

Controls on modern and paleo-shell weights of *G. bulloides* in the SW Pacific Ocean

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Shell weights of the planktic foraminifera *G. bulloides* have been used to track changes in near-surface ocean carbonate ion concentrations over the past 50 kyr in the Atlantic Ocean [1], and to hypothesize that anthropogenic atmospheric CO₂ increases and ocean acidification resulted in decreases in modern *G. bulloides* shell weights as compared to mean Holocene weights in the Southern Ocean [2]. We have carried out a study of the test sizes and weights, and trace element chemistry of 'modern' *G. bulloides* in sediment core-tops from the SW Pacific Ocean (latitudes 33-53°S; T=7-19°C). Mean size-normalized shell weights (SNW) correlate negatively with near-surface ocean temperature in the SW Pacific Ocean ($T = 31.8 \times e^{-30.5 \times \text{SNW}}$) and, unlike the study of [1], shell weights are heaviest in southernmost sites of lowest temperatures and lowest carbonate ion concentrations. Similar suites of data have been obtained for *G. bulloides* from sites offshore of eastern New Zealand for the past 25 kyr covering the last deglaciation, and MIS-33 to MIS-29 encompassing the warm MIS-31 interglacial when collapse of the Ross Ice Shelf and substantive ice loss from West Antarctica may have occurred [3]. Hypothetical *G. bulloides* SNW can be calculated for these paleo-records using the modern relationship between ocean temperature and SNW, Mg/Ca paleo-ocean temperatures, and then compared with measured SNW. In the current interglacial (<10 kyr) and the MIS-29 interglacial, measured SNW are in good agreement (within 10%) of predicted values. However, during the last and MIS-30 glacial periods, measured SNW are often more different (up to 30%) than predicted SNW, although the modern ocean temperature-SNW relationship is still the prominent control on SNW. During and prior to MIS-31, measured SNW deviate significantly (up to 100%) from predicted values and, in fact, correlate positively with Mg/Ca paleo-ocean temperatures and, presumably, are largely controlled by carbonate ion concentrations. These results demonstrate the complexity in attributing changes in *G. bulloides* SNW to one process both in different ocean settings and also back in time at a single site in the SW Pacific Ocean.

[1] Barker & Elderfield (2002) *Science* **297**, 833–836. [2] Moy *et al.* (2009) *Nature Geoscience* **2**, 276–280. [3] Pollard & deConto (2009) *Nature* **458**, 329–332.

Water dynamics in clay as a function of temperature: Coupling Neutron Spin Echo and molecular dynamics

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In the context of underground storage of radioactive waste, investigating water molecules dynamics in swelling clays considered in engineered barriers is of prime importance. In the vicinity of the canisters containing the nuclear waste, the temperature can reach more than 350K. Swelling clay minerals are lamellar alumino-silicates with permanent negative charge compensated by exchangeable cations situated between clay layers. In contact with water, the cations hydrate, leading to the formation of one, two or more layers of water confined between clay surfaces.

We study the translational dynamics of water in clays in low hydrated states by coupling quasi-elastic neutron scattering experiments (Neutron Spin Echo or NSE) and molecular dynamics (MD) on a large scale of temperature range where water remains liquid. As the natural montmorillonite clay of interest is complex to analyze because of interstratification, we chose to model it by a synthetic clay with well-defined states of hydration [1]. The activation energies of the diffusion processes determined by NSE are around 6 kJ/mol higher than for bulk water, for both the hydration states studied. The simulations are found to be in good agreement with experiments for relevant set of conditions [2] and they allow more insight into the origin of the observed dynamics, like the influence of hydrogen bonding and specific interactions with the surfaces.

[1] Malikova, N. *et al.* (2007) *J. Phys. Chem. C* **111**, 17603–17611. [2] Marry, V. *et al.* (2011) *Environ. Sci. Technol.* **45**, 2850–2855.