

# Key problems of the four-dimensional Earth system

Cite as: Matter Radiat. Extremes 5, 038102 (2020); doi: 10.1063/1.5139023

Submitted: 17 November 2019 • Accepted: 31 March 2020 •

Published Online: 28 April 2020



View Online



Export Citation



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**Note:** This paper is part of the Special Issue on High Pressure Science.

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## ABSTRACT

Compelling evidence indicates that the solid Earth consists of two physicochemically distinct zones separated radially in the middle of the lower mantle at ~1800 km depth. The inner zone is governed by pressure-induced physics and chemistry dramatically different from the conventional behavior in the outer zone. These differences generate large physical and chemical potentials between the two zones that provide fundamental driving forces for triggering major events in Earth's history. One of the main chemical carriers between the two zones is H<sub>2</sub>O in hydrous minerals that subducts into the inner zone, releases hydrogen, and leaves oxygen to create superoxides and form oxygen-rich piles at the core–mantle boundary, resulting in localized net oxygen gain in the inner zone. Accumulation of oxygen-rich piles at the base of the mantle could eventually reach a supercritical level that triggers eruptions, injecting materials that cause chemical mantle convection, superplumes, large igneous provinces, extreme climate changes, atmospheric oxygen fluctuations, and mass extinctions. Interdisciplinary research will be the key for advancing a unified theory of the four-dimensional Earth system.

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## I. OVERVIEW

Beginning from Alfred Wegener's original picture of continental drift, the plate tectonics revolution in the 1960s unified crustal observations, including seismic belts, island arcs, orogenic systems, midocean ridges, magnetic reversal stripes, and other diverse surface features into a powerful two-dimensional global model. Subsequent efforts over the following half century in geophysics, geodynamics, and high-pressure mineral physics have revealed an array of large-scale structures and phenomena occurring deep in the Earth's mantle and core. Meanwhile, research in geochemistry, petrology, stratigraphy, geochronology, paleoclimatology, and paleontology has identified a number of pivotal catastrophic events throughout the planet's 4.6 Gyr time dimension, including Wilson cycles,<sup>1</sup> large igneous provinces (LIPs),<sup>2</sup> the Great Oxidation Event (GOE),<sup>3</sup> subsequent oxygen fluctuations, snowball Earth events,<sup>4</sup> and mass extinctions. We are now in the position to explore fundamental understanding of our four-dimensional (4D) Earth system. The present article raises key questions inspired by recent paradigm-changing observations in high-pressure mineral physics<sup>5–11</sup> and

proposes a new set of hypotheses and key tests. The focus is on understanding the altered physicochemical world in the depth dimension that needs to be fully appreciated and integrated with surficial events that have occurred in the time dimension.

### A. Are Earth's catastrophic, surficial events a manifestation of its deep internal processes?

Observations of the 4D Earth have left us with many long-standing, unanswered questions: What is the material origin of life? How did inorganic compounds convert to the organic ingredients necessary for starting indigenous life forms on Earth? What were the oxygen sources for the GOE and subsequent large oxygen fluctuations? What caused episodic mass extinctions and the emergence of new lifeforms? What triggered catastrophic environmental climate changes? Why did our planet go through glacial and interglacial cycles? What caused the massive melting of the lithosphere that generated the flood basalts of LIPs? What perturbed steady-state mantle convection and triggered the merging and rifting of supercontinents? Successions of gradual progressions and catastrophic

revolutions have been meticulously identified and correlated with one another in time and space, yet wildly different, unrelated mechanisms ranging from asteroid impacts,<sup>12</sup> to microbial photosynthesis,<sup>13</sup> to superplumes,<sup>14</sup> etc. have been proposed. Most of the diverse hypotheses are based on surficial or external origins of stochastic nature, with little consideration of deep Earth processes. The atmosphere, biosphere, hydrosphere, and lithosphere represent only a minor fraction of the Earth: the bulk of our planet's mass is hidden at depth. Could there be an overarching internal driving force that dictates the surficial behavior of the 4D Earth system?

