- [31] Jacobsen SD, Smyth JR, Spetzler H, et al. Sound velocities and elastic constants of iron-bearing hydrous ringwoodite. *Phys Earth Planet Inter*. 2004;143:47–56. doi:[10.1016/j.pepi.2003.07.019](https://doi.org/10.1016/j.pepi.2003.07.019)
- [32] Ringwood A, Major A. High-pressure reconnaissance investigations in the system Mg₂SiO₄–MgO–H₂O. *Earth Planet Sci Lett*. 1967;2(2):130–133. doi:[10.1016/0012-821X\(67\)90114-8](https://doi.org/10.1016/0012-821X(67)90114-8)
- [33] Finger L, Ko J, Hazen R, et al. Crystal chemistry of phase B and an anhydrous analogue: implications for water storage in the upper mantle. *Nature*. 1989;341(6238):140–142. doi:[10.1038/341140a0](https://doi.org/10.1038/341140a0)
- [34] Finger LW, Hazen RM, Prewitt CT. Crystal structures of Mg₁₂Si₄O₁₉ (OH)₂ (phase B) and Mg₁₄Si₅O₂₄ (phase AnhB). *Am Mineral*. 1991;76(1–2):1–7.
- [35] Gasparik T. Phase relations in the transition zone. *J Geophys Res: Solid Earth*. 1990;95(B10):15751–15769. doi:[10.1029/JB095iB10p15751](https://doi.org/10.1029/JB095iB10p15751)
- [36] Prewitt CT, Parise JB. Hydrous phases and hydrogen bonding at high pressure. *Rev Mineral Geochem*. 2000;41(1):309–333. doi:[10.2138/rmg.2000.41.11](https://doi.org/10.2138/rmg.2000.41.11)

- [37] Liu L-g. Phase transformations in serpentine at high pressures and temperatures and implications for subducting lithosphere. *Phys Earth Planet Inter.* **1986**;42(4):255–262. doi:[10.1016/0031-9201\(86\)90028-2](https://doi.org/10.1016/0031-9201(86)90028-2)
- [38] Liu L-g. Effects of H₂O on the phase behaviour of the forsterite-enstatite system at high pressures and temperatures and implications for the Earth. *Phys Earth Planet Inter.* **1987**;49(1–2):142–167. doi:[10.1016/0031-9201\(87\)90138-5](https://doi.org/10.1016/0031-9201(87)90138-5)
- [39] Yang H, Prewitt CT, Frost DJ. Crystal structure of the dense hydrous magnesium silicate, phase D. *Am Mineral.* **1997**;82(5–6):651–654. doi:[10.2138/am-1997-5-627](https://doi.org/10.2138/am-1997-5-627)
- [40] Ohtani E, Mizobata H, Kudoh Y, et al. A new hydrous silicate, a water reservoir, in the upper part of the lower mantle. *Geophys Res Lett.* **1997**;24(9):1047–1050. doi:[10.1029/97GL00874](https://doi.org/10.1029/97GL00874)
- [41] Frost DJ, Fei Y. Stability of phase D at high pressure and high temperature. *J Geophys Res: Solid Earth.* **1998**;103(B4):7463–7474. doi:[10.1029/98JB00077](https://doi.org/10.1029/98JB00077)
- [42] Shieh SR, Mao H-K, Hemley RJ, et al. Decomposition of phase D in the lower mantle and the fate of dense hydrous silicates in subducting slabs. *Earth Planet Sci Lett.* **1998**;159(1–2):13–23. doi:[10.1016/S0012-821X\(98\)00062-4](https://doi.org/10.1016/S0012-821X(98)00062-4)
- [43] Kanzaki M. Stability of hydrous magnesium silicates in the mantle transition zone. *Phys Earth Planet Inter.* **1991**;66(3–4):307–312. doi:[10.1016/0031-9201\(91\)90085-V](https://doi.org/10.1016/0031-9201(91)90085-V)
- [44] Tsuchiya J. First principles prediction of a new high-pressure phase of dense hydrous magnesium silicates in the lower mantle. *Geophys Res Lett.* **2013**;40(17):4570–4573. doi:[10.1002/grl.50875](https://doi.org/10.1002/grl.50875)
- [45] Ewing F. The crystal structure of diaspor. *J Chem Phys.* **1935**;3(4):203–207. doi:[10.1063/1.1749634](https://doi.org/10.1063/1.1749634)
- [46] Suzuki A, Ohtani E, Kamada T. A new hydrous phase δ -AlOOH synthesized at 21 GPa and 1000 C. *Phys Chem Miner.* **2000**;27:689–693. doi:[10.1007/s002690000120](https://doi.org/10.1007/s002690000120)
- [47] Coes L Jr. Synthesis of minerals at high pressures, Modern very high pressure techniques (1962) 137–150.
- [48] Wunder B, Medenbach O, Krause W, et al. Synthesis, properties and stability of Al₃Si₂O₇(OH)₃ (phase Pi), a hydrous high-pressure phase in the system Al₂O₃-SiO₂-H₂O (ASH). *Eur J Mineral.* **1993**;5(4):637–649. doi:[10.1127/ejm/5/4/0637](https://doi.org/10.1127/ejm/5/4/0637)
- [49] Wunder B, Rubie D, Ross C, et al. Synthesis, stability, and properties of Al₂SiO₄(OH)₂: A fully hydrated analogue of topaz. *Am Mineral.* **1993**;78(3–4):285–297.
- [50] Kanzaki M. Crystal structure of a new high-pressure polymorph of topaz-OH. *Am Mineral.* **2010**;95(8–9):1349–1352. doi:[10.2138/am.2010.3555](https://doi.org/10.2138/am.2010.3555)
- [51] RA E, JN B, AE R. High pressure synthesis of a new aluminium silicate: Al₅Si₅O₁₇(OH). *Geochem J.* **1978**;12(3):191–194. doi:[10.2343/geochemj.12.191](https://doi.org/10.2343/geochemj.12.191)
- [52] Wirth R, Vollmer C, Brenker F, et al. Inclusions of nanocrystalline hydrous aluminium silicate “Phase egg” in superdeep diamonds from Juina (Mato Grosso State, Brazil). *Earth Planet Sci Lett.* **2007**;259(3–4):384–399. doi:[10.1016/j.epsl.2007.04.041](https://doi.org/10.1016/j.epsl.2007.04.041)
- [53] Ballaran TB, Frost DJ, Miyajima N, et al. The structure of a super-aluminous version of the dense hydrous-magnesium silicate phase D. *Am Mineral.* **2010**;95(7):1113–1116. doi:[10.2138/am.2010.3462](https://doi.org/10.2138/am.2010.3462)
- [54] Ransome FL. On Lawsonite, a new rock-forming mineral: from the Tiburon Peninsula. Oakland: Marin Co., Cal, The University Press; **1895**.
