Determining the utility of rhenium as a novel redox tracer in carbonate-rich sediments

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Local redox conditions should be evaluated and considered when interpreting U isotope fractionation and its validity for understanding global seawater redox conditions[1]. Redoxsensitive trace metals (RSM) have been useful for indicating local changes in redox conditions in marine sediments. In particular, rhenium (Re) has been a particularly useful tracer in marine sediments due to its accumulation in sediments coincident with Fe(III) and sulfate reduction[2]. Rhenium has an extremely low concentration in oxic marine sediments (0.1 ppb[3]). With this low detrital background, it is possible to discern an unmistakable authigenic signal. However, the usefulness of Re as a tracer in carbonate-rich sediments is less well understood because it is unknown whether Re incorporates into the carbonate lattice and/or is only retained in the noncarbonate matrix. The likelihood of the dissolution of host phases containing Re needs to be considered under a variety of conditions in concert with the dissolution of the carbonate fraction, metal/Ca ratios, and U isotopic fractionation. We focused on five complementary samples: a pure limestone standard, two samples with lower (<20%) non-carbonate content and minimal evidence for diagenesis, and two samples with greater non-carbonate content (20-30%) and evidence for diagenesis under sulfidic conditions. Variables included acid type (nitric and acetic), concentration (0.08 M and 2 M), and acid addition to achieve a targeted percent carbonate dissolution (from 20-200%). Simultaneous measurements of Sr, Mn, Fe, Al and U provided additional context so as to evaluate the measured Re concentrations. Together, these samples and metal analyses provide an appropriate context for evaluating the effects of Re release during carbonate dissolution. Preliminary results reveal higher Re concentrations and Re/Ca ratios in samples with previous exposure to sulfidic conditions when those samples were treated with excess 2 M nitric acid relative to samples treated with 0.08 M nitric or acetic acids. In contrast, the U isotope fractionation appears to be consistent regardless of acid type, concentration, or amount.

References:

[1] Chen et al. (2018) Geochim. Cosmochim. Acta. 237, 294-311. [2] Morford et al. (2012) Chem. Geol. 324-325, 73-86.[3] Koide et al. (1986) Appl. Geochemistry 1, 705-714.