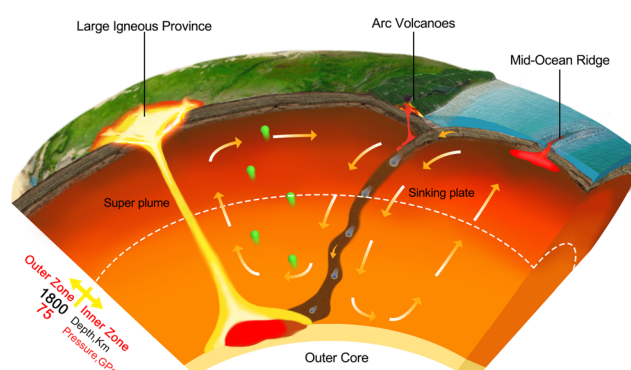
## B. Two key regimes in the Earth

The effects of the depth dimension are dominated by pressure  $P$ . Discovery of the quartz–coesite transition at 3.5 GPa in 1953<sup>15</sup> marked the realization that an ordinary mineral such as quartz could change into a new mineral by structural rearrangement under the high- $P$  conditions corresponding to a moderate depth. High- $P$  mineral physics has come a long way from its initial focus on the discovery of new minerals to the exploration of new physics and new chemistry present in the new phases and an evaluation of their impacts on the Earth system. From the crust down to the upper portion of the lower mantle, high- $P$  phases are formed by structural alteration, but the guiding rules of physics and chemistry remain unchanged. Further down at greater depth, however, phase transitions are often associated with pressure-induced paradigm changes in the chemical and physical guidelines. For instance, the conventional wisdom on the stoichiometry of minerals being based on the ionic valences of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cl}^-$ ,  $\text{O}^{2-}$ , etc. is no longer a constraint; surprising chemistry, such as  $\text{Na}_3\text{Cl}$ ,  $\text{NaCl}_3$ ,<sup>16</sup> and  $\text{FeO}_2$ ,<sup>8</sup> appears. The general concept of hard-sphere atomic packing in crystallography gives way to complex structures reflecting non-spherical electronic configurations. Pressure enhances and changes the electronic configuration of  $3d$  electrons from magnetic spin-parallel to spin-paired.<sup>17</sup> The Bernal–Fowler ice rule is no longer followed for hydroxyls and is replaced by symmetric hydrogen bonding at high- $P$  low- $T$ <sup>18</sup> and to superionic hydrogen at high  $P$ – $T$ .<sup>19</sup>

From the chemical and physical point of view, therefore, the solid Earth can be divided at approximately 1800 km depth (75 GPa) into two distinct regimes: the outer zone (OZ) where the ordinary rules apply, and the inner zone (IZ) where new high- $P$  behaviors emerge (Fig. 1). Common physicochemical variations within a system provide mechanisms to drive countless interesting processes, such as Carnot cycles, thermoelectric heat pumps, electrochemical batteries, convection, dynamos, etc. The contrasts between the OZ and IZ with similar bulk compositions yet dramatically different physical and chemical operating rules certainly provide previously unexpected driving potentials for major events. Based on new knowledge of the contrasts, here we will explore their consequences and point out key problems that open new research directions.

## C. Two key boundaries

The Earth's surface boundary where lithosphere, atmosphere, hydrosphere, and biosphere meet is the habitable zone. Its complexity is well appreciated and has been extensively studied. The steep temperature gradient in the lithosphere creates the condition for partial melting and crystallization that leads to Bowen's



**FIG. 1.** The division between the outer zone (OZ) and inner zone (IZ). Blue droplets denote  $\text{H}_2\text{O}$  in hydrous minerals subducting with a sinking plate into the IZ, and reacting with Fe in the deep lower mantle [reaction (1)] to form  $\text{FeO}_2\text{H}_x$  and release hydrogen (green droplets).

differentiation and fractionation series in the rocks that make up oceanic and continental crusts.

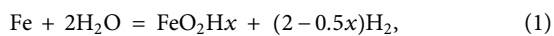
On the other hand, inside the Earth, the inaccessible core–mantle boundary (CMB) lies 2900 km beneath the surface, where the molten iron core meets the solid silicate/oxide mantle (Fig. 1). The CMB is a thermochemical boundary layer, with the greatest contrast in physical and chemical properties in the Earth,<sup>20,21</sup> but is very poorly understood. It is the interface where plates end and plumes originate. Its extremely steep temperature gradient provides the heating plate for driving plate tectonics. It is safe to postulate that major activities at the CMB must have far-reaching impacts on Earth's surface, yet such impacts are rarely considered owing to our lack of understanding of the CMB, which is further obscured by the previously unknown physics and chemistry of the IZ. Therefore, it is crucial to understand the nature of the CMB and its role in surface events. This requires challenging research efforts that address a number of important questions: How do core and mantle interact, react, and equilibrate? What are the solid and liquid phase assemblages at the CMB? How do they differentiate and fractionate to form the enigmatic  $D''$  layer, which is sometimes viewed as an “anticrust”? What are the mechanisms that stabilize or drastically perturb the CMB layer? What are the surface manifestations of CMB activity?

## D. Key reactions

Facing the new frontier of IZ physics and chemistry, we start with the most basic system, H–O–Fe, which represent the key elements of the volatiles, mantle, and core, respectively. Volatile components of the Earth are responsible for major events that have occurred in the atmosphere, hydrosphere, and biosphere. It is therefore essential to understand their circulation, storage, and reactions in the deep interior. Hydrogen is the most abundant element in the Universe. Although the majority of H was likely lost early during Earth's formation, it is still the key element in the hydrosphere and biosphere. It is by far the most mobile element and is responsible for volatile transport in the mantle. Oxygen is the most abundant element by number of atoms in the Earth, and is concentrated in the silicate/oxide mantle. It plays dual roles as the backbone of the strong,

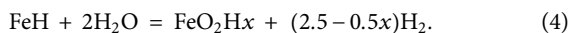
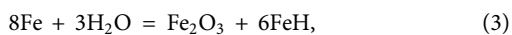
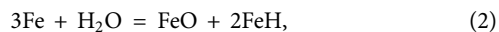
refractory ceramic minerals and in volatile compounds with H, C, N, S, etc. in the atmosphere and throughout the mantle. Iron is the most abundant element in the Earth by weight, and the early separation of the iron core from the rocky mantle is the most significant differentiation event in Earth's history—defining to first order the chemical distribution in the planet. The unfilled *d* orbitals, multiple oxidation states, and magnetism that result in the rich physics and chemistry of Fe are particularly amenable to the pressure effects. While we focus our consideration on the three principal elements H, O, and Fe, the following discussions can be expanded to include other major elements such as Mg, Si, and Al, as well as minor elements.

