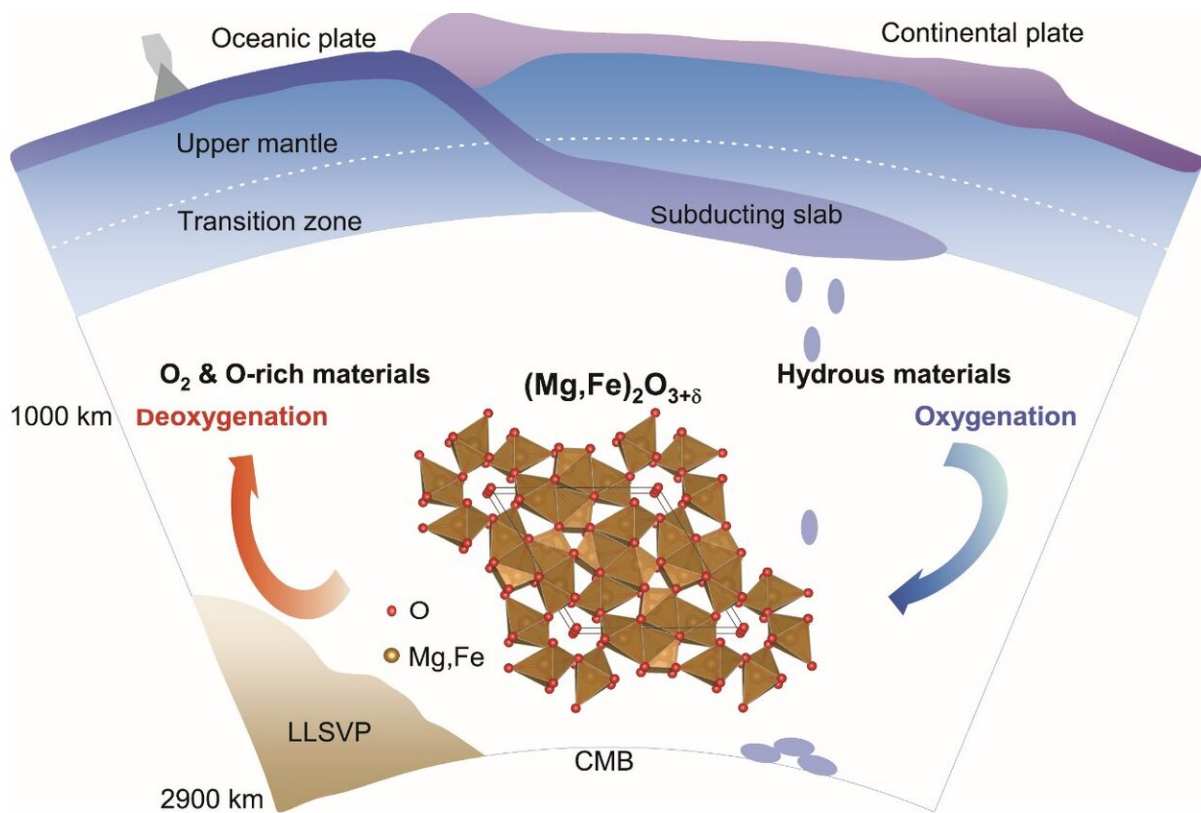


Oxygen-excess oxides in Earth's mid-mantle facilitate the ascent of deep oxygen

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A schematic diagram of the Earth's deep oxygen factory shows the oxygenation and deoxygenation processes of hydrous mantle materials in the lower mantle across the ~1000 km depth beneath Earth's surface. Under the conditions of Earth's middle mantle, scientists discovered an oxygen-excess phase, $(\text{Mg,Fe})_2\text{O}_{3+\delta}$ (0 1000 kilometers depths. Those oxygen-excess materials may have long-termly oxidized the shallow mantle and the crust, which is essential to allow free oxygen to build up in Earth's atmosphere. Credit: Science China Press

Subduction of hydrous materials imposes great influence on the structure, dynamics, and evolution of our planet. However, it is largely unclear how subducting slabs chemically interact with the middle mantle. Recently, an oxygen-excess phase $(\text{Mg,Fe})_2\text{O}_{3+\delta}$ was discovered under conditions similar to the Earth's middle mantle (~1000-2000 km) by a team of scientists from the Center of High Pressure Science and Technology Advanced Research (HPSTAR) and Stanford University.

