Using atomistic simulation to study the interaction of water and carbonate with oxide surfaces

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With recent environmental concerns, understanding the interactions of carbon with mineral surfaces is essential for the effective use of carbon sequestration. The adsorption of carbon dioxide can be considered through surface carbonation on the model surfaces of magnesium and calcium oxide. In addition, understanding the role water has on this process is also essential.

Potential based atomistic simulation techniques can be utilised for this purpose, due to their speed and effciency compared with other techniques. The screening of a large number of different surface configurations allow for the evaluation of free energies as well as the identification of important surfaces.

The calculation of vibrational frequencies can give information regarding the mode of carbonate adsorption. Results suggest that whilst the adsorption of a single carbonate leads to incorporation *into* the surface, higher concentrations will give rise to the formation of a mineral carbonate layer.

We have also modelled the mixed adsorption of carbonate and water on the low index surfaces of these simple oxides. Water adsorption has also been considered as both associative (hydration) and dissociative (hydroxylation). Through the modelling of varying surface coverage, the generation of surface phase diagrams is possible, showing the variation of surface composition with changing chemical potential of water and carbon dioxide.

The key results indicate the feasibility of these materials for a role in carbon sequestration. In particular, calcium oxide surfaces are more susceptible to surface carbonation at standard conditions than their magnesium equivalents. Also, the stepped {310} surface shows that it can take up more carbonate than a flat surface. However, the preference of the polar {111} surface to hydroxylate makes it unsuitable for carbon uptake.

Finally, we examine the effect surface carbonation has on the mineral – water interface using molecular dynamics. The results indicate that the water layering, which is evident in the uncarbonated surface, is severly disrupted upon carbonation.

Tracing terrestrial organic matter by δ^{34}S and δ^{13}C signatures in an Arctic and a subarctic estuary

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Arctic regions holds a third of the world's soil carbon [1]. A major concern is that thawing permafrost would lead to a release of this stored organic carbon and an increased discharge to the Arctic Ocean. However, the fate of terrestrially derived organic carbon in the marine environment is poorly understood [2]. One significant problem has been to precisely estimate the fraction of terrestrially derived carbon in marine dissolved organic matter (DOM). We have developed a method using δ^{34}S signatures, in addition to δ^{13}C signatures, to trace DOM in coastal environments. The values for dissolved organic S ($\delta^{34}S_{DOS}$) have twice the range between terrestrial and marine endmembers compared to those for dissolved organic C ($\delta^{13}C_{DOC}$); hence, the share of terrestrial DOM in the total estuarine DOM can be calculated more precisely. Also, $\delta^{34}S_{DOS}$ from estuarine primary production has a typical marine δ^{34}S signature, so terrestrial organic matter can be distinguished from both marine- and estuarine-produced organic matter. In contrast, a significant fraction of the C in estuarine primary production can be assimilated terrestrial dissolved inorganic C (DIC), which cannot be readily distinguished from terrestrially derived organic matter.

We have measured $\delta^{34}S_{DOS}$, first in DOM of the Gulf of Bothnia [3], and now also of the Laptev Sea in a transect from the Lena River. While the Northern Baltic Sea is a constrained system with known hydrological fluxes, the Laptev Sea is an open system, where it is harder to estimate fluxes of DOC, but by precise and accurate estimates of the fraction terrestrial, marine-produced and estuarine-produced DOC the fate of terrestrial organic carbon could better be described.

[1] Gorham (1991) *Ecol. Appl.* **1**, 182–195. [2] Hedges & Benner (1997) *Org. Geochem.* **27**, 195–212. [3] Alling *et al.* (2008) *Limnol. Oceanogr.* **53**, 2594–2602.