The key reaction in the H–O–Fe system under IZ *P–T* conditions involves the reaction of iron with H<sub>2</sub>O to form hydrogenated iron-bearing superoxides (HISOs), FeO<sub>2</sub>H<sub>*x*</sub>, and release hydrogen.<sup>5–8</sup> In simplified form, this reaction is

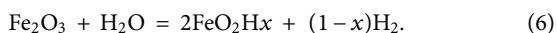
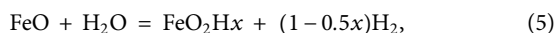


where  $0 \leq x \leq 1$ . The name superoxide refers to excessive oxygen above what can be balanced by ferric or ferrous iron, indicating the presence of O–O dimers. The Fe in a HISO may be partially substituted by other ions, such as Mg<sup>2+</sup> and Al<sup>3+</sup>.<sup>22</sup>

If the supply of H<sub>2</sub>O is insufficient, reaction (1) may stop at intermediate steps, producing less-oxidized iron oxides and iron hydride, which can later react further with H<sub>2</sub>O to reach the final state of HISO and release hydrogen:



The Fe in reaction (1) could also be replaced by iron oxides, and H<sub>2</sub>O could come from hydrous minerals. For instance, iron oxides with varying stoichiometries could be further oxidized by H<sub>2</sub>O to produce the HISO and release hydrogen:



Experimentally,<sup>5,7</sup> the final product is the surprising assemblage of a HISO with a very high oxygen-to-cation ratio coexisting with the presumably reducing H<sub>2</sub>. These reactions have the important consequence of splitting H<sub>2</sub>O, releasing hydrogen, which migrates upward, and storing extra oxygen in the IZ (Fig. 1).

## E. Key technology

Advances in deep Earth mineral physics have been enabled by advances in high *P–T* technology.<sup>23,24</sup> One of the key elements, iron, is uniquely suited for a plethora of *in situ* high-*P* synchrotron probes.<sup>25</sup> The electronic configuration in relation to the crystal field energy and its effects on the thermal and electrical conductivity of iron-bearing minerals can be investigated by high-*P* optical spectroscopy and electrical probes.<sup>26,27</sup> Magnetism in iron-bearing minerals can be investigated by high-*P* neutron diffraction and synchrotron x-ray magnetic circular dichroism and by Mössbauer

spectroscopy.<sup>28</sup> Being a Mössbauer isotope, <sup>57</sup>Fe enables the use of nuclear-resonant x-ray forward scattering for studying high-*P* magnetism, valence states, and site occupancy of iron, as well as nuclear-resonant inelastic x-ray scattering for probing the high-*P* phonon density of states for comparison with seismological observations in the mantle<sup>6,29</sup> and the determination of iron force constants for constraining geochemical models of iron alloys of light elements.<sup>30,31</sup> The phonon dispersion of an iron-bearing mineral can be determined at high *P* by high-resolution nonresonant inelastic x-ray scattering for comparison with seismological longitudinal-wave observations.<sup>32</sup> The iron valence state and site occupancy are also revealed by high-*P* x-ray absorption spectroscopy near the Fe K-edge, and the spin-pairing transition of iron can be unequivocally identified by monitoring the Fe Kβ fluorescence peak shoulder using high-*P* x-ray emission spectroscopy.<sup>17</sup> The continuous development of a range of characterization tools is essential for continuing advances in our understanding of this key element.

Most volatiles in the lithosphere are hidden in minor minerals within rocks that represent a complex mineral assemblage typically composed of three to five major minerals and a dozen minor and accessory minerals. Although the *P–T* conditions of the entire Earth's deep interior can now be reached with laser-heated diamond anvil cells (DACs), the standard petrographic tools, such as petrographic microscopy and electron and ion microprobes, are incompatible with an ultrahigh pressure environment. For a long time, the only possible probe for *in situ* high *P–T* structure identification has been polycrystalline x-ray diffraction, which typically produces less than a dozen useful distinctive powder diffraction rings at *d* spacings greater than 1 Å. At smaller *d* spacings, a large number of additional weak rings may exist, but they often overlap and merge into a continuum, thus becoming undistinguishable. The usable information is far less than the required constraints for uniquely defining the dozen or so unknown minerals in a rock. A solution is, however, in sight with the newly developed methodology of multigrain crystallography (MGC).<sup>33</sup> Using a computational approach that can sort out thousands of diffraction spots for hundreds of individual crystallites, in principle, all diffraction spots, regardless of large or small *d* spacings, can yield a great deal of information that not only can enable unique determination of crystallographic parameters of the new unknown minerals, but also can provide a redundancy check many times over for robustness.<sup>34</sup>

Another important parameter in petrology is texture information for constituent minerals, which has been unavailable in ordinary DAC experiments. The recent development of nanoscale transmission x-ray microscopy has enabled imaging of the size and shape of individual minerals with a spatial resolution of tens of nanometers, as well as determination of the dihedral angle of an iron melt in a silicate matrix under lower-mantle pressure conditions.<sup>35</sup> Now we can hope to conduct realistic petrographic studies under the conditions of the IZ.

