

## GEOCHEMISTRY

## A journey to the oxidized centre of the Earth

The formation of the Earth and the subsequent evolution of its layers are two processes that have long fascinated geochemists and geophysicists. Ho-kwang Mao and co-workers have added an additional piece to the puzzle by studying the dehydrogenation of goethite ( $\text{FeO}_2\text{H}$ ) under conditions typical of the Earth's deep lower mantle. They show that the existence of hydrogen in the mantle — contrary to the traditional assumption — can be independent of water, allowing us to explore interesting new scenarios for our planet's evolution.

Unlike in Jules Verne's classic tale, we lack direct access to the deep interior of the Earth. Unsurprisingly, determining the exact compositions and relevant chemical processes in such a remote region is very challenging, although it can be addressed

by experimentation and simulation. Studying the response of representative minerals to high pressures and temperatures — conditions typical of the deep interior — is one of the main approaches used by scientists to gain knowledge of the Earth's deep secrets. Such studies have taught us that cycles of iron, oxygen and hydrogen control the redox equilibrium in the Earth's mantle. It is therefore important to understand the interplay of these cycles.

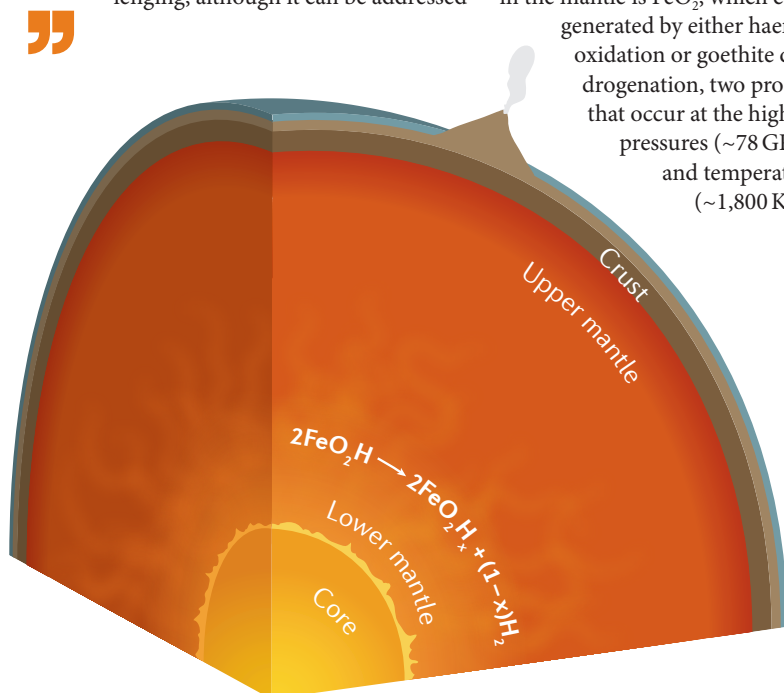
Iron is present in various forms in the different layers of the Earth — metallic iron in the core, bridgmanite ( $(\text{Mg,Fe})\text{SiO}_3$ ) and ferropericlase ( $(\text{Mg,Fe})\text{O}$ ) in the mantle, and olivine ( $(\text{Mg,Fe})_2\text{SiO}_4$ ), haematite ( $\text{Fe}_2\text{O}_3$ ) and goethite in the crust. Another form of iron that is present in the mantle is  $\text{FeO}_2$ , which can be generated by either haematite oxidation or goethite dehydrogenation, two processes that occur at the high pressures ( $\sim 78$  GPa) and temperatures ( $\sim 1,800$  K)

in the deep lower mantle of the Earth. In previous work, the Mao group found that the unit cell of the  $\text{FeO}_2$  mineral derived from goethite dehydrogenation was quite variable owing to the presence of residual hydrogen in the form of  $\text{FeO}_2\text{H}_x$ . Mao and co-workers have now moved forward: by combining diamond anvil cell compressions, state-of-the-art X-ray diffraction measurements and first-principles simulations, they have quantified the amount of hydrogen lost by goethite and proposed a two-step mechanism for goethite dehydrogenation.

When goethite is compressed to between 71 and 133 GPa, and subsequently heated to 2,000 K, only 19–61% of the mineral undergoes dehydrogenation. Complete dehydrogenation and conversion to  $\text{FeO}_2$  occurs when the partially dehydrogenated goethite is exposed to prolonged heat in the deep mantle. The liberation of  $\text{H}_2$  leaves regions rich in  $\text{FeO}_2$ ; the oxidizing nature of this compound has important consequences for the redox balance in the Earth's inner layers. This research shows that, in the crust and mantle, the hydrogen and water cycles may not be completely equivalent. The authors note that geochemists did (and still do) consider the lower mantle close to the liquid iron core as being highly reducing. However, this study shows that water-bearing minerals such as goethite can release hydrogen, which migrates to the upper mantle and leaves highly oxidizing islands of metal peroxides at the core–mantle boundary. “This totally unexpected chemistry will lead to many new scenarios that will take years to unravel,” concludes Mao.

Gabriella Graziano

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Rachael Tremlett/Macmillan Publishers Limited

**ORIGINAL ARTICLE** Hu, Q. *et al.* Dehydrogenation of goethite in Earth's deep lower mantle. *Proc. Natl Acad. Sci. USA* <http://dx.doi.org/10.1073/pnas.1620644114> (2017)  
**FURTHER READING** Hu, Q. *et al.*  $\text{FeO}_2$  and  $\text{FeOOH}$  under deep lower-mantle conditions and Earth's oxygen–hydrogen cycles. *Nature* **534**, 241–244 (2016)