- [55] Güven N. The crystal structures of 2 M 1 phengite and 2 M 1 muscovite. *Zeitschrift für Kristallographie-Crystalline Materials.* **1971**;134(3–4):196–212. doi:[10.1524/zkri.1971.134.3-4.196](https://doi.org/10.1524/zkri.1971.134.3-4.196)
- [56] Ohira I, Ohtani E, Sakai T, et al. Stability of a hydrous δ -phase, AlOOH–MgSiO₂ (OH)₂, and a mechanism for water transport into the base of lower mantle. *Earth Planet Sci Lett.* **2014**;401:12–17. doi:[10.1016/j.epsl.2014.05.059](https://doi.org/10.1016/j.epsl.2014.05.059)
- [57] Bindi L, Bendeliani A, Bobrov A, et al. Incorporation of Mg in phase Egg, AlSiO₃OH: toward a new polymorph of phase H, MgSiH₂O₄, a carrier of water in the deep mantle. *Am Mineral.* **2020**;105(1):132–135. doi:[10.2138/am-2020-7204](https://doi.org/10.2138/am-2020-7204)

- [58] Pernet M, Joubert J, Berthet-Colominas C. Etude par diffraction neutronique de la forme haute pression de FeOOH. *Solid State Commun.* **1975**;17(12):1505–1510. doi:[10.1016/0038-1098\(75\)90983-7](https://doi.org/10.1016/0038-1098(75)90983-7)
- [59] Zhang L, Yuan H, Meng Y, et al. Discovery of a hexagonal ultradense hydrous phase in (Fe, Al) OOH. *Proc Nat Acad Sci.* **2018**;115(12):2908–2911. doi:[10.1073/pnas.1720510115](https://doi.org/10.1073/pnas.1720510115)
- [60] Nishi M, Kuwayama Y, Tsuchiya J, et al. The pyrite-type high-pressure form of FeOOH. *Nature.* **2017**;547(7662):205–208. doi:[10.1038/nature22823](https://doi.org/10.1038/nature22823)
- [61] Hu Q, Kim DY, Yang W, et al. FeO₂ and FeOOH under deep lower-mantle conditions and Earth's oxygen–hydrogen cycles. *Nature.* **2016**;534(7606):241–244. doi:[10.1038/nature18018](https://doi.org/10.1038/nature18018)
- [62] Thompson EC, Davis AH, Brauser NM, et al. Phase transitions in ϵ -FeOOH at high pressure and ambient temperature. *Am Mineral.* **2020**;105(12):1769–1777. doi:[10.2138/am-2020-7468](https://doi.org/10.2138/am-2020-7468)
- [63] Thompson EC, Campbell A, Tsuchiya J. Elasticity of ϵ -FeOOH: seismic implications for Earth's lower mantle. *J Geophys Res: Solid Earth.* **2017**;122(7):5038–5047. doi:[10.1002/2017JB014168](https://doi.org/10.1002/2017JB014168)
- [64] Zhuang Y, Gan B, Cui Z, et al. Mid-mantle water transportation implied by the electrical and seismic properties of ϵ -FeOOH. *Sci Bull.* **2022**;67(7):748–754. doi:[10.1016/j.scib.2021.12.002](https://doi.org/10.1016/j.scib.2021.12.002)
- [65] Gan B, Zhang Y, Huang Y, et al. Partial deoxygenation and dehydration of ferric oxyhydroxide in Earth's subducting slabs. *Geophys Res Lett.* **2021**;48(17):e2021GL094446. doi:[10.1029/2021GL094446](https://doi.org/10.1029/2021GL094446)
- [66] Hu Q, Liu J. Deep mantle hydrogen in the pyrite-type FeO₂-FeO₂H system. *Geosci Front.* **2021**;12(2):975–981. doi:[10.1016/j.gsf.2020.04.006](https://doi.org/10.1016/j.gsf.2020.04.006)
- [67] Liu J, Hu Q, Kim DY, et al. Hydrogen-bearing iron peroxide and the origin of ultralow-velocity zones. *Nature.* **2017**;551(7681):494–497. doi:[10.1038/nature24461](https://doi.org/10.1038/nature24461)
- [68] Williams Q, Hemley RJ. Hydrogen in the deep Earth. *Annu Rev Earth Planet Sci.* **2001**;29(1):365–418. doi:[10.1146/annurev.earth.29.1.365](https://doi.org/10.1146/annurev.earth.29.1.365)
- [69] Morris RV, Klingelhofer G, Bernhardt B, et al. Mineralogy at Gusev crater from the Mossbauer spectrometer on the Spirit rover. *Science.* **2004**;305(5685):833–836. doi:[10.1126/science.1100020](https://doi.org/10.1126/science.1100020)
- [70] Goldshtaub S. Étude de quelques dérivés de l'oxyde ferrique (FeO. OH, FeO₂Na, FeOCl); détermination de leurs structures. *Bulletin de Minéralogie.* **1935**;58(1):6–76.
- [71] Hoppe W. Über die Kristallstruktur von α -AlOOH (Diaspor) und α -FeOOH (Nadeleisenerz). *Zeitschrift für Kristallographie-Crystalline Materials.* **1941**;103(1–6):73–89. doi:[10.1524/zkri.1941.103.1.73](https://doi.org/10.1524/zkri.1941.103.1.73)
- [72] Yang H, Lu R, Downs RT, et al. Goethite, α -FeO(OH), from single-crystal data. *Acta Crystallographica Section E: Structure Reports Online.* **2006**;62(12):i250–i252. doi:[10.1107/S1600536806047258](https://doi.org/10.1107/S1600536806047258)
- [73] Hahn T, Shmueli U, Arthur JW. *International tables for crystallography.* Dordrecht: Reidel; **1983**.
- [74] Nagai T, Kagi H, Yamanaka T. Variation of hydrogen bonded O...O distances in goethite at high pressure. *Am Mineral.* **2003**;88(10):1423–1427. doi:[10.2138/am-2003-1005](https://doi.org/10.2138/am-2003-1005)
- [75] Forsyth J, Hedley I, Johnson C. The magnetic structure and hyperfine field of goethite (α -FeOOH). *J Phys C Solid State Phys.* **1968**;1(1):179. doi:[10.1088/0022-3719/1/1/321](https://doi.org/10.1088/0022-3719/1/1/321)
- [76] Jeffrey G. *An Introduction to Hydrogen Bonding*: Oxford University Press: New York, 1997, Google Scholar There is no corresponding record for this reference (1997) 220–225.