## II. TRANSPORT AND REACTIONS IN THE INNER ZONE

### A. How much water enters the inner zone?

Reaction (1) relies on the availability of H<sub>2</sub>O, in the form of hydroxyls in hydrates and hydrous minerals as well as free H<sub>2</sub>O. The key question is thus the net amount of H<sub>2</sub>O entering the IZ. The total

amount of H<sub>2</sub>O in a subducting slab was estimated by Peacock to be  $1 \times 10^{12}$  kg/yr.<sup>36</sup> van Keken *et al.*<sup>37</sup> estimated that 70% of the H<sub>2</sub>O returns to the surface through island arc volcanism (Fig. 1), and approximately  $3 \times 10^{11}$  kg/yr continues down into the mantle transition zone (MTZ, 400–670 km depth). The MTZ is generally thought to be the wettest region in the Earth, because its main minerals, ringwoodite ( $\gamma$ -phase) and wadsleyite ( $\beta$ -phase)<sup>38</sup> can accommodate several weight percent H<sub>2</sub>O. The slab descending through the wet MTZ is therefore more likely to absorb additional H<sub>2</sub>O and carry more than  $3 \times 10^{11}$  kg/yr H<sub>2</sub>O into the lower mantle. In addition, there could be a primordial H<sub>2</sub>O reservoir in the IZ.<sup>39</sup> We will use the value of  $3 \times 10^{11}$  kg/yr for an order-of-magnitude estimate.

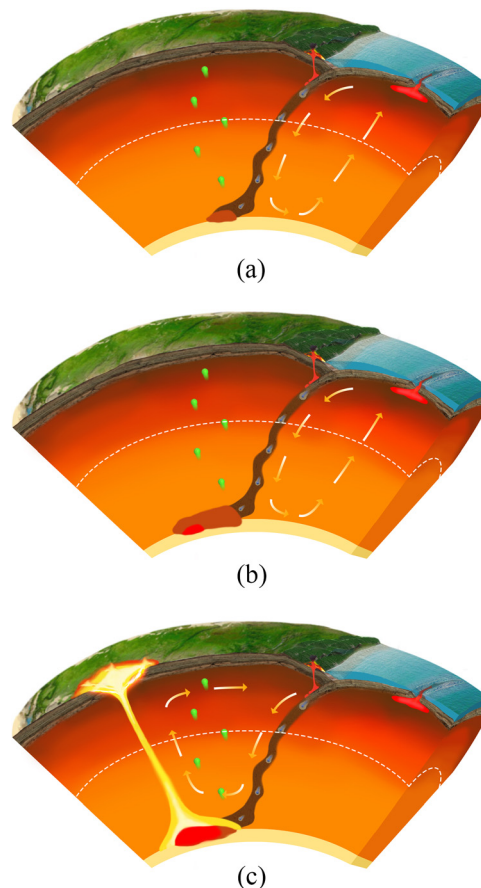
We have very little information on H<sub>2</sub>O in the lower mantle. Only six years ago, the lower mantle was considered dry owing to the lack of H<sub>2</sub>O-bearing minerals: all known hydrous minerals broke down at the high  $P$ - $T$  conditions of the lower mantle. With the discoveries in 2014 of the dense hydrous phase-H and  $\delta$ -phase,<sup>40,41</sup> hydration of the lower mantle has become a more plausible scenario,<sup>42,43</sup> and the case for this scenario has been further strengthened by the stream of subsequent observations of high  $P$ - $T$  hydrogen-bearing phases.<sup>7,22,44</sup> It should also be noted that the breakdown of water-bearing wadsleyite and ringwoodite to bridgmanite and ferropericlase and release of H<sub>2</sub>O does not necessarily prevent the descent of H<sub>2</sub>O, which could be carried down as fluid inclusions in minerals<sup>45,46</sup> or trapped between grain boundaries. Whether a significant fraction of H<sub>2</sub>O will escape at grain boundaries or be trapped as fluid inclusions depends upon the dihedral angle relationship with the host minerals at high  $P$ - $T$ , which can be investigated by new mineral physics techniques.<sup>35</sup>

## B. What happens to the ascending hydrogen?

The primary consequence of H<sub>2</sub>O entering the IZ is the reaction with iron and iron-bearing oxides to form HISOs and release hydrogen [reaction (1)].<sup>7,8,47</sup> The  $3 \times 10^{11}$  kg/yr of H<sub>2</sub>O will produce  $1.7 \times 10^{10}$  kg/yr of free hydrogen, which is very mobile and will diffuse or infiltrate upward. The HISOs will also release additional hydrogen. The deep Earth's hydrogen cycle will thus take the form of water-down and hydrogen-up [Fig. 2(a)].

The released hydrogen will react with the materials along the ascending path to form hydrides or remain as free H<sub>2</sub>, depending upon the chemistry under the  $P$ - $T$  conditions. Hydrogen forms hydrides with practically all elements at low  $T$  and high  $P$ , but most hydrides, except for some light-element hydrides, will dehydrogenate and release H<sub>2</sub> under the high- $T$  conditions of the deep Earth geotherm. In the OZ, hydrogen reacts with carbon, nitrogen, and oxygen to form organic compounds with strong covalent CH, NH, and OH bonds that can survive the geotherm  $T$ . Owing to their low-density buoyancy, these compounds will ascend and constitute an important source of hydrogen and hydrocarbons for deep natural gas reservoirs. This is a natural consequence of the water–hydrogen cycling process, regardless of the biogenic–abiogenic controversy regarding shallow petroleum resources.

