Evaluating ocean acidification using stable isotope fractionation of fossil scallop shells

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As ocean pH declines, due to increased atmospheric carbon dioxide, the saturation states of carbonate polymorphs is expected to decline. Fractionation of oxygen, carbon, and sulfur stable isotopes in growing shells in response to these changes, whether direct or indirect, could provide a new tool for reconstruction of paleoenvironments. In the laboratory bay scallops were reared (*Argopecten irradians*) under low pH conditions induced by high CO_2 (pH = 7.8, 7.6, 7.4, and 7.2). Carbonate chemistry was measured/modeled as well as other water quality parameters. Animals were sacrificed over a 1 month period and growth (length, buoyant weight) was measured. New shell was excised and $\delta1^{3}C$, $\delta^{18}O$, and $\delta^{34}S$ as well as total C and S were measured. Fractionation of C and O associated with pH was observed as was fractionation of S though, in the case of S, the fractionation was not significantly associated with pH. A C-O fractionation model was developed that predicted pH treatment. This model was then tested on Pliocene scallop fossils (*Carolinapecten eboreus*; Pinecrest Sand, Florida). The Pinecrest was deposited in the Late Pliocene as the final closure of the Central America Isthmus was occuring and ocean circulation patterns were changing as a result. Decline in pH associated with these changes has been suggested. Given the exceptional preservation of these fossils we tested our experimentally determined pH stable isotope model and evaluated the potential for this model to predict changes in pH in the Late Pliocene ocean.

Large Mo isotope variations before the Great Oxidation Event

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Molybdenum (Mo) isotopes are efficiently removed under euxinic conditions and therefore may directly record contemporaneous seawater in ancient organic-rich shales. Removal of Mo in other environments (i.e., anoxic and oxic) is less efficient and accompanied by a significant negative isotope fractionation, where $\Delta^{98}Mo_{SW-SED}$ is typically 1 to 3 ‰ [1,2]. It is generally accepted that before the Great Oxidation Event (GOE) at ca. 2.3 Ga the transfer of Mo to the oceans was primarily in detrital form. This is in accordance with the available sedimentary data showing a narrow range of isotopic compositions corresponding to the crustal reservoir. As atmospheric oxygen started to rise, Mo was chemically weathered from continental sources and transported to the oceans as oxidized molybdate (MoO_4^{2-}). There, it was removed to sediments via several fractionating mechanisms, depending on the redox conditions. Consequently, Proterozoic and Phanerozoic black shales record a wide range of Mo isotopic values, reflecting variations in the isotopic composition of seawater as determined by the mass balance between the different sinks.

We measured Mo concentrations and isotopic compositions of black shales from several Neoarchean and Paleoproterozoic sections (2.7 Ga - Belingwe Fm., Zimbabwe; 2.63 Ga - Jeerinah Fm., Western Australia; 2.52 Ga - Gamohaan Fm., South Africa; 2.15 Ga - Sengoma Argillite Fm., Botswana; 2.06 Ga – Zaonega Fm., Karelia). The data show large isotopic variations and significantly elevated $\delta^{98}Mo$ values in sections dated up to 400 Myr before the GOE. Moreover, these pre-GOE sections show Mo concentrations which are higher than those typically found in older sections [3,4], but still lower than those found in post-GOE Proterozoic sections[5,6]. These observations imply a process of chemical weathering, transport and sedimentation of Mo, which was accompanied by significant isotope fractionation. We propose that such a process may be driven by either (a) low and fluctuating oxygen levels which led to episodes of continental Mo weathering, or (b) enhanced atmospheric sulfur levels after volcanic events which may initiate removal of Mo from the continental crust to the oceans.

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