- [77] Piermarini G, Block S, Barnett J. Hydrostatic limits in liquids and solids to 100 kbar. *J Appl Phys.* **1973**;44(12):5377–5382. doi:[10.1063/1.1662159](https://doi.org/10.1063/1.1662159)
- [78] Gleason AE, Jeanloz R, Kunz M. Pressure-temperature stability studies of FeOOH using X-ray diffraction. *Am Mineral.* **2008**;93(11–12):1882–1885. doi:[10.2138/am.2008.2942](https://doi.org/10.2138/am.2008.2942)
- [79] Grocholski B, Jeanloz R. High-pressure and-temperature viscosity measurements of methanol and 4: 1 methanol: ethanol solution. *J Chem Phys.* **2005**;123(20):204503. doi:[10.1063/1.2110068](https://doi.org/10.1063/1.2110068)
- [80] Mao H-K, Shu J, Hu J, et al. High-pressure X-ray diffraction study of diaspor. *Solid State Commun.* **1994**;90(8):497–500. doi:[10.1016/0038-1098\(94\)90053-1](https://doi.org/10.1016/0038-1098(94)90053-1)
- [81] Anderson DL, Anderson OL. The bulk modulus-volume relationship for oxides; 1988.

- [82] Bendeliani N, Baneyeva M, Poryvkin D. Synthesis of new modification of FeO(OH), stable at high pressure. *Geochem Int.* **1972**;9:589–590.
- [83] Bendeliani N, Baneyeva M, Poryvkin D. Synthesis of a new FeO(OH) modification being stable at high-pressure, Rossiiskaya Akad Nauk Savelevskii Per, 13 Octozhenka, 119034 Moscow, RUSSIA, 1972, pp. 871–+.
- [84] Bolotina N, Molchanov V, Dyuzheva T, et al. Single-crystal structures of high-pressure phases FeOOH, FeOOD, and GaOOH. *Crystallogr Rep.* **2008**;53:960–965. doi:[10.1134/S1063774508060084](https://doi.org/10.1134/S1063774508060084)
- [85] Voigt R, Will G. The system Fe₂O₃-H₂O under high-pressures. *Neues Jahrbuch Fur Mineralogie-Monatshefte.* **1981**;2:89–96.
- [86] Wiethoff F, Grevel K-D, Marler B, et al. Pvt behavior of FeO(OH) and MnO(OH). *Phys Chem Miner.* **2017**;44:567–576. doi:[10.1007/s00269-017-0884-3](https://doi.org/10.1007/s00269-017-0884-3)
- [87] Liu K, Dai L, Li H, et al. Pressure-induced phase transitions for goethite investigated by Raman spectroscopy and electrical conductivity. *High Press Res.* **2019**;39(1):106–116. doi:[10.1080/08957959.2019.1572751](https://doi.org/10.1080/08957959.2019.1572751)
- [88] Jeanloz R. Finite-strain equation of state for high-pressure phases. *Geophys Res Lett.* **1981**;8(12):1219–1222. doi:[10.1029/GL008i012p01219](https://doi.org/10.1029/GL008i012p01219)
- [89] Suzuki A. High-pressure X-ray diffraction study of ϵ -FeOOH. *Phys Chem Miner.* **2010**;37:153–157. doi:[10.1007/s00269-009-0319-x](https://doi.org/10.1007/s00269-009-0319-x)
- [90] Xu W, Greenberg E, Rozenberg GK, et al. Pressure-induced hydrogen bond symmetrization in iron oxyhydroxide. *Phys Rev Lett.* **2013**;111(17):175501. doi:[10.1103/PhysRevLett.111.175501](https://doi.org/10.1103/PhysRevLett.111.175501)
- [91] Kawazoe T, Ohira I, Ishii T, et al. Single crystal synthesis of δ -(Al, Fe) OOH. *Am Mineral.* **2017**;102(9):1953–1956. doi:[10.2138/am-2017-6153](https://doi.org/10.2138/am-2017-6153)
- [92] Ikeda O, Sakamaki T, Ohashi T, et al. Sound velocity measurements of ϵ -FeOOH up to 24 GPa. *J Mineral Petrol Sci.* **2019**;114(3):155–160. doi:[10.2465/jmps.181115b](https://doi.org/10.2465/jmps.181115b)
- [93] Xu C, Nishi M, Inoue T. Solubility behavior of δ -AlOOH and ϵ -FeOOH at high pressures. *Am Mineral.* **2019**;104(10):1416–1420. doi:[10.2138/am-2019-7064](https://doi.org/10.2138/am-2019-7064)
- [94] Tang R, Chen J, Zeng Q, et al. Study on the high-pressure behavior of goethite up to 32 GPa using X-ray diffraction, Raman, and electrical impedance spectroscopy. *Minerals.* **2020**;10(2):99. doi:[10.3390/min10020099](https://doi.org/10.3390/min10020099)
- [95] Gualtieri AF, Venturelli P. In situ study of the goethite-hematite phase transformation by real time synchrotron powder diffraction. *Am Mineral.* **1999**;84(5–6):895–904. doi:[10.2138/am-1999-5-624](https://doi.org/10.2138/am-1999-5-624)
- [96] Morris RV, Lauer HV Jr. Stability of goethite (α -FeOOH) and lepidocrocite (γ -FeOOH) to dehydration by UV radiation: implications for their occurrence on the Martian surface. *J Geophys Res: Solid Earth.* **1981**;86(B11):10893–10899. doi:[10.1029/JB086iB11p10893](https://doi.org/10.1029/JB086iB11p10893)
- [97] Walter D, Buxbaum G, Laqua W. The mechanism of the thermal transformation from goethite to hematite. *J Therm Anal Calorim.* **2001**;63:733–748. doi:[10.1023/A:1010187921227](https://doi.org/10.1023/A:1010187921227)
- [98] Ruan H, Frost R, Klopogge J, et al. Infrared spectroscopy of goethite dehydroxylation. II. Effect of aluminium substitution on the behaviour of hydroxyl units. *Spectrochim Acta, Part A.* **2002**;58(3):479–491. doi:[10.1016/S1386-1425\(01\)00556-X](https://doi.org/10.1016/S1386-1425(01)00556-X)
- [99] Ruan H, Frost R, Klopogge J, et al. Infrared spectroscopy of goethite dehydroxylation: III. FT-IR microscopy of in situ study of the thermal transformation of goethite to hematite. *Spectrochim Acta, Part A.* **2002**;58(5):967–981. doi:[10.1016/S1386-1425\(01\)00574-1](https://doi.org/10.1016/S1386-1425(01)00574-1)
- [100] Langmuir D. Particle size effect on the reaction goethite = hematite+ water. *Am J Sci.* **1971**;271(2):147–156. doi:[10.2475/ajs.271.2.147](https://doi.org/10.2475/ajs.271.2.147)
- [101] Majzlan J, Grevel K-D, Navrotsky A. Thermodynamics of Fe oxides: Part II. enthalpies of formation and relative stability of goethite (α -FeOOH), lepidocrocite (γ -FeOOH), and maghemite (γ -Fe₂O₃). *Am Mineral.* **2003**;88(5–6):855–859. doi:[10.2138/am-2003-5-614](https://doi.org/10.2138/am-2003-5-614)
- [102] Majzlan J, Lang BE, Stevens R, et al. Thermodynamics of Fe oxides: Part I. entropy at standard temperature and pressure and heat capacity of goethite (α -FeOOH), lepidocrocite (γ -FeOOH), and maghemite (γ -Fe₂O₃). *Am Mineral.* **2003**;88(5–6):846–854. doi:[10.2138/am-2003-5-613](https://doi.org/10.2138/am-2003-5-613)

- [103] Goss C. The kinetics and reaction mechanism of the goethite to hematite transformation. *Mineral Mag.* **1987**;51(361):437–451. doi:[10.1180/minmag.1987.051.361.11](https://doi.org/10.1180/minmag.1987.051.361.11)
- [104] Wolska E, Schwertmann U. Nonstoichiometric structures during dehydroxylation of goethite. *Zeitschrift für Kristallographie-Crystalline Materials.* **1989**;189(1–4):223–238. doi:[10.1524/zkri.1989.189.3-4.223](https://doi.org/10.1524/zkri.1989.189.3-4.223)
- [105] Wolska E, Szajda W. Structural and spectroscopic characteristics of synthetic hydrohaematite. *J Mater Sci.* **1985**;20:4407–4412. doi:[10.1007/BF00559329](https://doi.org/10.1007/BF00559329)
- [106] Zhou X, Chen T, Zhang P, et al. Structural characterization of the heat treatment products of natural goethite. *J Chin Ceram Soc.* **2013**;41(10):1442–1446.