The hydride and organic chemistry under IZ  $P$ - $T$  conditions is a vast unknown research area that needs to be explored. Only a very tiny fraction of the  $20 \times 10^6$  known organic compounds have been investigated at high  $P$ .<sup>48,49</sup> The  $s$ - $p$  bonding of C and N and hydrogen bonding will be dramatically changed in the IZ, and should be the



**FIG. 2.** The OZ–IZ interaction processes. (a) A steady-state process of reaction (1) brings H<sub>2</sub>O in the sinking plate to react with Fe, form oxygen-rich patches (ORPs), and release hydrogen. (b) The ORPs accumulate, partially melt, and form oxygen-rich magma (ORM) chambers (red). (c) A catastrophic event of ORM eruption, forming superplumes, perturbing thermal convections, generating chemical convections, and causing large-scale melting in the lithosphere.

focus for future investigations. It has been proposed that a descending slab would lose its hydrogen by dissolution into the liquid outer core,<sup>43</sup> but the endurance of oceans throughout the Earth's history indicates the return of hydrogen and minimal loss to the core. Extension of the very low- $P$  study of hydrogen partitioning in molten iron<sup>50</sup> to the CMB  $P$ - $T$  conditions will be key to solving this problem.

## C. High- $P$ crystal chemistry of iron

As a transition element with partially filled  $3d$  orbitals, iron in minerals controls their redox potential, magnetism, electrical conductivity, optical spectroscopy, etc. Iron is a secondary element in the OZ, but has a greater impact in comparison with the more abundant oxygen, silicon, and magnesium. In the IZ, iron is the predominant constituent, and its significance is further magnified by the  $P$ -induced dramatic changes in its fundamental physics and chemistry.

Iron in metallic (Fe<sup>0</sup>), ferrous (Fe<sup>2+</sup>), and ferric (Fe<sup>3+</sup>) states is the key variable that mediates the full range of redox behaviors from minerals to organisms. However, the ferrous/ferric ratio alone does

not define the oxygen fugacity:<sup>51</sup> it must be considered within the specific host mineral phase assemblage. For instance, under pressure,  $\text{Fe}^{2+}$  in a mineral can disproportionate into  $\text{Fe}^{3+}$  and metallic iron ( $\text{Fe}^0$ ),<sup>52,53</sup> and the disproportionation transitions become more common at higher  $P$ , as shown by the abundant  $\text{Fe}^{3+}$  in high- $P$  bridgmanite of the lower mantle.<sup>54</sup>

According to Hund's rule, the five degenerate  $3d$  orbitals of an iron atom are filled with electrons that maximize the parallel magnetic spin. In a crystal, however, the anions surrounding the iron exert a crystal field that splits the degenerate energies of the five  $3d$  orbitals. The crystal field splitting energy increases with increasing  $P$ , and, under the extreme pressure of the IZ, it exceeds Hund's exchange coupling energy and forces the parallel spins into opposite-spin pairs, thus minimizing the net spin. The "spin-pairing transition" or "high-spin to low-spin transition" changes the elemental affinity,<sup>17</sup> ionic radius, magnetism, etc. and results in a totally new set of physical and chemical properties as though the iron has become a new element. The definition of siderophile will take a different new meaning, and we should expect a whole new set of iron compounds of "unusual stoichiometry" with other cations and anions, and especially with volatile elements, including chalcogens, halides, and noble gases.<sup>55</sup>

#### D. High- $P$ crystal chemistry of oxygen

Oxidation–reduction (redox) is the key chemical reaction that dictates all inorganic, organic, and biochemical processes of the 4D Earth. The molecular  $\text{O}_2$  in the atmosphere and hydrosphere sustains aerobic life forms in the biosphere through redox reactions between  $\text{O}^0$  and  $\text{O}^{2-}$ . The oxygen fugacity is defined for the activity of  $\text{O}_2$  ( $\text{O}^0$ ), and is experimentally measured by a series of calibrated oxide buffers such as iron–wüstite, wüstite–magnetite, nickel–nickel oxide, fayalite–magnetite–quartz (FMQ), and magnetite–hematite. In the lithosphere, asthenosphere and throughout the OZ, oxygen in oxides is present in the form of  $\text{O}^{2-}$ , with very little  $\text{O}_2$  molecules. All minerals in the buffer system, such as FM, become unstable under the high  $P$ – $T$  conditions, but the same notion is still useful to describe the oxygen fugacity on an abstract scale relative to the FMQ.<sup>51</sup>

Further down into the IZ, the redox reaction is controlled not only by the valence of iron but also by oxygen itself. The oxygen is no longer limited to the  $-2$  valence state. The excess oxygen forms  $\text{O}_2$  dimers mimicking the presence of molecular oxygen in a mineral.<sup>56,57</sup> The oxygen molecules in the pure element change from  $\text{O}_2$  to  $\text{O}_8$  under high pressure,<sup>58,59</sup> making the definition of redox potential based on  $\text{O}_2$  activity in a series of unstable buffers even more hypothetical. In the solid Earth, redox is not a global parameter, but is relevant only within the local rock system. A more tangible description of redox potential is thus the total amount of oxygen relative to the cations. For this purpose, we call the oxide with excess oxygen a superoxide.

