

## Deep ocean carbonate chemistry on millennial to Milankovitch time scales

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Deep ocean carbonate ion concentration is intimately linked to ocean processes that regulate atmospheric CO<sub>2</sub> over glacial time scales. Well dated records of CaCO<sub>3</sub> preservation in deep-sea sediments provide valuable clues about these processes.

Building upon previous studies of CaCO<sub>3</sub> preservation in Cape Basin sediments [1, 2], we find that <sup>230</sup>Th-normalized fluxes of CaCO<sub>3</sub> are well correlated with the abundance of CaCO<sub>3</sub> during the last glacial period (LGP), allowing us to use the entire record of ODP-1089 CaCO<sub>3</sub> content [1] to infer changes in deep water carbonate ion concentration.

During the LGP, peaks in CaCO<sub>3</sub> preservation exhibit features that are reminiscent of warm intervals in Antarctic ice cores. Initially we linked increased CaCO<sub>3</sub> preservation to ventilation of deep waters via the Southern Ocean, which increased during Antarctic warm periods [3]. However, precise dating of Cape Basin sediments revealed that CaCO<sub>3</sub> preservation peaks are associated with vigorous North Atlantic Deep Water (NADW) formation following the Antarctic warm periods rather than by ventilation from the Southern Ocean during these warm periods [2]. Thus, the link between deepwater formation and atmospheric CO<sub>2</sub> is complicated by the complementary impacts of ventilation at opposite ends of the earth.

Millennial scale features in the CaCO<sub>3</sub> record of the Cape Basin are also observed in North Pacific sediments during the LGP, indicating the widespread impact of NADW formation on deepwater carbonate ion concentration.

Finally, we also find an intriguing correlation over longer time scales to suggest that precession forcing [4] and millennial events share some common impacts on deep water carbonate ion via NADW formation.

[1] Hodell *et al.* (2001) *Earth. Planet. Sci. Lett.* **192**, 109-124.

[2] Barker *et al.* (2010) *Nature Geosci.* **3**, 567-571.

[3] Anderson *et al.* (2009) *Science* **323**, 1443-1448. [4]

Lisiecki *et al.* (2008) *Nature* **456**, 85-88.

## How acidic is water on calcite?

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Mineral dissolution and precipitation take place primarily on undercoordinated sites on the solid surface, in particular kink sites. Most theoretical studies are performed using molecular mechanics assuming that only water is present at the surface. We have used density functional theory in combination with the COSMO-RS implicit solvent model to calculate pK<sub>a</sub> values of water on various sites on a calcite surface. The mineral surfaces were modelled by 80 atom clusters and we have checked convergence of the pK<sub>a</sub> values with respect to both cluster size and number of relaxed surface atoms. For kink sites, we found that water is acidic with a pK<sub>a</sub> value as low as 3.5. At equilibrium, kink sites are thus covered with hydroxyl ion and water. Our results are relevant for future theoretical studies of dissolution and precipitation of minerals, where the correct equilibrium structure should be modelled.

We also calculated the pK<sub>a</sub> values for ethanol adsorbed on terrace, step and kink sites on calcite and compared the free energies of adsorption of ethanol and water. Ethanol was found to bind stronger than water on the {10.4} terrace and on the obtuse step, equally strongly on the acute step, whereas on kink sites, water (in the form of hydroxyl ions) binds more strongly than ethanol (in the form of ethoxide). This is consistent with recent experimental data using atomic force microscopy showing that ethanol hinders recrystallization on the {10.4} terrace.