- [107] Yoshino T, Baker E, Duffey K. Fate of water in subducted hydrous sediments deduced from stability fields of FeOOH and AlOOH up to 20 GPa. *Phys Earth Planet Inter.* **2019**;294:106295. doi:[10.1016/j.pepi.2019.106295](https://doi.org/10.1016/j.pepi.2019.106295)
- [108] Chen H, Xie S-Y, Ko B, et al. A new hydrous iron oxide phase stable at mid-mantle pressures. *Earth Planet Sci Lett.* **2020**;550:116551. doi:[10.1016/j.epsl.2020.116551](https://doi.org/10.1016/j.epsl.2020.116551)
- [109] Wolska E. Relations between the existence of hydroxyl ions in the anionic sublattice of hematite and its infrared and X-ray characteristics. *Solid State Ionics.* **1988**;28:1349–1351. doi:[10.1016/0167-2738\(88\)90385-2](https://doi.org/10.1016/0167-2738(88)90385-2)
- [110] Bykova E, Dubrovinsky L, Dubrovinskaia N, et al. Structural complexity of simple Fe₂O₃ at high pressures and temperatures. *Nat Commun.* **2016**;7(1):10661. doi:[10.1038/ncomms10661](https://doi.org/10.1038/ncomms10661)
- [111] Koemets E, Fedotenko T, Khandarkhaeva S, et al. Chemical stability of FeOOH at high pressure and temperature, and oxygen recycling in early Earth history. *Eur J Inorg Chem.* **2021**;2021(30):3048–3053. doi:[10.1002/ejic.202100274](https://doi.org/10.1002/ejic.202100274)
- [112] Martens R, Freund F. The potential energy curve of the proton and the dissociation energy of the OH[−] ion in Mg(OH)₂. *Physica status solidi (a).* **1976**;37(1):97–104. doi:[10.1002/pssa.2210370112](https://doi.org/10.1002/pssa.2210370112)
- [113] Tunega D. Theoretical study of properties of goethite (α -FeOOH) at ambient and high-pressure conditions. *J Phys Chem C.* **2012**;116(11):6703–6713. doi:[10.1021/jp2091297](https://doi.org/10.1021/jp2091297)
- [114] Holzapfel W. On the symmetry of the hydrogen bonds in ice VII. *J Chem Phys.* **1972**;56(2):712–715. doi:[10.1063/1.1677221](https://doi.org/10.1063/1.1677221)
- [115] Kuribayashi T, Sano-Furukawa A, Nagase T. Observation of pressure-induced phase transition of δ -AlOOH by using single-crystal synchrotron X-ray diffraction method. *Phys Chem Miner.* **2014**;41:303–312. doi:[10.1007/s00269-013-0649-6](https://doi.org/10.1007/s00269-013-0649-6)
- [116] Sano-Furukawa A, Kagi H, Nagai T, et al. Change in compressibility of δ -AlOOH and δ -AlOOD at high pressure: A study of isotope effect and hydrogen-bond symmetrization. *Am Mineral.* **2009**;94(8–9):1255–1261. doi:[10.2138/am.2009.3109](https://doi.org/10.2138/am.2009.3109)
- [117] Sano-Furukawa A, Yagi T, Okada T, et al. Compression behaviors of distorted rutile-type hydrous phases, MOOH (M = Ga, In, Cr) and CrOOD. *Phys Chem Miner.* **2012**;39:375–383. doi:[10.1007/s00269-012-0487-y](https://doi.org/10.1007/s00269-012-0487-y)
- [118] Panero WR, Caracas R. Stability of phase H in the MgSiO₄H₂-AlOOH-SiO₂ system. *Earth Planet Sci Lett.* **2017**;463:171–177. doi:[10.1016/j.epsl.2017.01.033](https://doi.org/10.1016/j.epsl.2017.01.033)
- [119] Gleason A, Quiroga C, Suzuki A, et al. Symmetrization driven spin transition in ϵ -FeOOH at high pressure. *Earth Planet Sci Lett.* **2013**;379:49–55. doi:[10.1016/j.epsl.2013.08.012](https://doi.org/10.1016/j.epsl.2013.08.012)
- [120] Fujihara T, Ichikawa M, Gustafsson T, et al. Powder-neutron diffraction studies of geometric isotope and hydrogen-bonding effects in β -CrOOH. *J Phys Chem Solids.* **2002**;63(2):309–315. doi:[10.1016/S0022-3697\(01\)00147-0](https://doi.org/10.1016/S0022-3697(01)00147-0)
- [121] Sano-Furukawa A, Hattori T, Komatsu K, et al. Direct observation of symmetrization of hydrogen bond in δ -AlOOH under mantle conditions using neutron diffraction. *Sci Rep.* **2018**;8(1):1–9. doi:[10.1038/s41598-018-33598-2](https://doi.org/10.1038/s41598-018-33598-2)
- [122] Vanpeteghem CB, Ohtani E, Kondo T, et al. Compressibility of phase egg AlSiO₃OH: equation of state and role of water at high pressure. *Am Mineral.* **2003**;88(10):1408–1411. doi:[10.2138/am-2003-1002](https://doi.org/10.2138/am-2003-1002)
- [123] Tsuchiya J, Tsuchiya T, Tsuneyuki S. First-principles study of hydrogen bond symmetrization of phase D under high pressure. *Am Mineral.* **2005**;90(1):44–49. doi:[10.2138/am.2005.1628](https://doi.org/10.2138/am.2005.1628)

