

## Stable isotopic trends in Neoproterozoic oceans: A record of global Snowballs, global Slushballs, global methane, global diagenesis, and/or palaeogeography?

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The Neoproterozoic (1000 – 543 Ma) is a period of extraordinary Earth System change marked by extreme climatic fluctuations and hallmark biological innovations (advent of metazoans). Stable isotopic trends (C-O-B) associated with Neoproterozoic marine carbonate rocks display large amplitude fluctuations which many studies have shown are broadly reproducible worldwide and stratigraphically systematic. Amongst the most intriguing of these are from cap carbonates (carbonate rocks which rest directly on glaciogenic rocks, and/or the surface representing palaeo-glacial episodes) which show sharp negative C isotopic excursions (in many localities down to -6 ‰) followed by recovery to more positive values and concomitant B-isotopic excursions (about 9‰); these have generated lively debate and been used for innovative models addressing C cycling and ocean acidification during times of extreme Earth System change. However, no consensus has emerged over the mechanisms driving these isotopic fluctuations, or their exact timing.

We have amassed a C-O-B dataset on cap carbonates from Namibia, North America and northern Europe that shows that  $\delta^{13}\text{C}_{\text{carbonate}}$  trends can be distinguished based on location and inferred palaeobathymetric position within an individual basin. Along individual craton margins trends are systematic and variations can be reasonably attributed to varying palaeoenvironmental setting, i.e., they are self-consistent and compatible with the geology. However, inter-craton comparisons show that stratigraphic (temporal) patterns and amplitudes differ between basins. Although the duration of cap carbonate precipitation remains contentious, it is likely that deposition was relatively rapid (i.e.,  $10^{3-4}$  years rather than  $10^{4-5}$  years). Our data can be used to imply that the isotopic composition of water masses varied from place to place in Neoproterozoic oceans. This suggests that cap carbonates and their isotopic signatures were a likely product of a dynamic interplay between palaeogeography and palaeoceanic circulation.

## Adsorption and dynamics of ions at rutile and cassiterite surfaces

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The interface between aqueous solutions of ions (mostly  $\text{Rb}^+$ ,  $\text{Na}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$ ) and metal oxide surfaces, represented by rutile and cassiterite, is studied using molecular dynamics computer simulations. The previously published results for adsorption of these ions at negatively charged surfaces at 25°C are extended to cover higher temperatures up to 150°C and the effect of pH-dependent surface charge density. The effect of the temperature and pH on occupancy of different types of adsorption sites will be compared with predictions of Multi Site Complexation models (MUSIC). The competition between adsorption of several cationic species present in mixed solutions used in titration experiments (e.g.  $\text{Rb}^+$  and  $\text{Sr}^{2+}$ ) and the adsorption dynamics of ions will be also discussed.

### References

- Z. Zhang, P. Fenter, L. Cheng, N. C. Sturchio, M. J. Bedzyk, M. Předota, A. Bandura, J. Kubicki, S. N. Lvov, P. T. Cummings, A. A. Chialvo, M. K. Ridley, P. Bénézeth, L. Anovitz, D. A. Palmer, M. L. Machesky, D. J. Wesolowski: “Ion Adsorption at the Rutile-Water Interface: Linking Molecular and Macroscopic Properties, *Langmuir* **20**, 4954-4969, (2004).
- M. Předota, P. T. Cummings, Z. Zhang, P. Fenter, and D. J. Wesolowski: “Electric double layer at the rutile (110) surface. 2. Adsorption of ions from molecular dynamics and X-ray experiments”, *J. Phys. Chem. B* **108**, 12061 (2004).
- L. Vlcek, Z. Zhang, M. L. Machesky, P. Fenter, J. Rosenqvist, D. J. Wesolowski, L. M. Anovitz, M. Předota, and P. T. Cummings: “Electric Double Layer at Metal Oxide Surfaces: Static Properties of the Cassiterite-Water Interface”, *Langmuir* **23**, 4925 (2007).