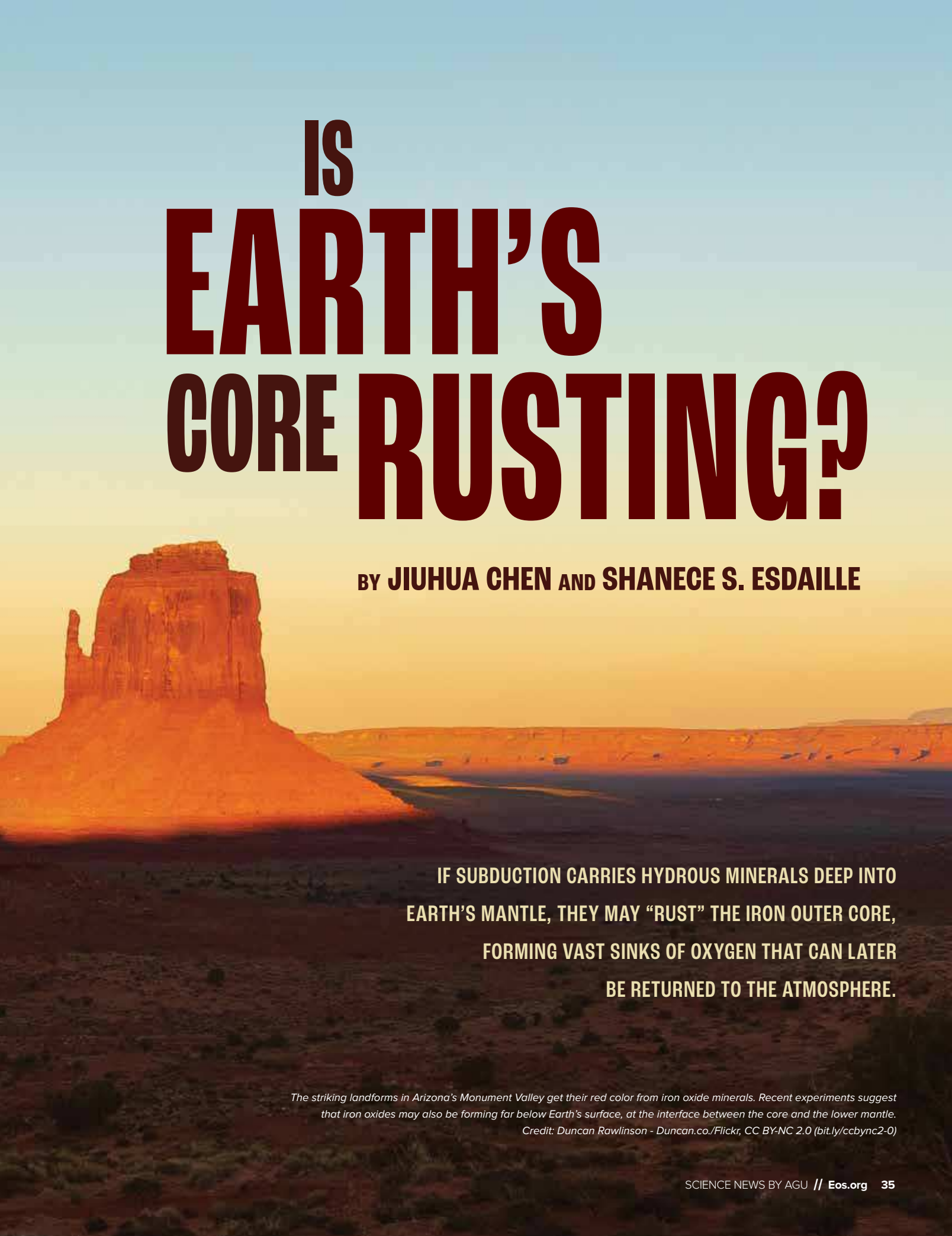






IS EARTH'S CORE RUSTING?

BY JIUHUA CHEN AND SHANECE S. ESDAILLE

IF SUBDUCTION CARRIES HYDROUS MINERALS DEEP INTO
EARTH'S MANTLE, THEY MAY "RUST" THE IRON OUTER CORE,
FORMING VAST SINKS OF OXYGEN THAT CAN LATER
BE RETURNED TO THE ATMOSPHERE.

