Upper ocean deoxygenation and denitrification at the end of the last ice age

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The solubility of gases in the ocean decreased at the end of the last ice age, as ocean temperatures gradually rose, which would be expected to have increased water column denitrification rates. However, proxy records from marine sediments have shown that changes in oceanic oxygen contrations across this interval were not globally uniform, implying an important role for accumulated changes in oxygen consumption through the respiration of settling organic matter. A global compilation of marine sediment proxy records reveals that the upper ocean generally deoxygenated, but this included pauses and even reversals, consistent with changes in both temperature and oxygen consumption. [1] A new global nitrogen isotope compilation is consistent with a doubling of the rate of denitrification in the anoxic cores of oxygen-minimum zones across the deglaciation. This compilation is also consistent with a deglacial increase of nutrient supply via leakage from nitrate-rich upwelling regions, most notably the Southern Ocean, as previously suggested [2]. It seems likely that this increased nitrate supply contributed to the deglacial de-oxygenation by enhancing export and oxygen consumption, while also intensifying denitrification in anoxic waters. This analysis suggests that the nutrient flux across the thermocline is a key determinant of oxygenation and denitrification, in addition to temperature-driven solubility changes.

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Computing the thermodynamics and reactivity of carbonates from solid state to speciation

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Being able to compute the thermodynamics and reactivity of carbonate minerals and their solution species from atomistic simulation has long been a goal of geochemical modelling. The objective of this presentation is to address the question of how far can we go towards achieving this with present models and resources? Here a number of problems in carbonate geochemistry will be examined to demonstrate to what extend we can reproduce experimental data for the solid state and therefore be predictive for more complex environments, such as those for solution speciation.

A first test for any theoretical method is the polymorphism of crystalline calcium carbonate where the thermodynamics is well known. Examination of the performance of various first principles methods shows that reproducing the relative stabilities of calcite, aragonite and vaterite is sensitive to the choice of functional. Beside the quantitative thermodynamics, such methods offer new insights into the disorder within vaterite [1]. While there are also many force field models for carbonate minerals in the literature, most also fail to yield accurate thermodynamics unless explicitly considered during fitting [2]. If care is taken, force field models are found to provide a good description of cation-mixing in carbonate solid solutions.

More challenging than the bulk is the interface between carbonates and solution, including the influence of pH. Here the thermodynamics and reactivity of calcium carbonate in solution can be accurately predicted by atomistic methods. Computed free energies for ion pairing and formation of stable pre-nucleation clusters [3] are found to agree well with data from experimental speciation models [4]. Furthermore, simulations predict that nanoparticles of amorphous calcium carbonate are more stable than their crystalline counterparts below a critical size, depending on the degree of water incorporation [5]. The final challenge is to be able to compute rates of growth and dissolution for carbonates; this is now feasible with the use of enhanced sampling techniques [6].

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