

First principles investigation of manganese oxide surface chemistry

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Manganese oxides, which are ubiquitous in geological settings, play an important role in heavy metal adsorption and oxidation in the environment. In particular, the ability of manganese oxides to oxidize trivalent chromium to hexavalent chromium has garnered considerable attention, but questions remain concerning the mechanism of oxidation. To accurately model hexavalent chromium transport and its fate in the environment, the specific interactions between chromium ions and manganese oxide surfaces must be ascertained. Because structure, composition, and chemical properties of surfaces are intimately related to reactivity, a fundamental understanding of manganese oxide surface reconstructions and redox behavior lays the foundation for investigating oxidation mechanisms involving manganese oxides. However, detailed structural analyses of manganese oxide surfaces under environmentally relevant conditions are scarce.

We have combined periodic density functional theory calculations and *ab initio* thermodynamics to identify stable surface terminations of the β -MnO₂ (110) and γ -MnOOH (010) surfaces and to determine their redox behavior in response to varying oxygen and water chemical potentials. Reduction of the surfaces produces interesting surface reconstructions driven by the competition between lattice constraints and optimal *d*-orbital occupation and manganese coordination geometry. Multiple oxidation states are found at the surfaces due to Jahn-Teller effects. Under ambient conditions, oxidation of the γ -MnOOH (010) surfaces is predicted to be favorable, while the reduced β -MnO₂ (110) and γ -MnOOH (010) surfaces are not stable but may become relevant during heavy metal oxidation processes at the surface. Molecular and dissociative adsorption of water on the clean surfaces significantly lower the surface free energies. Binding sites for trivalent chromium on the hydrated surfaces will be presented with a focus on the effect of manganese oxidation state on adsorption geometry.

Modeling oceanic anoxia/euxinia induced by massive CO₂ injection

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Atmosphere-ocean biogeochemical cycle model

Rapid global warming caused by large igneous provinces (LIPs) has been suggested as the cause of ocean anoxia. To constrain the required conditions for the occurrence of oceanic anoxic event (OAE) and investigate the climate change during OAE, we constructed the atmosphere-ocean biogeochemical cycle model. The ocean model [1] can reproduce the vertical distribution of several dissolved components (e.g. PO₄, O₂, H₂S, DIC, Alk) in the water column. We also consider the kinetic treatment of carbonate dissolution in the ocean. Hence, carbonate compensation depth (CCD) can also be calculated. The simplified chemical (carbonate and silicate) weathering on land and air-sea exchange of CO₂ were also included.

Results and discussions

We conducted the sensitivity analyses of CO₂ injection event systematically with several initial conditions (we especially focused on *p*CO₂, *p*O₂, SST, and shelf area) because climate and geographical setting would affect the required amount of CO₂ and behaviour of climate change. Simulations indicate that (1) enhanced nutrient (phosphorus) input to ocean effectively promote the oceanic productivity, resulting in an expansion of oxygen minimum zone and nutrient efflux from the surface sediments to the bottom waters, (2) global eutrophication (and anoxia) can be induced by a positive feedback loop among anoxia, phosphorus regeneration, and surface productivity, (3) once global anoxia achieve, enhanced accumulation of organic carbon in marine sediments acts as a buffer against global warming, resulting in climate cooling during OAE in some cases.

In this presentation, we will also discuss the effect of initial conditions on the required amount of CO₂ for the occurrence of global anoxia. We conclude that historical background has an important role in the required conditions for OAEs.

[1] Ozaki, Tajika & Tajika (2011) *EPSL* **304**, 270–279.