This oxygen-excess phase is fully recoverable to [ambient conditions](#) for ex-situ investigation using transmission electron microscopy. It contains ferric iron as in hematite (Fe_2O_3) which is the most oxidized form of iron on the Earth's surface, but this new phase holds more oxygen than hematite through interactions between [oxygen atoms](#). The peculiar nature of oxygen in this new phase may revise our view on the mantle redox chemistry.

"We employed laboratory techniques to simulate the conditions deep inside the Earth and found an oxygen-excess phase emerged when hydrous mineral assemblages (e.g., ferropicicase mixed with brucite) were exposed to laser heating at pressures greater than 40 million times the atmospheric pressure on the Earth's surface" said Dr. Jin Liu from HPSTAR. "The formation of this new phase provides strong evidence that water acts as a strong oxidant at high pressure."

"This phase could coexist with the pyrite-type phase hydrogen-bearing FeO_2 at deep mantle conditions, whereas the two phases are distinct in crystal chemistry," added Dr. Qingyang Hu from HPSTAR. "Unlike the formation of the pyrite-type phase which usually forms in deep lower mantle and requires a large quantity of water, this oxygen-excess phase can be formed with a moderate amount of water at mid-mantle conditions. The flexible formation conditions make it potentially a more widespread phase at depths greater than 1000 km in Earth's mantle, occupying almost 2/3 of the mantle." Furthermore, this oxygen-excess

phase can co-exist with the major mantle minerals, bridgmanite and ferropericlavite, under Earth's lower-mantle conditions.

"The widespread presence of the oxygen-excess phase makes it and other oxygen-enriched oxides an important subject for the full range of future geochemistry and mineral physics studies," suggested Dr. Hongkwang Mao, director of HPSTAR. "Remarkably, this new phase is quenchable. As a matter of fact, most compounds synthesized under the lower mantle conditions and quenchable back to ambient conditions have been discovered and named as minerals such as bridgmanite $(\text{Mg,Fe})\text{SiO}_3$ and seifertite SiO_2 . Hence, this presents an opportunity to search for this oxygen excess phase in nature as diamond inclusions or meteorite shock products."

The crystal structure of this oxygen excess phase may represent a structure prototype which will accommodate other Earth-abundant components (e.g. Al, Ca, Ti, and Ni). At the same time, the channel space in this oxygen-excess phase could offer a great flexibility not only for excess oxygen, but also for other volatiles (e.g. N, S, F, and Cl). Considering its structural versatility, the new phase could be an important volatile carrier in the deep mantle over geological time. More importantly, together with excess Fe_3^+ from the primordial lower mantle, those oxygen-excess materials may have in the long term oxidized the shallow mantle and the crust, which is fundamental to the evolution and habitability of complex life on the Earth's surface.

These results suggest that the oxygen-excess phase may facilitate oxygen-excess reservoirs out of hydrated slab remnants at depths greater than 1000 km. Oceanic crusts in the mid-mantle thus might deeply regulate the rise of oxygen in Earth's atmosphere and global habitability, like shallowly-recycled fluids. Such intriguing chemistry of deep oxygen sheds light on chemical and dynamic models of [mantle](#) slab remnants as well as the interaction and coevolution of Earth's interior and surface.

More information: Jin Liu et al, Evidence for oxygenation of Fe-Mg oxides at mid-mantle conditions and the rise of deep oxygen, *National Science Review* (2020). [DOI: 10.1093/nsr/nwaa096](https://doi.org/10.1093/nsr/nwaa096)

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