

High resolution rare earth element (REE) study on mussel shells, a proxy for the geochemical cycling at the coastal region?

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Trace and minor element variations in biogenic calcium carbonate shells have been widely applied in reconstruction of past environmental conditions [1,2,3]. Successively deposited biogenic calcareous shells, such as mussel shells, may have the potential to provide high resolution records of temporally resolved variability to investigate changes in climatic configurations and/or geochemical cycling where instrumental records are non-existent. In our previous work, we developed a high precision analytical method, using laser ablation coupled with sector field inductively coupled plasma mass spectrometry (LA-ICP-MS), to obtain high resolution time series of a suite of element/Ca ratios for mussel shells [4]. Here, we investigate the potential of one species of mussels, *Mytilus californianus*, to provide high-resolution records of coastal geochemical changes.

Mussel shell samples used in this study are from Tatoosh Island, Washington, USA, a coastal upwelling region where 11 years of instrumental records are available to calibrate shell chemistry on modern shells. Age models of the shells are anchored by stable isotope analysis on seasonally resolved micromilled shell material. An anti-correlated relationship between rare earth element (REE)/Ca and $\delta^{18}\text{O}$ is apparent upon comparison of the two records. A reliable shell age model is then constructed by combining both high resolution REE/Ca records and the seasonally resolved $\delta^{18}\text{O}$ records. Multi-Taper Method (MTM) spectral analysis was applied to identify significant quasi-periodic variability in shell REE/Ca records [5]. An intra-annual (3-5 cycles/year) periodic component has been identified in both modern and midden shells; similar periodic variability was also observed in the high resolution instrumental data for environmental parameters, such as upwelling and temperature. Calculated Ce anomalies (Ce*), a proxy for redox state in the water column, show similar ranges of variations in modern and ancient shells. Our results indicate REE/Ca ratios in mussel shells have the potential to serve as a proxy for the geochemical cycling at this coastal area and could possibly offer hints for explaining the recent and dramatic pH declines at this location [6].

[1] Klein et al. (1996) *Geology* **24**, 415-418. [2] Lea et al. (1999) *GCA* **63**, 2369-2379. [3] Wyndham et al. (2004) *GCA* **68**, 2067-2080. [4] Bian et al. (2012) *GCA*, submitted. [5] Mann and Lees (1996) *Climate Change* **33**, 409-445. [6] Wootton et al. (2008) *PNAS* **105**, 18848-18853.

Molecular structure and acidity

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Surface complexation models (SCMs) are often capable of fitting the same macroscopic data (e.g., titration data) by employing substantially different assumptions about molecular-scale reactions. This has been addressed by constraining SCMs with 1) more macroscopic data and information about molecular-scale processes obtained from 2) advanced spectroscopic techniques, 3) molecular modeling studies, and 4) quantitative structure-activity relationships (QSARs) like MUSIC [1]. All of these are reasonable, but even given the first three options, QSARs would still be necessary to provide a conceptual framework for interpreting the other types of results.

A problem with QSARs is that they assume only certain aspects of the molecular structure determine a particular type of reactivity. Sometimes, however, other structural features are important, but were roughly constant in the calibration set. E.g., MUSIC is calibrated on a certain set of (hydr)oxo-monomers, and assumes only the metal-oxygen bond valences and coordination numbers are important for determining functional group acidities. The model is then applied to the acidities of oxide surface functional groups, which are much more difficult to experimentally determine.

Are the MUSIC predictions always accurate for oxide surface functional group acidity, or are some important structural features missing from the model? Our previous work [2] used an expanded calibration set of solution monomers to show that in addition to bond valence and coordination number, the electronegativity of the metal atoms is also necessary to accurately predict acidity, but we provided no compelling structural explanation.

We are now assembling a complete potential energy model, based largely on the Bond-Valence Model (BVM), to guide development of QSARs based on the BVM. Our model combines the predictions of the VSEPR model of molecular geometry with the BVM, using the concept of bond valence vectors [3], along with van der Waals and electrostatic potentials to describe non-bonded interactions. So far, we have been able to show that changes in Me-H van der Waals potential energies due to structural relaxation are likely to be important for determining acidity in our calibration set of oxyacids, and that this effect is highly correlated with the electronegativity of the metal atoms. Thus, we have found a way to explain our previous results in structural terms, and a way to determine how an acidity QSAR based on bond valence, coordination number, and acidity might be successfully transferred to oxidized surfaces. This kind of theoretical guidance for creating and transferring QSARs is essential for systems like mineral-water interfaces, where it is often difficult to check the veracity of model results at the molecular scale.

[1] Hiemstra et al. (1996) *J. Colloid Interface Sci.*, **184**, 680-692. [2] Bickmore et al. (2006) *GCA* **70**, 4057-4071. [3] Harvey et al. (2006) *Acta Crystallographica*, B62, 1038-1042.