- [124] Hushur A, Manghnani MH, Smyth JR, et al. Hydrogen bond symmetrization and equation of state of phase D. *J Geophys Res: Solid Earth*. 2011;116:B06203. doi:10.1029/2010JB008087
- [125] Lin JF, Speziale S, Mao Z, et al. Effects of the electronic spin transitions of iron in lower mantle minerals: implications for deep mantle geophysics and geochemistry. *Rev Geophys*. 2013;51(2):244–275. doi:10.1002/rog.20010
- [126] Verma AK, Modak P, Stixrude L. New high-pressure phases in MOOH (M = Al, Ga, In). *Am Mineral*. 2018;103(12):1906–1917. doi:10.2138/am-2018-6634
- [127] Liu X, Matsukage KN, Li Y, et al. Aqueous fluid connectivity in subducting oceanic crust at the mantle transition zone conditions. *J Geophys Res: Solid Earth*. 2018;123(8):6562–6573. doi:10.1029/2018JB015973
- [128] Nishihara Y, Matsukage KN. Iron-titanium oxyhydroxides as water carriers in the Earth's deep mantle. *Am Mineral*. 2016;101(4):919–927. doi:10.2138/am-2016-5517
- [129] Hu H, Dai L, Li H, et al. Influence of dehydration on the electrical conductivity of epidote and implications for high-conductivity anomalies in subduction zones. *J Geophys Res: Solid Earth*. 2017;122(4):2751–2762. doi:10.1002/2016JB013767
- [130] Lu C, Chen C. High-pressure evolution of crystal bonding structures and properties of FeOOH. *J Phys Chem Lett*. 2018;9(9):2181–2185. doi:10.1021/acs.jpclett.8b00947
- [131] Fan D, Li B, Chen W, et al. Progress on the equation of state of garnet group minerals. *Chin Phys Soc J*. 2018;32(01):4–16.
- [132] Kim Y-H, Yi Z. High pressure X-ray diffraction study on a goethite using synchrotron radiation. *J Min Soc Korea*. 1997;10:75–81.
- [133] Kim Y, Hwang G, Do J. Compression study of goethite at room temperature. *J Mineral Soc Korea*. 2007;20(4):261–266.
- [134] Suzuki A. Pressure–volume–temperature equation of state of ϵ -FeOOH to 11 GPa and 700 K. *J Mineral Petrol Sci*. 2016;111(6):420–424. doi:10.2465/jmps.160719c
- [135] Suzuki A. Thermal equation of state of goethite (α -FeOOH). *High Press Res*. 2017;37(2):193–199. doi:10.1080/08957959.2017.1301938
- [136] Ohira I, Jackson JM, Solomatova NV, et al. Compressional behavior and spin state of δ -(Al, Fe) OOH at high pressures. *Am Mineral: J Earth Planet Mater*. 2019;104(9):1273–1284. doi:10.2138/am-2019-6913
- [137] Ohira I, Jackson JM, Sturhahn W, et al. The influence of δ -(Al, Fe) OOH on seismic heterogeneities in Earth's lower mantle. *Sci Rep*. 2021;11(1):12036. doi:10.1038/s41598-021-91180-9
- [138] Dai L, Li H, Hu H, et al. Experimental study of grain boundary electrical conductivities of dry synthetic peridotite under high-temperature, high-pressure, and different oxygen fugacity conditions. *J Geophys Res: Solid Earth*. 2008;113:B12211. doi:10.1029/2008JB005820
- [139] Guo X, Yoshino T. Pressure-induced enhancement of proton conduction in brucite. *Geophys Res Lett*. 2014;41(3):813–819. doi:10.1002/2013GL058627
- [140] Liu J, Wang C, Lv C, et al. Evidence for oxygenation of Fe-Mg oxides at mid-mantle conditions and the rise of deep oxygen. *Natl Sci Rev*. 2021;8(4):nwaa096.
- [141] Yoshino T, Noritake F. Unstable graphite films on grain boundaries in crustal rocks. *Earth Planet Sci Lett*. 2011;306(3–4):186–192. doi:10.1016/j.epsl.2011.04.003
- [142] Yoshino T, Katsura T. Electrical conductivity of mantle minerals: role of water in conductivity anomalies. *Annu Rev Earth Planet Sci*. 2013;41:605–628. doi:10.1146/annurev-earth-050212-124022
- [143] Yoshino T, Ito E, Katsura T, et al. Effect of iron content on electrical conductivity of ferropericlase with implications for the spin transition pressure. *J Geophys Res: Solid Earth*. 2011;116:B04202. doi:10.1029/2010JB007801
- [144] Zhuang Y, Su X, Salke NP, et al. The effect of nitrogen on the compressibility and conductivity of iron at high pressure. *Geosci Front*. 2021;12(2):983–989. doi:10.1016/j.gsf.2020.04.012
- [145] Shen W. Conductivity studies of mantle minerals at high temperatures and pressures. Jilin: Jilin University; 2019.