#### E. Hydrogenated iron-bearing superoxides (HISOs)

HISOs comprise a new class of materials playing a key role in the IZ. They represent a group of minerals of different structures and compositions, sharing the common character of three key ingredients: superprotonic hydrogen, low-spin ferrous or ferric iron, and an unconventionally high amount of oxygen. Here the charge of the oxygen anion is variable and significantly less than 2, leading to a

variable and high oxygen stoichiometry.<sup>56</sup> After the initial discovery of  $\text{FeO}_2\text{H}_x$  with the pyrite structure, a growing number of HISOs with the general form  $\text{FeO}_y\text{H}_x$  in pyrite and hexagonal structures have been observed, with a variable high number of  $y$  and possible cation substitution of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  by  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$ . HISOs are chemically very accommodating to a wide range of substitutions. Preliminary experiments and theories have indicated that their Fe can be substituted with Al, Mg, and other cations,<sup>22</sup> their O with other anions, and their H with He<sup>55</sup> and other small atoms and inert gases. Many new discoveries of different phases and a variety of new structures are expected to emerge.

The low-spin  $\text{Fe}^{2+}$  has ionic radii similar to  $\text{Mg}^{2+}$ , but with considerably higher atomic weight, making it a high-density oxide that can gravitationally settle at the bottom of the mantle above the liquid core. With  $3 \times 10^{11}$  kg/yr of  $\text{H}_2\text{O}$  descending to meet an unlimited reservoir of Fe from the core, the total amount of excess oxygen left in HISOs would be  $1.2 \times 10^{21}$  kg over the history of the Earth, which could accumulate into a 4 km thick HISO layer on top of the CMB [5,6],<sup>5,6</sup> and this layer would be thicker if it were mixed with other mantle materials [Fig. 2(b)].

In the hydroxyl group of hydrous minerals, hydrates, and  $\text{H}_2\text{O}$  in the OZ, the hydrogen atom is bonded with an oxygen atom to form a strong O–H covalent bond and with another oxygen in the opposite direction by a weak hydrogen bond. At high- $P$  low- $T$ , the covalent and hydrogen bonding changes to O–H–O symmetrical hydrogen bonding.<sup>18</sup> Under the high  $P$ – $T$  conditions in the IZ, the hydrogen in HISOs becomes a superionic proton,<sup>19</sup> moving freely in the  $\text{O}^{2-}$  lattice and thus changing the name from hydrous to hydrogenated.

Reaction (1) divides the total amount of hydrogen into two portions: the ascending released hydrogen and the descending hydrogen in HISOs. The HISOs may further release a portion or all of their hydrogen, depending upon the  $P$ – $T$  conditions. The residual superprotonic hydrogen in HISOs is often nonstoichiometric.<sup>7</sup> In the OZ, hydrogen is known to affect electrical and thermal conductivities. In the IZ, the superprotonic hydrogen could play a dominant role in electrical and thermal transport properties, as well as the magnetism of the geodynamo and other geophysical phenomena.<sup>19</sup>

#### F. Mantle heterogeneity and mass transport

The Earth is a chemically heterogeneous system radially, laterally, and locally. Seismology defines the spherical shell structure of the crust, upper mantle, transition zone, lower mantle, outer core and inner core with first-order chemical differences and/or depth-induced phase transitions that are manifested as seismic discontinuities. Subducting slabs and rising plumes can penetrate the spherical shell boundaries and introduce materials into chemically foreign regions. Chemical reactions occur to reach local equilibrium at the interfaces and within the intrusives that enter a new  $P$ – $T$  regime. Local mass transport is driven by chemical potentials and limited by the diffusion mobility of the elements.

In the HISO-bearing provinces, the superprotonic behavior is particularly important. It implies that hydrogen moves freely in HISOs and equalizes the hydrogen fugacity of the IZ. By contrast, the diffusion rate of oxygen in HISOs is expected to be similar to that of  $\text{Mg}^{2+}$  in oxides, which is practically immobile over geological time.<sup>60</sup> This implies that oxygen fugacity is highly heterogeneous within a solid slab, and a very large range of oxygen fugacity can exist owing to

chemical zoning and local equilibrium layers analogous to metasomatic zoning.<sup>61</sup> Instead of defining the overall oxygen fugacity for the lower mantle or large provinces, a practical approach would be to account for the overall budget of excess oxygen resulting from the water-down hydrogen-up global water cycle, which turns into a net oxygen pump down into the IZ.

The mantle is predominantly solid, with local occurrences of partial melting, which are more common near the CMB owing to the higher  $T$  and the proximity to the liquid iron core. Depending upon the melt fraction and the intergranular dihedral angle, infiltration and intergranular fluid diffusion could be a major mechanism for mass transport. Gravitational sorting and large-scale differentiation to form HISO-rich provinces would be feasible. Analogous to the magmatic differentiation that generated the heterogeneous crust, reaction (1) and the formation of HISO-bearing patches may play a key role in generating the complexity and heterogeneity of the D'' layer on top of the CMB.<sup>20</sup> Seismology reveals large-scale, laterally heterogeneous regions such as large low-shear-velocity provinces (LLSVPs) and ultralow-velocity zones (ULVZs), which have been proposed as mixtures of HISOs and other mantle materials.<sup>5,6</sup> Extensive experimental efforts are needed to understand the mineralogical and compositional nature of these heterogeneous regions.