*The striking landforms in Arizona's Monument Valley get their red color from iron oxide minerals. Recent experiments suggest that iron oxides may also be forming far below Earth's surface, at the interface between the core and the lower mantle.
Credit: Duncan Rawlinson - [Duncan.co./Flickr](https://www.flickr.com/photos/duncanrawlinson/), CC BY-NC 2.0 (bit.ly/ccbync2-0)*

If rust is actually present where the outer core meets the mantle, scientists may need to update their view of Earth's interior and its history.

Iron on Earth's surface—whether in simple nails or mighty girders—is altered gradually when exposed to moist air or oxygenated water through a chemical reaction known as oxidation. The reddish-brown product of this reaction, rust, can consist of various forms of hydrous (water-bearing) iron oxides and iron oxide-hydroxide materials. In nature, the red rocks found in the arid climes of the southwestern United States and elsewhere similarly owe their color to the iron oxide mineral hematite, whereas in wetter environments, iron ore minerals like hematite weather to form the iron oxide-hydroxide mineral goethite (FeOOH).

Deep below Earth's surface—2,900 kilometers deep, to be precise—is a mass of mostly molten iron forming the planet's outer core. Could it rust as well?

In experiments, scientists have recently shown that when iron meets moisture—as water or in the form of hydroxyl-bearing minerals—at pressures close to 1 million atmospheres, similar to pressures in the deep lower mantle, it forms iron peroxide or a high-pressure form of iron oxide-hydroxide with the same structure as pyrite (i.e., pyrite-type FeOOH) [Hu *et al.*, 2016; Mao *et al.*, 2017]. In other words, the oxidation reactions in these experiments do, indeed, form high-pressure rust.

If rust is actually present where the outer core meets the mantle (the core-mantle boundary, or CMB), scientists may need to update their view of Earth's interior and its history. This rust could shed light on the deep-water cycle in the lower mantle and the enigmatic origins of ultralow-velocity zones (ULVZs)—small, thin regions atop Earth's fluid core that slow seismic waves significantly (Figure 1). It could also help answer questions about the Great Oxidation Event (GOE), which marked the beginning of

Earth's oxygen-rich atmosphere some 2.5 billion to 2.3 billion years ago, and the Neoproterozoic Oxygenation Event (NOE), which brought atmospheric free oxygen to its present levels 1 billion to 540 million years ago.

But how do we know whether rusting has been happening at the CMB?

SEISMIC SIGNATURES AT THE CORE-MANTLE BOUNDARY

Although we can't mine the minerals at the CMB, we can examine them in other ways. If the core rusts over time, a layer of rust may have accumulated at the CMB, exhibiting certain seismic signatures.

Laboratory studies indicate that iron oxide-hydroxide core rust (i.e., FeOOH_x , where x is 0–1) may cause significant reductions in the velocities of seismic shear waves (V_s) and compressional waves (V_p) that pass through it, much like the rocks (or partial melts, if present) in ULVZs do [Liu *et al.*, 2017]. In fact, core rust could slow seismic wave velocities by as much as 44% for V_s and 23% for V_p , compared with the average seismic velocities as a function of depth represented in the preliminary reference Earth model. These large velocity reductions would make the core rust recognizable in seismic tomography if it accumulated into piles thicker than 3–5 kilometers.

