Derivation of an accurate force-field for the simulation of carbonates

PAOLO RAITERI[1,*], RAFFAELLA DEMICHELIS[1] AND JULIAN D. GALE[1]

[1]Curtin University, Department of Chemistry, PO Box 1987, Perth WA 6845, Australia, p.raiteri@curtin.edu.au (* presenting author)

In recent years computational methods have become increasingly important in the study of geochemical processes due to the atomistic insight they are able to provide. In particular, force-field simulations are arguably the natural candidates to study processes that occur at the nano-scale due to their ability to approach the experimental conditions. However, the predictive power of force-field simulation strictly depends on the empirical parameters used in the simple formulae that mimic the atomistic interactions, which need to be derived with considerable care.

This work presents the approach followed in our group to derive force-field parameters based on a combination of static and free energy calculations, which are able to reproduce the thermodynamics of minerals in water [1]. Advantages and limitations of this approach will be illustrated, also in view of possible errors in the experimental thermodynamc quantities that are used to train the force field. The application of this approach to the study of carbonates in an aqueous environment will also be presented.

Although force field simulations do not naturally allow for chemical reactions, different approaches to simulate proton reactivity have been proposed in the past years. In this work an overview of two methods, ReaxFF[2,3] and MSEVB[4,5], is also presented.

[1] P. Raiteri *et al.* (2010) *J. Phys. Chem. C*, **114**, 5997–6010.
[2] A. C. T. van Duin, S. Dasgupta, F. Lorant and W. A. Goddard III. (2001), *J. Phys. Chem. A*, **105**, 9396–9409
[3] J. D. Gale, P. Raiteri A. C. T. van Duin (2011) *Phys. Chem. Chem. Phys.*, **13**, 16666–16679
[4] U. W. Schmitt and G. A. Voth (1999), *J. Chem. Phys* **111,** 9361.
[5] P. Raiteri, J. D. Gale and G. Bussi (2011), *J. Phys.: Condens. Matter* **23**, 334213

Cenozoic boron isotope variations in benthic foraminifers

M. RAITZSCH[1*] AND B. HÖNISCH[2]

[1]Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany, raitzsch@awi.de (* presenting author)
[2]Lamont-Doherty Earth Observatory of Columbia University, Palisades, USA, hoenisch@ldeo.columbia.edu

Background

One of the proxies at the forefront of estimating past CO_2 from marine archives is the boron isotopic composition recorded in shells ($\delta^{11}B_c$) of surface-dwelling foraminifers [e.g. 1], which reflects surface seawater pH and relates to atmospheric CO_2. A prerequisite for translating $\delta^{11}B_c$ into pH is the knowledge of the $\delta^{11}B$ of seawater ($\delta^{11}B_{sw}$), which is essentially unknown prior to the Pleistocene. Whereas boron in seawater has a long residence time of 10-20 My, modeling results suggest that $\delta^{11}B_{sw}$ may have changed considerably over millions of years [2,3], thus restricting paleo-pCO_2 reconstructions beyond the Pleistocene to interpretation of relative shifts rather than quantitative estimates.

Estimating $\delta^{11}B_{sw}$ from $\delta^{11}B_c$

Our benthic foraminiferal $\delta^{11}B_c$ approach is based on (i) the observation that deep-sea pH is quasi-constant below 1000 m water depth and (ii) the assumption that past variations in deep-sea pH were muted compared to surface seawater, similar to the dominant control of ice volume on the oxygen isotopic composition of benthic foraminifer shells. Because the distribution of dissolved boron and its isotopes in seawater is conservative, ocean-wide changes in benthic $\delta^{11}B_c$ should thus primarily reflect changes in $\delta^{11}B_{sw}$. The synthesis of multiple individual estimates from spatially distant core locations thus avoids bias due to regional variations in carbonate chemistry, which likely differed between ocean basins. However, modeling studies based on independent evidence from the CCD history of the ocean and atmospheric CO_2 estimates suggest that deep-sea pH has not remained constant over the Cenozoic. To scale our averaged benthic $\delta^{11}B_c$ record to $\delta^{11}B_{sw}$, we therefore account for a linear 0.45 units pH-increase [4] from 50 Ma until today.

Results & Conclusions

Our 50 My benthic foraminiferal $\delta^{11}B_c$ stack, composed of seven core sites from all ocean basins and various water depths, yields a remarkably consistent record. Although a general influence of whole ocean pH-variation has to be accounted for, the history of CCD-variations is not uniform in all ocean basins [5] and would have caused non-uniform changes in pH and thus in benthic $\delta^{11}B_c$. We do not observe such inter-basin differences in $\delta^{11}B_c$ and hence conclude that our record primarily reflects secular variations in $\delta^{11}B_{sw}$. Accordingly, our estimates suggest that $\delta^{11}B_{sw}$ increased by ~2.5‰ since the late Eocene, superimposed on oscillating variations with amplitudes of up to 2‰ over the entire record.

[1] Hönisch et al. (2009) *Science* **12**, 1551-1554. [2] Lemarchand et al. (2000) *Nature* **408**, 951-954. [3] Simon et al. (2006) *Chemical Geology* **225**, 61-76. [4] Tyrrell and Zeebe (2004) *Geochimica et Cosmochimica Acta* **68**, 3521-3530. [5] Van Andel (1975) *Earth and Planetary Science Letters* **26**, 187-194.