8 February 2016

The Earth’s mantle produces oxygen

EMBARGOED UNTIL 11 FEBRUARY 1100hrs CET

Studies of iron oxides under extreme conditions by an international team at the ESRF reveal a possible novel mechanism of oxygen recycling in the Earth’s interior with potentially great impact on geochemical processes. This work is published in Nature Communications today.

The Earth’s interior is still a mystery. Reproducing the conditions of high pressure and temperature inside our planet is a challenge. At the ESRF, researchers can get as close as it gets to studying what goes on underneath our feet. A team from the University of Bayreuth (Germany), the ESRF, DESY's X-ray light source PETRA III, the University of Chicago have managed to apply pressures over 100 GPa (1 million times the standard atmospheric pressure) and temperatures above 2500K (2227°C) on a kind of iron oxide inside the Earth, Fe_2O_3, to see how it behaves in the mantle. Despite simple chemical composition, this oxide, one of the main components of rocks industrially important for iron production, has been in the focus of studies due to the enigmatic structural and electronic transitions that it shows at elevated pressures and temperatures. Numerous publications have so far failed to provide a consistent picture of high pressure behaviour of this material.

The team found that Fe_2O_3 is chemically unstable at high pressures and temperatures: if heated at pressures above ~60 GPa, it is transformed into the known post-perovskite structure, which then releases oxygen and forms a novel compound, Fe_5O_7.

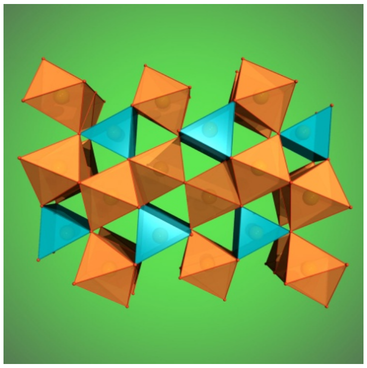

Image 2. High-pressure experiments reveal chemical complexity of Fe_2O_3. At pressures above 60 GPa iron oxides lose oxygen producing novel structures such as Fe_5O_7.

The results of this work have important implications not only for fundamental high-pressure chemistry, but also for the understanding of the global rock development processes. The so-called Banded Iron Formations (BIFs) and ironstones are huge sedimentary rock formations occurring on all continents (and the main source of iron for our civilisation). BIFs may reach up to several hundred metres in thickness and hundreds of kilometres in length.

Deposited in the world's oceans about two billion years ago, BIFs as part of the ocean floor are recycled into the Earth's interior by subduction (process by which one tectonic plate moves under another tectonic plate and sinks into the mantle) to depths extending possibly to the core-mantle boundary region. According to the present study, hematite and magnetite, two of the main components of the BIFs, would undergo numerous phase transformations upon subduction of BIFs into the lower mantle and produce oxygen. Based on estimates of the amount of BIFs subducted into the Earth's mantle, the amount of oxygen produced can be as high as 8 to 10 times the mass of oxygen in the modern atmosphere. The study suggests the presence of an oxygen-rich fluid in the deep Earth's interior that can significantly affect geochemical processes by changing oxidation states and mobilising trace elements.

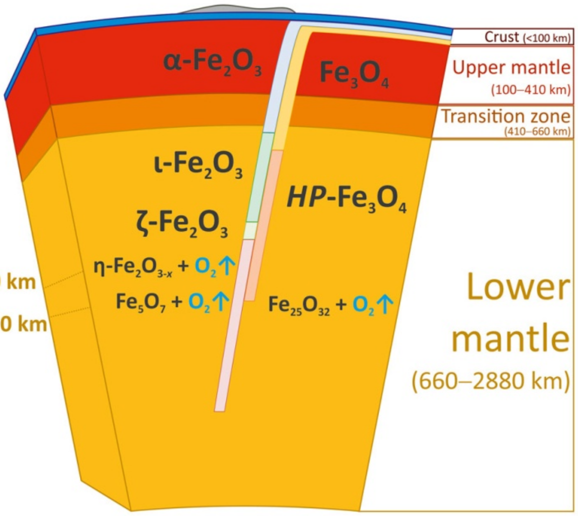

Figure 1. Possible consequence of phase transitions of Fe_2O_3 and Fe_3O_4 in a BIF subducted to the lower mantle.

***"This possible mechanism of oxygen recycling in the Earth's interior is a game changer. Any global models of the past and future of the Earth, including models of evolution of climate, should take into account the new findings"*, explains Leonid Dubrovinsky,** University of Bayreuth.

Single-crystal X-ray diffraction (XRD) is the most powerful method for studying structures of solids. "*When I started my PhD project five years ago, single crystal diffraction studies at pressures over 15 GPa even at ambient temperatures were hardly possible. Now the development of the technique of high pressure generation, laser heating in diamond anvil cells, and methodology of data collection and processing (like at ID09 at the ESRF) make possible the determination and refinement of crystal structures of materials compressed to over 150 GPa (1.5 million atmospheres) and heated at thousands of degrees. These conditions correspond to the Earth outer core. Moreover, as we demonstrate in our work, now we are able to perform quantitative in situ characterization of a chemical composition of matter and, at ESRF ID18 beamline, an electronic state of compounds subjected to extreme conditions. So, we not only found some new and unexpected iron oxides, but opened up a door in the whole new world of amazing chemistry at high pressures and temperatures,*" **says Elena Bykova, University of Bayreuth, corresponding author of the paper.**

"On the ID09A beamline of the ESRF we have been working hard, to expand the limits of crystallographic studies at extreme conditions of pressure and temperature, allowing us for example to explore in detail processes relevant for the functioning of our earth", **adds Michael Hanfland, scientist in charge of the former ID09A beamline, soon to be replaced by ID15B.**

Principal publication and authors

E. Bykova et al, *Nature Communications*, 2016; doi: 10.1038/NCOMMS10661

About the ESRF:
The ESRF – the European Synchrotron – is a large scale international research instrument, located in Grenoble, France. It is one of the world's most intense source of X-rays. The extremely bright light that the ESRF provides to scientists from around the globe enables them to explore matter in many disciplines. Founded in 1988, the ESRF is a model of European and International cooperation with 21 partner countries, of which 13 are Members, and 8 are Scientific Associates.