The difficulty lies in distinguishing whether seismic anomalies in ULVZs are

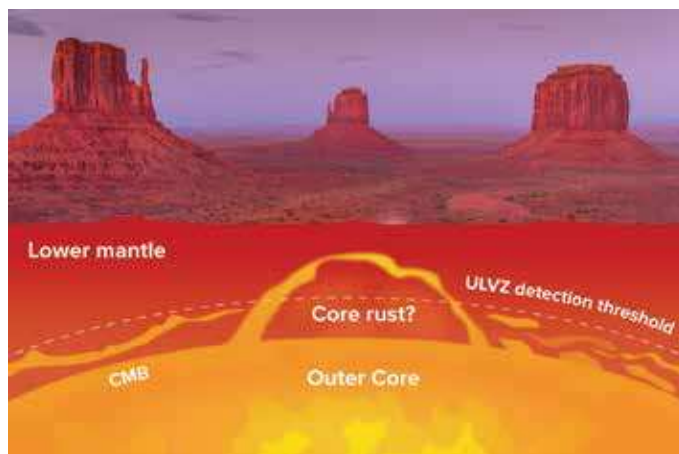


Fig. 1. The coloration of red rocks on Earth's surface—as seen here near West Mitten Butte, East Mitten Butte, and Merrick Butte in Arizona—mainly results from the oxidized iron minerals hematite and goethite. Possible core rust deposits at the core-mantle boundary (CMB), 2,900 kilometers below Earth's surface, could be made of iron oxide-hydroxide minerals with a pyrite-like structure. This rust material could explain the detections of ultralow-velocity zones (ULVZs) in seismic data. The ULVZ detection threshold indicates the resolution of current seismic tomography. Credit: Top: Ken Cheung/Pexels; Bottom: Mary Heinrichs/AGU

caused by core rust or whether they have other origins. For example, partial melting, which is commonly believed to occur at the base of the lower mantle and to be responsible for ULVZs [Williams and Garnero, 1996], could give rise to seismic velocity reductions similar to those caused by core rust.

Scientists should be able to use seismic tomograms to differentiate between core rust and partial melting at the CMB. A seismic tomogram is normally produced through a mathematical inversion process that matches calculated and observed seismic waveforms. The inversion process requires determining possible mathematical solutions that fit the data and then choosing a “best” solution from among these on the basis of additional considerations.

Each possible mathematical solution corresponds to a distinct set of model parameters related to the physical properties of the materials involved—for example, the relative differences in V_s , V_p , and density between a material of interest and the average of the mantle surrounding that material.

These differences can vary with the amount of the material in the mantle, but each material usually exhibits a characteristic range of values for the differential logarithmic ratio of V_s to V_p ($\delta \ln V_s : \delta \ln V_p$) [Chen, 2021], which can be used to distinguish materials in seismic tomograms (Figure 2). It’s known from mineral physics experiments that this ratio ranges from a lower limit of 1.2:1 to an upper limit of 4.5:1 for all possible materials explaining the origin of ULVZs. Within this broader range, ratios for core rust (pyrite-type FeOOHx) fall between 1.6:1 and 2:1 and are distinct from the other materials.

EVIDENCE OF CORE RUST ORIGINS

So far, seismologists have sampled about 60% of the CMB in their search for ULVZs, and they have identified nearly 50 locations of seismic anomalies, accounting for as much as 20% of the CMB area, that could represent ULVZs. Most of these areas are coupled with large low shear velocity provinces (LLSVPs) in the lowermost mantle and display a $\delta \ln V_s : \delta \ln V_p$ of around 3:1, which suggests partial melting (Figure 2).

However, some of them, located at the margins of or outside the LLSVP beneath the Pacific, display a best fit ratio of about 2:1 [Chen, 2021]. For example, a ULVZ at the northern border of the Pacific LLSVP (at about 9°N, 151°W) [Hutko et al., 2009] and a

cluster of ULVZs beneath northern Mexico (at about 24°N, 104°W) [Havens and Revenaugh, 2001] each have $\delta \ln V_s : \delta \ln V_p$ ratios that suggest the presence of pyrite-type FeOOHx.

A common feature of these ULVZs is that they are located in a region of the CMB where temperatures are relatively low—a

Scientists should be able to use seismic tomograms to differentiate between core rust and partial melting at the core-mantle boundary.

few hundred kelvins lower than average temperatures within the LLSVP. The low temperatures suggest that these zones were produced by a mechanism other than melting. Of note, the region beneath northern Mexico has been identified as comprising the remnants of deep subduction deposited roughly 200 million years ago to the west of North and Central America, which supports the notion that water released from the subducting slab could have rusted the outer core at the CMB.

