Boron isotope systematics of calcitic gorgonian corals and their response to ocean acidification

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Cold-water corals are thought to be especially susceptible to CO_2-driven climate change and ocean acidification given that many live near the aragonite saturation horizon in the deep oceans. Recently, however, boron isotope analysis of aragonitic (scleractinian) cold-water corals revealed their capacity to modulate internal pH and aragonite saturation state at the site of calcification, which enables these species to maintain higher rates of calcification and potentially escape the effects of ocean acidification [1].

Here we investigate the boron isotopic systematics of a suite of calcitic gorgonian corals from a wide range of environments to determine their potential to modulate the pH of the calcifying fluid, their sensitivity to future climate change scenarios, and their utility as archives of seawater pH. These calcitic corals are lower in boron concentration as well as isotopic composition ($\delta^{11}B$) than aragonitic cold-water corals, with $\delta^{11}B$ values lying along or near the seawater borate equilibrium curve. This shows that, unlike aragonitic corals, these calcitic species have limited if any ability to modify the calcifying fluid and thereby precipitate their calcitic skeletons close to ambient seawater pH. serve as an archive of continuous seawater pH over centennial to millennial timescales, is especially important given the lack of continuous long-term records and the need to understand the natural variability of seawater pH on longer timescales.

[1] McCulloch *et al.* (2012) Geochim. Cosmochim., 87, 21-34.

Impact of As(V) on abiotic reduction of U(VI) by mackinawite

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Arsenic and uranium are commonly found together in areas of historic uranium mining activity because they can be released during the mining of uranium ore. Studying the behavior of these elements together under anoxic conditions is necessary to understand their mobility in natural sediments. Recent studies have shown that mackinawite produced through activity of sulfate reducing bacteria is one of the major reductants of U(VI) in subsurface environments [1]. Although reduction of uranyl species by mackinawite has been shown to occur, the reduction of U(VI)-carbonates or U(VI)-arsenates has not been investigated. U(VI) and As(V) can form uranyl arsenate mineral precipitates or surface precipitates depending on their relative concentrations [2]. This study examines the reducibility of U(VI)-carbonates and U(VI)-arsenates under varying U/carbonate and U/As ratios in the presence of mackinawite.

Anoxic batch experiments were conducted including mackinawite with U(VI) and As(V) at concentrations ranging between 50 to 500 μM, including treatments with 5 mM and 30 mM dissolved carbonate. After 48 hours, mackinawite was collected for analysis by X-ray absorption fine structure (XAFS) spectroscopy to determine speciation and binding environment of U and As. Results showed that the extent of U(VI) reduction was not affected by the formation of U(VI)-carbonato complexes. U(VI) reduction was only shown to be limited by As(V) at concentrations at or above 500 μM, where the formation of uranyl arsenate mineral precipitates is favored. Although little influence of U(VI)-carbonate and U(VI)-arsenate species was observed on U(VI) reduction, As(V) reduction was limited in the presence of all tested U(VI) concentrations due to preferential reduction of U(VI). When remediating natural environments containing both As and U, As(V) does not prevent U(VI) reduction by mackinawite under environmentally relevant concentrations.

[1] Bargar *et al.* (2013) *PNAS* **110,** 4506-4511. [2] Tang *et al.* (2009) *ES&T* **43,** 4452-4458.

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