Redox reactions and Earth's volatile cycle

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Previous studies predicted the presence of iron metal in Earth's mantle at depths greater than 250 km, resulting from disproportionation of ferrous iron in silicate minerals and glasses [1]. On the other hand, deep mantle has long been considered a potential water reservoir containing structural water equivalent to the mass of many oceans [2]. Iron and hydrous phases are known to react at high pressure and high temperature [3]. Here we show that partitioning of hydrogen between iron metal and nominally hydrous silicate depends on the iron to water ratio and the pressure and temperature conditions. In the iron-rich case, the reaction may produce iron hydrite FeH_x and iron oxide FeO [4]. Segregation of FeH_x may have facilitated the operation of oxygen "pump", leading to oxidation of the shallow mantle and rise of oxygen level in the atmosphere [5-6]. If water is abundant, the reaction may release hydrogen fluid H_2, causing dehydration and oxidation of the mantle without net loss of iron to the core. At pressures greater than 70 GPa, the reaction may produce peroxide FeO_2 [7], with profound consequences for the mantle oxidation state and Earth's volatile cycle.

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