THE CONSEQUENCES OF A RUSTED CORE

It is thought that the dominant mineral in Earth’s lower mantle, bridgmanite, has little ability to host water. However, rusting of the core could produce a high-capacity water reservoir at the CMB—the FeOOHx rust may contain about 7% water by weight [Tang et al., 2021]. Because core rust is heavier than the average mantle, this water reservoir would tend to stay at the CMB. Thus, water can theoretically be transported and stored just outside the core, at least until mantle convection carries it away from the

cooler regions near the remnants of subducted slabs and makes it thermally unstable (Figure 3).

Whether and when this deep water cycles back to the surface would depend largely on the thermal stability of the core rust. Some scientists, on the basis of experimental work, have claimed that FeOOHx can survive only up to 2,400 K under the pressure at the CMB [Nishi et al., 2017], whereas others have observed the presence of FeOOHx at 3,100–3,300 K at a similar pressure [Liu et al., 2017]. But whatever the maximum temperature FeOOHx can withstand, it’s likely that when core rust migrates to hotter regions of the CMB, following the flow of mantle convection, it would decompose into hematite, water, and oxygen. This process offers a possible alternative explanation for the oxygenation history of Earth’s atmosphere.

Geological, isotopic, and chemical evidence suggests that Earth’s atmosphere was mostly or entirely anoxic during the Archean eon. Following the Archean, the first introduction of molecular oxygen into the atmosphere began about 2.4 billion years ago in the GOE. The second major rise in atmospheric oxygen, the NOE, then occurred about 750 million years ago, bringing concentrations close to today’s level.

The causes of these oxygenation events remain uncertain. One possible explanation of the GOE is the emergence of cyanobacteria, the early photosynthesizing precursor to plants. The NOE, occurring almost 2 bil-

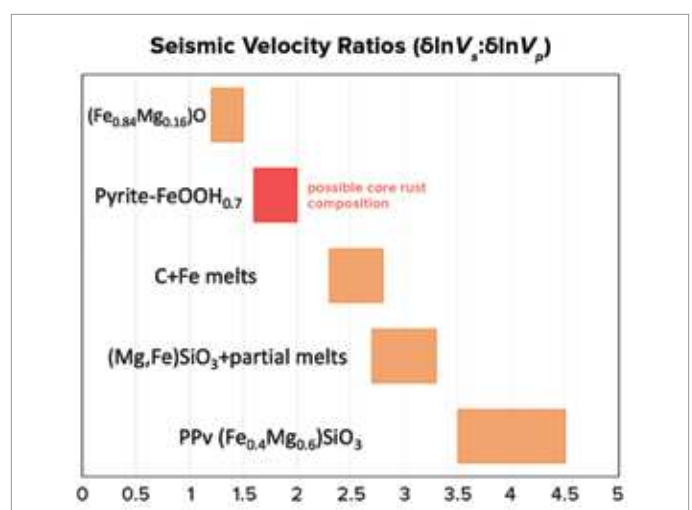


Fig. 2. The ranges (orange and red) of seismic velocity ratios ($\delta \ln V_s : \delta \ln V_p$) for different materials proposed as sources of ULVZs are shown here: iron-rich oxide, (Fe_{0.84}Mg_{0.16})O; pyrite-type FeOOH_{0.7} (possible core rust composition); carbon-iron melts, C+Fe melts; silicate perovskite and mantle partial melts, (Mg,Fe)SiO₃+partial melts; and postperovskite solid silicate, PPv (Fe_{0.4}Mg_{0.6})SiO₃.

lion years later, has been attributed to a rapid increase in marine photosynthesis and to an increased photoperiod (i.e., longer daylight hours) [Klatt *et al.*, 2021].

But these explanations are far from impeccable. For example, besides a large mismatch in timing between the appearance of cyanobacteria on Earth and the GOE, several studies have indicated the possibility that a large increase in atmospheric oxygen at the beginning of the GOE was followed by a deep plunge to lower levels that extended over a few hundred million years. So far, there is no convincing explanation for this rise and fall based on cyanobacterial photosynthesis.