- [146] Wang R, Yoshino T. Electrical conductivity of diasporite, δ -AlOOH and ϵ -FeOOH. *Am Mineral: J Earth Planet Mater*. 2021;106(5):774–781. doi:10.2138/am-2021-7605

- [147] Ohta K, Cohen RE, Hirose K, et al. Experimental and theoretical evidence for pressure-induced metallization in FeO with rocksalt-type structure. *Phys Rev Lett.* **2012**;108(2):026403. doi:[10.1103/PhysRevLett.108.026403](https://doi.org/10.1103/PhysRevLett.108.026403)
- [148] Matsuoka T, Hirao N, Ohishi Y, et al. Structural and electrical transport properties of FeH_x under high pressures and low temperatures. *High Press Res.* **2011**;31(1):64–67. doi:[10.1080/08957959.2010.522447](https://doi.org/10.1080/08957959.2010.522447)
- [149] Kaneko K, Inoue N, Ishikawa T. Electrical and photoadsorptive properties of valence-controlled. α -iron hydroxide oxide. *J Phys Chem.* **1989**;93(5):1988–1992. doi:[10.1021/j100342a056](https://doi.org/10.1021/j100342a056)
- [150] Zhuang Y, Dai L, Wu L, et al. Pressure-induced permanent metallization with reversible structural transition in molybdenum disulfide. *Appl Phys Lett.* **2017**;110(12):122103. doi:[10.1063/1.4979143](https://doi.org/10.1063/1.4979143)
- [151] Wang L, Ke F, Wang Q, et al. Effect of crystallization water on the structural and electrical properties of CuWO₄ under high pressure. *Appl Phys Lett.* **2015**;107(20):201603. doi:[10.1063/1.495978](https://doi.org/10.1063/1.495978)
- [152] Hall PG, Clarke NS, Maynard SC. Inelastic neutron scattering (TFXA) study of hydrogen modes in. α -FeOOH (Goethite) and. γ -FeOOH (Lepidocrocite). *J Phys Chem.* **1995**;99(15):5666–5673. doi:[10.1021/j100015a059](https://doi.org/10.1021/j100015a059)
- [153] Tsuchiya J, Tsuchiya T. Elastic properties of δ -AlOOH under pressure: first principles investigation. *Phys Earth Planet Inter.* **2009**;174(1–4):122–127. doi:[10.1016/j.pepi.2009.01.008](https://doi.org/10.1016/j.pepi.2009.01.008)
- [154] Tsuchiya J, Mookherjee M. Crystal structure, equation of state and elasticity of phase H (MgSiO₄H₂) at Earth's lower mantle pressures. *Sci Rep.* **2015**;5(1):1–8.
- [155] Gan B, Jiang G, Huang Y, et al. Phase diagram and thermoelastic property of iron oxyhydroxide across the spin crossover under extreme conditions. *Phys Rev B.* **2023**;107(6):064106. doi:[10.1103/PhysRevB.107.064106](https://doi.org/10.1103/PhysRevB.107.064106)
- [156] Xu Y, Schoonen MA. The absolute energy positions of conduction and valence bands of selected semiconducting minerals. *Am Mineral.* **2000**;85(3–4):543–556. doi:[10.2138/am-2000-0416](https://doi.org/10.2138/am-2000-0416)
- [157] Ding C, Li Y, Li Y, et al. Determination of the energy band structure of natural goethite by synchrotron radiation soft X-ray absorption and emission spectroscopy. *Acta Petrologica Et Mineralogica.* **2016**;35(02):349–354.
- [158] Fuente SA, Belevi PG, Castellani NJ, et al. Lda + U and GGA + U studies of Al-rich and bulk goethite (α -FeOOH). *Mater Chem Phys.* **2013**;137(3):1012–1020. doi:[10.1016/j.matchemphys.2012.11.017](https://doi.org/10.1016/j.matchemphys.2012.11.017)
- [159] Sherman DM, Randall SR. Surface complexation of arsenic (V) to iron (III)(hydr) oxides: structural mechanism from ab initio molecular geometries and EXAFS spectroscopy. *Geochim Cosmochim Acta.* **2003**;67(22):4223–4230. doi:[10.1016/S0016-7037\(03\)00237-0](https://doi.org/10.1016/S0016-7037(03)00237-0)
- [160] Williams Q, Guenther L. Pressure-induced changes in the bonding and orientation of hydrogen in FeOOH-goethite. *Solid State Commun.* **1996**;100(2):105–109. doi:[10.1016/0038-1098\(96\)00374-2](https://doi.org/10.1016/0038-1098(96)00374-2)
- [161] Verdonck L, Hoste S, Roelandt F, et al. Normal coordinate analysis of α -FeOOH—a molecular approach. *J Mol Struct.* **1982**;79:273–279. doi:[10.1016/0022-2860\(82\)85065-5](https://doi.org/10.1016/0022-2860(82)85065-5)
- [162] Blanch AJ, Quinton JS, Lenahan CE, et al. The crystal chemistry of Al-bearing goethites: an infrared spectroscopic study. *Mineral Mag.* **2008**;72(5):1043–1056. doi:[10.1180/minmag.2008.072.5.1043](https://doi.org/10.1180/minmag.2008.072.5.1043)
- [163] Schwarzmam E, Sparr H. Ultrarotspektrum von GaOOH. *Zeitschrift für Naturforschung B.* **1968**;23(6):767–770. doi:[10.1515/znb-1968-0602](https://doi.org/10.1515/znb-1968-0602)
- [164] Schwarzmam E, Sparr H. Die Wasserstoffbrückenbindung in Hydroxiden mit Diasporstruktur. *Zeitschrift für Naturforschung B.* **1969**;24(1):8–11. doi:[10.1515/znb-1969-0105](https://doi.org/10.1515/znb-1969-0105)
- [165] Schwertmann U, Cambier P, Murad E. Properties of goethites of varying crystallinity. *Clays Clay Miner.* **1985**;33:369–378. doi:[10.1346/CCMN.1985.0330501](https://doi.org/10.1346/CCMN.1985.0330501)
- [166] Oliveira LC, Ramalho TC, Souza EF, et al. Catalytic properties of goethite prepared in the presence of Nb on oxidation reactions in water: computational and experimental studies. *Appl Catal, B.* **2008**;83(3–4):169–176. doi:[10.1016/j.apcatb.2008.01.038](https://doi.org/10.1016/j.apcatb.2008.01.038)

- [167] Cambier P. Infrared study of goethites of varying crystallinity and particle size: I. Interpretation of OH and lattice vibration frequencies. *Clay Miner.* 1986;21(2):191–200. doi:10.1180/claymin.1986.021.2.08
- [168] Cambier P. Infrared study of goethites of varying crystallinity and particle size: II. crystallographic and morphological changes in series of synthetic goethites. *Clay Miner.* 1986;21(2):201–210. doi:10.1180/claymin.1986.021.2.09
- [169] Lewis D, Schwertmann U. The effect of [OH] on the goethite produced from ferrihydrite under alkaline conditions. *J Colloid Interface Sci.* 1980;78(2):543–553. doi:10.1016/0021-9797(80)90591-3
- [170] Ruan H, Gilkes R. Dehydroxylation of aluminous goethite: unit cell dimensions, crystal size and surface area. *Clays Clay Miner.* 1995;43:196–211. doi:10.1346/CCMN.1995.0430207
- [171] Schulze D, Schwertmann U. The influence of aluminium on iron oxides: XIII. Properties of goethites synthesised in 0.3 M KOH at 25° C. *Clay Miner.* 1987;22(1):83–92. doi:10.1180/claymin.1987.022.1.07
- [172] Schulze DG. The identification of iron oxides by differential X-ray diffraction and the influence of aluminum substitution on the structure of goethite, Technische Universitaet Muenchen (Germany); 1982.
