

Theoretical modeling of the $[\text{O}_2^{3-}/\text{M}^{3+}]$ defect centers and their precursors in stishovite and rutile

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Stishovite and rutile have been proposed to be important hosts of water in the lower mantle, and experimental studies have demonstrated the incorporation of elevated water contents in Al-rich stishovite. Electron paramagnetic resonance (EPR) spectroscopic study of gamma-ray-irradiated stishovite at 77 K revealed the presence of an aluminum-associated hole-like center. This aluminum hole center has been suggested to be an $[\text{O}_2^{3-}/\text{Al}^{3+}]$ defect, which may have formed from a hydrogen-associated precursor by the removal of the hydrogen atom and trapping of a hole during gamma-ray irradiation. Similarly, $[\text{O}_2^{3-}/\text{M}^{3+}]$ centers (where $\text{M} = \text{Fe}^{3+}$ and Ti^{3+}) have been suggested to occur in artificially irradiated rutile and may also originate from precursors linked to the incorporation of hydrogen. In this study, first-principle quantum-mechanical calculations have been made to evaluate the geometries, stabilities, electronic structures and magnetic properties of the proposed $[\text{O}_2^{3-}/\text{M}^{3+}]$ centers and their precursors in stishovite and rutile. In particular, the calculated magnetic properties (e.g. the ^{27}Al hyperfine coupling tensor for the $\text{O}_2^{3-}/\text{Al}^{3+}$ center in stishovite) are compared with experimentally-determined values. These results provide new insights into the incorporation of water in stishovite and rutile.

Abiotic sulfide oxidation via manganese fuels the deep biosphere

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The deep biosphere in marine sediments consists of large populations of metabolically active, mainly not described Bacteria and Archaea [1, 2]. Buried organic carbon as the main energy source for the deep biosphere is anaerobically oxidized via sulphate-, carbonate-, nitrate-, Fe(III)- or Mn(IV)-reduction [3, 4], however, the overall microbial activity is limited by the availability of organic carbon and oxidants. Sulphate reduction has been identified as the most important of these processes [3, 4], yet sulphate is typically quantitatively removed in the upper few meters of marine sediments. Stable isotope fractionation of sulphur and oxygen are particular useful to characterize biogeochemical processes upon sediment-pore fluid interactions [5, 6]. Here we used stable oxygen and sulphur isotope analysis to demonstrate that the oxidant sulphate is generated by anoxic sulphide oxidation in deeply buried sediments of the Cascadia margin and the Blake ridge, as well as in near-surface marine sediments. Experiments confirmed that Mn(IV)-containing oxide minerals abiotically oxidize iron sulfides such as pyrite and thereby producing ^{18}O depleted sulphate (with respect to water) in contrast to pyrite oxidation at low pH values. Oxidized manganese stored within the mineral fraction of marine sediments drives abiotic anaerobic sulphide oxidation, which together with microbial sulphate reduction, forms a closed sulphur cycle feeding the deep biosphere in marine sediments.

[1] Parkes *et al.* (2005) *Nature* **436**, 390. [2] Schippers *et al.* (2005) *Nature* **433**, 861. [3] D'Hondt *et al.* (2002) *Science* **295**, 2067. [4] D'Hondt *et al.* (2004) *Science* **306**, 2216. [5] Bottrell *et al.* (2000) *J. Geol. Soc.* **157**, 711. [6] Böttcher *et al.* (2006) *Proc. ODP, Sci. Res.* 201-109, 1.