Furthermore, although it is widely accepted that the GOE raised atmospheric oxygen concentrations only modestly compared with the rise during the NOE, laboratory experiments investigating the influence of photoperiod on the net oxygen export from microbial mats that host competitive photosynthetic and chemosynthetic communities suggest a contradictory result [Klatt *et al.*, 2021]. Instead of more oxygen emerging from such mats as a result of longer daylight in the NOE, the experiments indicated that the increase in day length,

from 21 to 24 hours, during the NOE may have led to only about half the rise in oxygen seen when the day length increased to 21 hours during the GOE.

Changes attributed to cyanobacteria and the length of the photoperiod thus do not provide a complete or consistent explanation for the atmospheric oxygen increases during the GOE or NOE, and alternative mechanisms for the origins of these events cannot be ruled out.

SUBDUCTION, MIGRATION, CONVECTION, ERUPTION

Decades of research have not produced conclusive evidence about when plate tectonics began on Earth. However, some recent studies indicate that subduction began bringing hydrous minerals down to the deep mantle before 3.3 billion years ago. And experimental studies have shown that hydrous minerals in subducting slabs are capable of relaying water all the way to the CMB [Ohtani, 2019]. If so, rusting might have happened as soon as the first ancient slab met the core. The core rust could have piled up gradually at the CMB, giving rise to ULVZs. As the pile migrated away from the cooler subduction region atop the molten

outer core, driven by mantle convection, it would have heated up and likely become unstable when it reached a hotter region where a mantle plume was rooted (Figure 3).

Just as typical volcanic eruptions occur intermittently, the temperature-driven decomposition of core rust could result in fitful bursts of oxygen at the surface. In contrast to the gradual increase in oxygen from cyanobacterial photosynthesis, such a burst might have released oxygen faster than the surface environment could respond and con-

sume it, causing a rapid initial rise and a subsequent fall of atmospheric oxygen levels.

The accumulation of a large core rust pile and its migration to the site of thermal decomposition could take a much longer time compared with the duration of eruptions of magma at the surface. Indeed, some piles that were formed may not have reached a region hot enough to cause decomposition, and their negative buoyancy amid the surrounding deep mantle would have kept them at the CMB. The geologic record suggests that Earth's surface was entirely covered by ocean until about 3.2 billion years ago. Net removal of water from the surface and storage in the deep mantle in core rust could have contributed to the emergence of continents in the Archean, although changes in surface topography driven by plate tectonics and the growth of buoyant continents also contributed to this emergence.

A POTENTIAL PARADIGM SHIFT

Although everyone can see that iron rusts at Earth's surface, unfortunately, no one can directly prove that Earth's liquid iron core 2,900 kilometers below the surface is similarly rusting. However, continuing studies will help scrape away layers of uncertainty and answer major questions, such as whether core rusting is responsible for the GOE and the NOE.

In particular, more laboratory experiments are needed to determine the precise limits of the thermal and compositional stability of core rust in equilibrium with molten iron at the conditions of the CMB. For example, we need to investigate the equilibrium between core rust and liquid iron at high pressure and high temperature. Other studies could examine core rust thermal stability at high pressures. These experiments are challenging but doable with the current experimental capabilities of laser-heated diamond anvil cells.

Furthermore, additional work is needed to resolve when subduction began and, specifically, when "wet subduction," which takes hydrous minerals into the deep interior, started. Geochemical evidence suggests that wet subduction did not start until 2.25 billion years ago, instead of 3.3 billion. This late a start of wet subduction may challenge the hypothesis that core rusting was the origin of the GOE.

Moreover, whether mantle convection involves layered circulations (i.e., separate convection cells in the lower and upper