- [173] Stiers W, Schwertmann U. Evidence for manganese substitution in synthetic goethite. *Geochim Cosmochim Acta.* 1985;49(9):1909–1911. doi:10.1016/0016-7037(85)90085-7
- [174] Stegmann M-C, Vivien D, Mazières C. Étude du spectre infrarouge des alumines de transition et du corindon. *Journal de Chimie Physique.* 1974;71:761–764. doi:10.1051/jcp/1974710761
- [175] Kagi H, Ushijima D, Iizuka R, et al. Micro-pellet method for infrared absorption spectroscopy using a diamond anvil cell under a quasi-hydrostatic condition. *High Press Res.* 2008;28(3):299–306. doi:10.1080/08957950802346868
- [176] Mashino I, Murakami M, Ohtani E. Sound velocities of δ -AlOOH up to core-mantle boundary pressures with implications for the seismic anomalies in the deep mantle. *J Geophys Res: Solid Earth.* 2016;121(2):595–609. doi:10.1002/2015JB012477
- [177] Pinney N, Morgan D. Ab initio study of structurally bound water at cation vacancy sites in Fe- and Al-oxyhydroxide materials. *Geochim Cosmochim Acta.* 2013;114:94–111. doi:10.1016/j.gca.2013.03.032
- [178] Kagi H, Ushijima D, Sano-Furukawa A, et al. Infrared absorption spectra of δ -AlOOH and its deuteride at high pressure and implication to pressure response of the hydrogen bonds, *Journal of Physics: Conference Series*, IOP Publishing, 2010, p. 012052.
- [179] Liu K, Dai L, Li H, et al. Migration of impurity level reflected in the electrical conductivity variation for natural pyrite at high temperature and high pressure. *Phys Chem Miner.* 2018;45:85–92. doi:10.1007/s00269-017-0904-3
- [180] San Juan-Farfán RE, Bayarjargal L, Winkler B, et al. Pressure dependence of the lattice dynamics of diasporite, α -AlO(OH), from Raman spectroscopy and density functional perturbation theory. *Phys Chem Miner.* 2011;38:693–700. doi:10.1007/s00269-011-0442-3
- [181] Kustova G, Burgina E, Sadykov V, et al. Vibrational spectroscopic investigation of the goethite thermal decomposition products. *Phys Chem Miner.* 1992;18:379–382. doi:10.1007/BF00199419
- [182] Legodi MA, de Waal D. The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste. *Dyes Pigm.* 2007;74(1):161–168. doi:10.1016/j.dyepig.2006.01.038
- [183] De Faria DL, Venâncio Silva S, De Oliveira M. Raman microspectroscopy of some iron oxides and oxyhydroxides. *J Raman Spectrosc.* 1997;28(11):873–878. doi:10.1002/(SICI)1097-4555(199711)28:11 < 873::AID-JRS177 > 3.0.CO;2-B
- [184] Liu H, Chen T, Zou X, et al. Effect of Al content on the structure of Al-substituted goethite: a micro-Raman spectroscopic study. *J Raman Spectrosc.* 2013;44(11):1609–1614. doi:10.1002/jrs.4376
- [185] Kubicki JD, Paul KW, Sparks DL. Periodic density functional theory calculations of bulk and the (010) surface of goethite. *Geochem Trans.* 2008;9(1):1–16. doi:10.1186/1467-4866-9-4

- [186] Janot C, Gibert H. Les constituants du fer dans certaines bauxites naturelles étudiées par effet Mössbauer. *Bulletin de Minéralogie*. 1970;93(2):213–223.
- [187] Schwertmann U, Carlson L. Aluminum influence on iron oxides: XVII. Unit-cell parameters and aluminum substitution of natural goethites. *Soil Sci Soc Am J*. 1994;58(1):256–261. doi:10.2136/sssaj1994.03615995005800010039x
- [188] Hazemann J, Manceau A, Sainctavit P, et al. Structure of the $\alpha\text{Fe}_x\text{Al}_{1-x}\text{OOH}$ solid solution: I. Evidence by polarized EXAFS for an epitaxial growth of hematite-like clusters in Fe-diaspore. *Phys Chem Miner*. 1992;19(1):25–38. doi:10.1007/BF00206797
- [189] Bazilevskaya E, Archibald DD, Aryanpour M, et al. Aluminum coprecipitates with Fe (hydr)oxides: does isomorphous substitution of Al^{3+} for Fe^{3+} in goethite occur? *Geochim Cosmochim Acta*. 2011;75(16):4667–4683. doi:10.1016/j.gca.2011.05.041
- [190] Martinez CE, McBride MB. Aging of coprecipitated Cu in alumina: changes in structural location, chemical form, and solubility. *Geochim Cosmochim Acta*. 2000;64(10):1729–1736. doi:10.1016/S0016-7037(00)00344-6
- [191] Fazey P, O'Connor B, Hammond L. X-ray powder diffraction Rietveld characterization of synthetic aluminum-substituted goethite. *Clays Clay Miner*. 1991;39:248–253. doi:10.1346/CCMN.1991.0390304
- [192] Schulze D. The influence of aluminum on iron oxides. VIII. Unit-cell dimensions of Al-substituted goethites and estimation of Al from them. *Clays Clay Miner*. 1984;32(1):36–44. doi:10.1346/CCMN.1984.0320105
- [193] Scheinost AC, Schulze DG, Schwertmann U. Diffuse reflectance spectra of Al substituted goethite: A ligand field approach. *Clays Clay Miner*. 1999;47:156–164. doi:10.1346/CCMN.1999.0470205
- [194] Ruan H, Gilkes R. Kinetics of thermal dehydroxylation of aluminous goethite. *J Therm Anal*. 1996;46:1223–1238. doi:10.1007/BF01979237
- [195] Schulze D, Schwertmann U. The influence of aluminium on iron oxides: X. Properties of Al-substituted goethites. *Clay Miner*. 1984;19(4):521–539. doi:10.1180/claymin.1984.019.4.02
- [196] Naono H, Fujiwara R. Micropore formation due to thermal decomposition of acicular microcrystals of $\alpha\text{-FeOOH}$. *J Colloid Interface Sci*. 1980;73(2):406–415. doi:10.1016/0021-9797(80)90086-7
- [197] Grygar T, Ruan I, Gilkes R. Re-examination of the kinetics of the thermal dehydroxylation of goethite. *J Therm Anal Calorim*. 1999;55:301–309. doi:10.1023/A:1010181416785
- [198] Heller-Kallai L, Rozenson L. Dehydroxylation of dioctahedral phyllosilicates. *Clays Clay Miner*. 1980;28:355–368. doi:10.1346/CCMN.1980.0280505
- [199] Wolska E, Schwertmann U. The mechanism of solid solution formation between goethite and diasporite. *Neues Jahrbuch für Mineralogie Monatshefte*. 1993;1993(5):213–223.
