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Redox Transfers at Subduction Zones: The Fluid-Melt-Rock Connection

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Oxygen fugacity (fO2) of mantle rocks and their derived magmas is a measure of their redox state, which influences the compositions of both minerals and fluids, and the fate of redox sensitive elements such as (noble) metals, iron, hydrogen, sulfur, carbon. fO2 is commonly expressed in log-unit relative to that buffered by the quartz-fayalite-magnetite mineral assemblage, FMQ. Many mantle regions have fO2 close to FMQ and produce magmas that are within the same range of fO2. Recent surveys have also concluded that the mantle redox state has been steady since the archean times. The mantle at subduction zones ($\sim$10% of global magmatism) is, however, much more oxidized and can display fO2 up to 2 log-units higher than FMQ. Because mantle redox state directly impacts on the one of melts and volcanic gases emitted at surface, how mantle fO2 can vary spatially and through the ages of the Earth is a fundamental issue for our understanding of the exchanges between the innermost and the outermost parts of our planet. Of prime interest is the question of the role of mantle redox state and the one of the derived volcanic gases on the atmospheric oxygen rise at 2.5 Ga.
At subduction zones, volatile-rich rocks are entrained with the oceanic lithosphere into the mantle where melting occurs. Water is the major volatile involved in the dynamic of subduction zones. The oxidized nature of subduction- or Arc-magmas might be related to their water-rich nature but this link remains unclear, as illustrated by the identification of hydrous magmas that can be strongly reduced in other geodynamic settings. From a thermodynamic point of view, water-rich fluids might be oxidizing if their equilibrium hydrogen fugacity is low (molar abundance much less than 1%). Water in subduction-magma mainly derives from serpentinite dehydration within the plunging lithosphere at depth. This dehydration takes place within rocks that have been oxidized by sea floor alteration prior to subduction.
We show that serpentinite dehydration produces an extremely oxidized water fluid, with hydrogen content of the order of 0.001 %. Based on experimental petrology and thermodynamic calculations, we estimate the fO2 of this water fluid at FMQ+4.5, mostly buffered by the magnetite-hematite redox buffer. Subsequently, the fluid migrates upward triggering a hyper-oxidative metasomatism of the mantle wedge (affecting sulfur and U/Th ratios), the production of arc-basalts and emission of oxidized volcanic gases into atmosphere. Upon percolation through the mantle wedge this fluid looses its hyper oxidant nature and reaches FMQ+2 when in the form of arc-basalts.
The dehydrated oxidized subducted rocks, which displays ferric to total iron around 60%, are entrained deeper in the mantle. Overall, subduction triggers an oxygen transfer from the surface to the interior of our planet and, therefore, could not have facilitated the oxidation of the atmosphere.