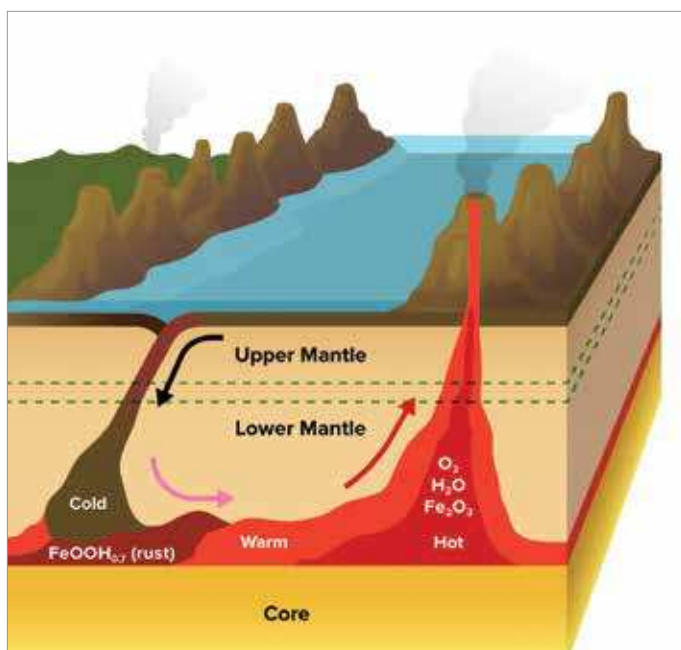
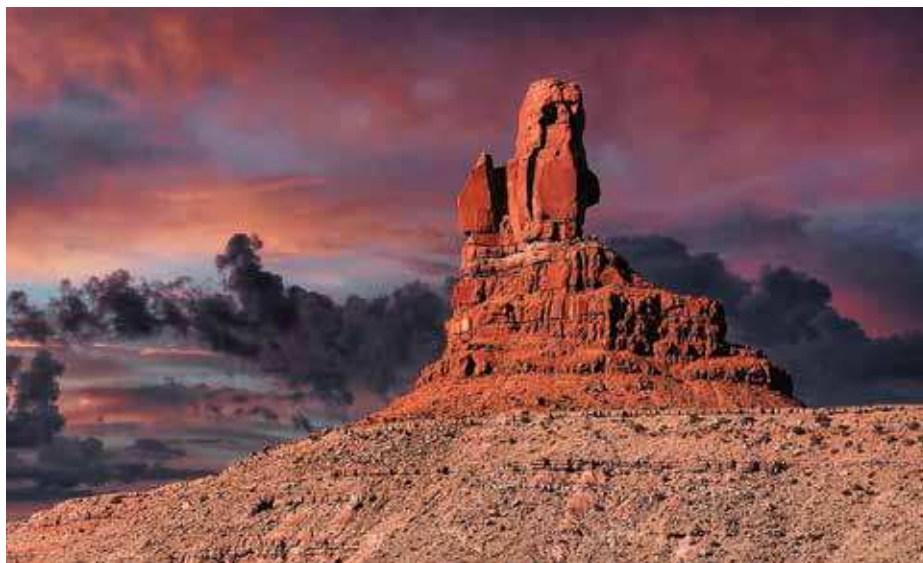


Fig. 3. Core rust ($\text{FeOOH}\cdot x\text{H}_2\text{O}$) could form when a relatively cold subducting slab carrying hydrous minerals meets the outer core. Driven by mantle convection, core rust deposits from this cold region could then migrate along the CMB to a hotter region at the root of a mantle plume, where it could become unstable and decompose into hematite (Fe_2O_3), water (H_2O), and oxygen (O_2). Credit: Mary Heinrichs/AGU



Owl Rock in Arizona's Monument Valley gets its red color from iron oxide minerals. Recent experiments suggest that iron oxides may also be forming far below Earth's surface, at the interface between the core and the lower mantle. Credit: G. Lamar/Flickr, CC BY 2.0 (bit.ly/ccby2-0)

mantle), whole-mantle circulation, or some hybrid of these scenarios still requires clarification. If layered circulation prevails in the mantle, then subducting slabs would be prevented from entering the lower mantle. Thus, either whole-mantle or hybrid convection [Chen, 2016] must exist for slabs—and the hydrous minerals they carry—to reach the CMB and potentially cause rusting.

If the pieces of the puzzle fall into place, then rusting of the core may, indeed, be a massive internal oxygen generator on Earth—and the next great atmospheric oxygenation event could be on its way. The possibility of such an event would raise all sorts of questions about the effects it could have

on environments, climate, and habitability in the future. In the near term, confirming that Earth's core rusts would cause a paradigm shift in our understanding of the planet's deep interior and how it has fundamentally influenced conditions and life at the surface.

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