### G. Oxygen reservoirs, temporary storage, and eruptions

Because the water cycle in the IZ releases hydrogen upward, it becomes a local oxygen injector, and oxygen will accumulate in the IZ over time. LLSVPs and ULVZs at the CMB may contain mixtures of HISOs with other mantle and core materials.<sup>6</sup> Nevertheless, HISOs increase the net oxygen budget beyond normal mantle oxides, thus continuously forming and stockpiling oxygen-rich patches (ORPs) that reach isostasy at the CMB [Fig. 2(b)]. The thickened ORPs span a large temperature range at the CMB, where a steep thermal boundary layer exists.<sup>20</sup> When the bottom of an ORP crosses its solidus melting point, partial melting occurs. Preliminary studies indicate that the incongruent melts will be particularly enriched in O and other volatiles: H, S, Cl, F, etc.; they may form oxygen-rich magma (ORM) chambers trapped in the solid ORP [Fig. 2(b)].

Small amounts of ORM may erupt regularly, but most ORM continues to grow and stockpile. Eventually, when a critical stockpile is reached, a huge eruption may occur to release the excess ORM [Fig. 2(c)]. This will then be followed by a period of tranquility after the ORM has been exhausted. This would provide an essential mechanism for steady-state and catastrophic cycles in the 4D Earth. The buildup–release cycles are analogous to smaller-scale catastrophes like volcanic eruptions and seismic events in the crust. In-depth understanding requires experimental petrology and melting studies of ORM under CMB conditions analogous to the Bowen's series studies of crustal rocks.

## III. KEY EVENTS

### A. Steady-state and catastrophic periods in mantle dynamics

The continental drift hypothesis inspired the plate tectonics revolution. The 2D merging and rifting of supercontinents has now been well documented over the Earth's history, but its mechanism is still poorly understood.<sup>14</sup> Thermal convection is generally thought to

be the steady-state mechanism of plate tectonics. The key question is then what perturbed the steady state and led to the merging and rifting of supercontinents?

The water–hydrogen cycles in the IZ provide a chemical convection mechanism for mantle convection. Ascending hydrogen and regular small ORM eruptions add buoyancy to the mantle plumes and enhance steady-state thermal convection. Large catastrophic eruptions perturb the steady state, and may create superplumes that can rift or merge supercontinents.<sup>14</sup> Here, the superplume may not be particularly larger or hotter than a regular plume, but may contain more oxygen, hydrogen, and possibly iron from ORM. Mineral physics studies of the composition and buoyancy of ORM, its compositional changes, and its equation of state during its ascent provide the key information needed for geodynamic computation to model chemical convection.

### B. Large igneous provinces (LIPs) in the lithosphere

Catastrophic eruption of ORM releases a large quantity of oxygen and volatile components to form a solidified or partially molten superplume rising through the mantle. The composition of the superplume may be altered through assimilation of the surrounding mantle materials along the 2900 km journey to the surface, but its enrichment in oxygen, hydrogen, and possibly iron still prevails. These ingredients will lower the melting temperature of the rocks at the bottom of the lithosphere, which is already close to the melting temperature. A large volume of magmas could then be generated, creating an episode of gigantic flood basalt [Fig. 2(c)].

The scenario of a catastrophic ORM superplume is consistent with the observations of episodic LIPs, which are well documented in Earth's history,<sup>2</sup> although their origins are poorly understood.<sup>62</sup> To further establish the ORM-based superplume hypothesis requires key mineral physics studies of the ORM components through the  $P$ – $T$ – $x$  journey from the CMB to the lithosphere, melting studies of ORM plume materials interacting with lithospheric rocks, and geochemical studies of LIPs in light of this possible deep origin.

### C. Environmental changes at the Earth's surface in the atmosphere and hydrosphere

The excess oxygen and hydrogen will be lost as volatiles when magma reaches the Earth's surface, leaving few clues in the rock, but having major impacts on the atmosphere and hydrosphere. The aforementioned potentially hidden  $1.2 \times 10^{21}$  kg of oxygen is three orders of magnitude greater than the total mass of oxygen ( $1.2 \times 10^{18}$  kg) in today's atmosphere. The steady-state flux of deep-source volatiles help to sustain a stable composition in the atmosphere and ocean, while catastrophic ORM eruptions can greatly disturb the balance. For instance, the internal source of oxygen from catastrophic ORM eruptions could provide an explanation for the Great Oxidation Event (GOE) that occurred  $\sim 2.3$ – $2.4$  Gyr ago when atmospheric oxygen increased dramatically from 0 to today's  $\sim 20\%$  level. Subsequent periods of ORM tranquility–eruption could also explain the large fluctuations in the oxygen level in the atmosphere and hydrosphere recorded throughout Earth's history.<sup>63–65</sup>

Earth's surface receives energy primarily from the Sun. Gas molecules and particles in the atmosphere may act as a sunscreen to block solar radiation or as a greenhouse to trap solar energy. Changes

in climate are therefore highly dependent upon atmospheric composition. Oxygenation,<sup>66</sup> other volatiles such as sulfur,<sup>67</sup> and volcanic ash are some of the culprits possible responsible for extreme temperature variations from global warming to snowball Earths. They would also be a natural consequence of the episodes of ORM-to-LIP volcanism.