- [200] Ruan H, Frost R, Klopogge JT. The behavior of hydroxyl units of synthetic goethite and its dehydroxylated product hematite. *Spectrochim Acta Part A. Mol Biomol Spectros*. 2001;57(13):2575–2586. doi:10.1016/S1386-1425(01)00445-0
- [201] Ohtani E, Amaike Y, Kamada S, et al. Stability of hydrous phase H MgSiO_4H_2 under lower mantle conditions. *Geophys Res Lett*. 2014;41(23):8283–8287. doi:10.1002/2014GL061690
- [202] Ohtani E, Toma M, Kubo T, et al. In situ X-ray observation of decomposition of superhydrous phase B at high pressure and temperature. *Geophys Res Lett*. 2003;30(2):1029. doi:10.1029/2002GL015549
- [203] Pamato MG, Myhill R, Boffa Ballaran T, et al. Lower-mantle water reservoir implied by the extreme stability of a hydrous aluminosilicate. *Nat Geosci*. 2015;8(1):75–79. doi:10.1038/ngeo2306
- [204] Nishi M, Irifune T, Tsuchiya J, et al. Stability of hydrous silicate at high pressures and water transport to the deep lower mantle. *Nat Geosci*. 2014;7(3):224–227. doi:10.1038/ngeo2074
- [205] Bindi L, Nishi M, Tsuchiya J, et al. Crystal chemistry of dense hydrous magnesium silicates: the structure of phase H, MgSiH_2O_4 , synthesized at 45 GPa and 1000 °C. *Am Mineral*. 2014;99(8–9):1802–1805. doi:10.2138/am.2014.4994

- [206] Walter MJ, Thomson AR, Wang W, et al. The stability of hydrous silicates in Earth's lower mantle: experimental constraints from the systems MgO-SiO₂-H₂O and MgO-Al₂O₃-SiO₂-H₂O. *Chem Geol.* **2015**;418:16–29. doi:[10.1016/j.chemgeo.2015.05.001](https://doi.org/10.1016/j.chemgeo.2015.05.001)
- [207] Yuan H, Zhang L, Ohtani E, et al. Stability of Fe-bearing hydrous phases and element partitioning in the system MgO-Al₂O₃-Fe₂O₃-SiO₂-H₂O in Earth's lowermost mantle. *Earth Planet Sci Lett.* **2019**;524:115714. doi:[10.1016/j.epsl.2019.115714](https://doi.org/10.1016/j.epsl.2019.115714)
- [208] Ohtani E, Yuan L, Ohira I, et al. Fate of water transported into the deep mantle by slab subduction. *J Asian Earth Sci.* **2018**;167:2–10. doi:[10.1016/j.jseaes.2018.04.024](https://doi.org/10.1016/j.jseaes.2018.04.024)
- [209] Nishi M, Tsuchiya J, Kuwayama Y, et al. Solid solution and compression behavior of hydroxides in the lower mantle. *J Geophys Res: Solid Earth.* **2019**;124(10):10231–10239. doi:[10.1029/2019JB018146](https://doi.org/10.1029/2019JB018146)
- [210] Sano A, Ohtani E, Kondo T, et al. Aluminous hydrous mineral δ -AlOOH as a carrier of hydrogen into the core-mantle boundary. *Geophys Res Lett.* **2008**;35:L03303. doi:[10.1029/2007GL031718](https://doi.org/10.1029/2007GL031718)
- [211] Mao H-K, Mao WL. Key problems of the four-dimensional Earth system. *Matter Radiat Extremes.* **2020**;5(3):038102. doi:[10.1063/1.5139023](https://doi.org/10.1063/1.5139023)
- [212] Gumsley AP, Chamberlain KR, Bleeker W, et al. Timing and tempo of the great oxidation event. *Proc Natl Acad Sci USA.* **2017**;114(8):1811–1816. doi:[10.1073/pnas.1608824114](https://doi.org/10.1073/pnas.1608824114)
- [213] Philippot P, Ávila JN, Killingsworth BA, et al. Globally asynchronous sulphur isotope signals require re-definition of the great oxidation event. *Nat Commun.* **2018**;9(1):2245. doi:[10.1038/s41467-018-04621-x](https://doi.org/10.1038/s41467-018-04621-x)
- [214] Warke MR, Di Rocco T, Zerkle AL, et al. The great oxidation event preceded a paleoproterozoic “snowball Earth”. *Proc Natl Acad Sci USA.* **2020**;117(24):13314–13320. doi:[10.1073/pnas.2003090117](https://doi.org/10.1073/pnas.2003090117)
- [215] Poulton SW, Bekker A, Cumming VM, et al. A 200-million-year delay in permanent atmospheric oxygenation. *Nature.* **2021**;592(7853):232–236. doi:[10.1038/s41586-021-03393-7](https://doi.org/10.1038/s41586-021-03393-7)
- [216] Wogan NF, Catling DC, Zahnle KJ, et al. Rapid timescale for an oxic transition during the great oxidation event and the instability of low atmospheric O₂. *Proc Natl Acad Sci USA.* **2022**;119(37):e2205618119. doi:[10.1073/pnas.2205618119](https://doi.org/10.1073/pnas.2205618119)
- [217] Luo C, Deng X, Wang W, et al. Wentzcovitch, cij: a python code for quasiharmonic thermoelasticity. *Comput Phys Commun.* **2021**;267:108067. doi:[10.1016/j.cpc.2021.108067](https://doi.org/10.1016/j.cpc.2021.108067)
- [218] Li Y, Vočadlo L, Brodholt JP. Elast: a toolkit for thermoelastic calculations. *Comput Phys Commun.* **2022**;273:108280. doi:[10.1016/j.cpc.2021.108280](https://doi.org/10.1016/j.cpc.2021.108280)
- [219] Wu Z, Wentzcovitch RM. Quasiharmonic thermal elasticity of crystals: An analytical approach. *Phys Rev B.* **2011**;83(18):184115. doi:[10.1103/PhysRevB.83.184115](https://doi.org/10.1103/PhysRevB.83.184115)
- [220] Zhao Y, Deng X, Chen L, et al. Is there a carbonated mid-lithosphere discontinuity in cratons? *J Geophys Res: Solid Earth.* **2024**;129(6):e2024JB028925. doi:[10.1029/2024JB028925](https://doi.org/10.1029/2024JB028925)
- [221] Deng X, Song J, Qian W, et al. Seismic signals induced by the Metasomatism of mantle wedge by siliceous melts: insights from the elasticity of orthopyroxene at high pressure and temperature. *Tectonophysics.* **2023**;846:229681. doi:[10.1016/j.tecto.2022.229681](https://doi.org/10.1016/j.tecto.2022.229681)