Unique redox behaviors induced by polysulfide and sulfide; Arsenic the latest example

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The polysulfide/sulfide (S_n^{2-}/HS^-) couple controls many redox processes in euxinic waters. At fixed pH, higher S_n^{2-}/HS^- shifts platinum electrode potentials in the positive direction and raises theoretical pE. However S_n^{2-}/HS^- mixtures affect individual metals and metal-oids in unexpected ways through complex formation; Sb^{III} is oxidized by higher S_n^{2-}/HS^-, as would be expected, but Mo^{VI} and Re^{VII} are reduced, counter to expectation. The latest curious example is As^{III}, which seems to be oxidized by HS^- even in the absence of S_n^{2-}. Much controversy surrounds this issue currently. Through a novel strategy that combines empirical data with *ab initio* computational results and estimated ionization constants, we have constructed a provisional thermodynamic model which predicts concentrations of thirty-two As^{III} and As^V oxythio monomers as a function pH, $\sum S^{-II}$ and $\sum As$ at any imposed pE. At the order of magnitude level, this model successfully predicts previously measured As_2S_3 solubilities. Assuming redox buffering by orpiment+realgar, the model predicts that As^V species contribute significantly to total solubility, especially at higher pH. Until now, papers discussing As species distributions claim that As thioanions must be either As^{III} or As^V species. The most important implication of the new model is that both kinds of thioanions are likely, even in the same solutions. The model rationalizes the counter-intuitive effect of sulfide on As redox chemistry, highlights critical information needs and provides a testable framework that can be used to guide future experimental studies.

In-run corrections for instrumental fractionation of boron isotopes by NTIMS: Filament material and loading matrix controls

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Maximizing the potential of the boron isotope paleo-pH proxy depends on precise analyses of very small samples. Negative thermal ionization mass spectrometry (NTIMS) allows analysis of <1ng, but controlling mass fractionation is a major challenge, addressed in our group by routinely analysing each sample multiple times. A promising strategy for mass fractionation correction has been proposed [1]. Reproducibility for NIST 951, seawater and corals on Pt filament wires was 2.3‰, 6.2‰ and 4.6‰, respectively, but improved to 0.67‰, 0.19‰ and 0.34‰ for the same analyses using a correction factor determined by measuring mass $^{45}(BO_2)$ in addition to $^{43}(BO_2)$ and $^{42}(BO_2)$.

While testing the Thermo Scientific Triton multi-collector thermal ionization mass spectrometer in Bremen, Germany, five of six NIST 951 samples on Re filaments produced isotope ratios on average 3‰ ±1.5‰ lower than the expected $^{43}(BO_2)/^{42}(BO_2)$ of 4.005 [2]. We took advantage of the multiple collector capability, and measured the isotopologues $^{44}(BO_2)$ and $^{45}(BO_2)$. On isotope cross plots [1] the very large deviations from expected ratios of NIST 951 analyses form a trend line (r^2=0.98). However, the slope of the trend line for Re filaments is very shallow, and correcting to the recommended NIST 951 value would yield an unreasonably high apparent $^{18}O/^{16}O$. Correcting to our best NIST 951 estimate yeilds an $^{18}O/^{16}O$ estimate of 0.00214, and applying the approach of [1] with this value improves the reproducibility to 0.21‰. In addition to the loading matrix control [1], it appears that the measured values are sensitive to filament material. It is apparent that a better understanding of the ionization process has tremendous potential for improving the precision and accuracy of boron isotope measurements.

[1] Shen & You (2003) *Anal. Chem.* **75**, 1972-1977. [2] Hemming & Hanson (1994) *Chem. Geol.* **114**, 147-156.