#### D. Emergence of life and mass extinction events in the biosphere

An intrinsically living planet must have a habitable surface environment and sufficient biochemical ingredients that can accumulate and interact to form living organisms. The key building blocks include hydrocarbons, ammonia, and water, which share a common element, hydrogen. Reaction (1) in the IZ releases a huge, steady flux of ascending hydrogen and provides the essential high hydrogen fugacity for the key building blocks that can be further combined and polymerized to form complex organic and biochemical materials. By contrast, planets such as Mars that do not meet the high-*P* requirement of reaction (1) will not have the water-down hydrogen-up cycle that provided the internal hydrogen source to create the building blocks of life, although they could still be habitable by external colonization. To test this hypothesis, the key studies require explorations of organic chemistry along the geotherm *P*-*T* conditions from the IZ to the surface. This is basically an unexplored research area. Such studies are valuable for understanding the origins of life and of deep hydrocarbon resources.

Living organisms are very sensitive to temperature and chemistry, and have little tolerance of fluctuations in atmospheric and ocean conditions, and thus they provide an excellent marker of environmental changes. Catastrophic ORM eruptions that triggered global environmental apocalypses, such as large swings of excessive and deficient oxygenation and glaciation, would be manifested by mass extinctions of existing biota and emergence of new ones.<sup>68</sup>

#### IV. SUMMARY AND DISCUSSION

Studies of the 4D Earth have revealed a rich array of enigmatic events and phenomena. In previous approaches, multiple theories were devised and tested to provide independent explanations for each individual such event or phenomenon. Some enigmas have led to a number of actively competing theories: for example, mass extinctions have variously been ascribed to asteroid impact,<sup>12</sup> LIP volcanism,<sup>69</sup> and sea level change,<sup>70</sup> among other causes. Other enigmas have generated many new ideas: for example, the GOE has variously been ascribed to tectonic erosion, growth of continents,<sup>71</sup> mantle oxygen inhomogeneity,<sup>72</sup> and ferric iron in bridgmanite,<sup>73</sup> although in this case the dominant explanation remains that based on cyanobacterial photosynthesis.<sup>13,74</sup> Some enigmas, such as the source of LIPs, still lack a tangible hypothesis. Previously, the causes of these seemingly diverse events were considered and studied separately. A very wide net has been cast, but convergence toward a common explanation is slow and challenging.

Instead of seeking separate answers for these diverse events and phenomena, here we focus on an approach that considers them as evidence or tests for our hypothesis. We identify a possible dominant, controlling mechanism in the Earth's deep interior: the great potential between the IZ and OZ, which represent fundamentally different regimes in physics and chemistry. Material transfer and interaction

between the two zones occur mainly through descending slabs, rising plumes, and infiltration of volatiles. Key to this process is reaction (1), which defines the reactions of the dominant components, H, O, and Fe, with a solid solution of Mg and Al in the presence of H<sub>2</sub>O. The water-down hydrogen-up cycle becomes the key steady-state transport process that stockpiles ORPs at the CMB and supplies plentiful ingredients enabling the emergence of life on Earth's surface. The seismologically enigmatic LLSVPs and ULVZs in the D'' layer could be supporting evidence for ORPs. The build-up of ORPs in the steep thermal boundary layer of the CMB must lead to fractionation melting, with the volatile components becoming concentrated in ORM.

The continuous growth of ORM chambers will eventually lead to a catastrophic eruption, forming superplumes. Episodic eruptions add a chemical driving force to the ongoing thermal convection in the mantle, perturb steady-state convection patterns, and cause the merging and rifting of supercontinents. A superplume enriched in oxygen, hydrogen, and other volatiles will lower the melting *T* of rocks in the lithosphere, leading to the formation of LIPs. Such igneous activity may have supplied the excess oxygen for the GOE and other oxygen fluctuations. The additional oxygen, other gases, and dust emission from the enormous volcanic activity may have been responsible for catastrophic climate changes in the past, to which the very fragile biota responded with the mass extinctions for which there is abundant evidence in the fossil record.

Although at a very primitive stage, this approach based on a single working theory could provide a natural unified explanation of all major geological events, in contrast to the approach whereby attempts are made to explain a single event with many different hypotheses. It still has gaps and weak links, but key studies have been suggested here to provide additional information to fill the gaps and strengthen the links. Most importantly, we hope with this article to inspire further interdisciplinary investigation to test the integrated 4D Earth theory, with emphasis on the depth dimension and the exciting new physics and chemistry of the inner zone.

#### ACKNOWLEDGMENTS

We thank Yu He, Qingyang Hu, Jin Liu, Duckyoung Kim, and Li Zhang for sharing preliminary information. W. L. Mao acknowledges support from NSF Geophysics Grant No. EAR 1446969. H.-k. Mao acknowledges supports from NSF Geochemistry Grant No. EAR-1447438 and NSF Geophysics Grant No. EAR-1722515. This work was also partially supported by the National Natural Science Foundation of China Grant No. U1530402 and U1930401.

H.-k. Mao and W. L. Mao declare that they have no conflicts of interest or financial conflicts to disclose.

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