

Microscopic Observations of Manganite Reductive Dissolution

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Manganese (hydr)oxide minerals are widely distributed at and near the earth's surface and are closely coupled to biological systems. The oxidation of organic compounds by manganese oxides is an important pathway for the release of the Mn micronutrient from its matrix into a bioavailable dissolved form. In the current work, the dissolution rate of manganite (γ -MnOOH) is investigated at several pH values and at several concentrations of the reductant, ascorbic acid. Changes in surface morphology are observed by atomic force microscopy, while the aqueous manganese concentration is simultaneously quantified by atomic absorption spectroscopy. The molecular dissolution mechanism exhibits several qualitatively different behaviours dependent on pH and reductant concentration. Above a critical pH value and reductant concentration, dissolution appears to occur incongruently because a precipitate, which is characterized by XPS, TEM/SAD, and XRD, is observed concurrently.

The role of deep sea temperature change in the glacial carbon cycle

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Measurements of benthic foraminiferal Mg/Ca from the deep eastern tropical Pacific (cores TR163-31P and 20B, 3.2 km water depth) are useful for estimating changes in mean ocean temperature during the last glacial period. Mg/Ca data imply temperature changes of $\sim 4^\circ\text{C}$ over the deglaciation, slightly larger than our previous estimates (Martin, 2002), and excursions of 1 to 2°C during Marine Isotope Stage (MIS) 3. Over the last 90,000 years, the oscillations in deep sea temperature show a general correlation with Antarctic air temperatures and atmospheric CO_2 . Comparison with a published high-resolution benthic foraminiferal O-18 record from the Atlantic (Shackleton et al., 2000) suggests that deep sea temperature excursions may be directly correlated with the well-defined sub-orbital atmospheric CO_2 events during MIS 3 (Indermuhle et al., 2000).

Two mechanisms simultaneously couple pCO_2 and ocean temperature: temperature-dependent CO_2 solubility and CO_2 -dependent radiative forcing of temperature. Each of these mechanisms leaves a unique slope of covariation between pCO_2 and deep ocean temperature, which we estimate using numerical models of climate and the carbon cycle. The pCO_2/T slopes derived from the data differ between the deglaciation and the shorter 5ky duration events in Marine Isotope Stage 3, revealing different mechanisms driving CO_2 variability. The deglaciation coincides with estimates for CO_2 forcing of temperature, while Marine Isotope Stage 3 is consistent with temperature-dependent solubility driving variations in atmospheric pCO_2 . Temperature-dependent solubility may also explain the small pCO_2 variations in the latter part of MIS 6.

References

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