

Sources of organic matter fueling As mobilization in groundwaters of West Bengal, India: Evidence from reactive transport modeling

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It is generally agreed that microbial reduction of Fe(III) oxides/oxyhydroxides coupled to organic matter (OM) oxidation is an important mechanism by which arsenic (As) is mobilized to groundwaters within the Bengal Basin of Bangladesh and West Bengal, India. Nonetheless, the source of the OM driving the respiratory processes remains contentious [1]. Some researchers argue that recently constructed perennial ponds are a major source of recharge waters, and hence dissolved organic matter (DOM) to the As affected groundwaters, whereas others maintain that the sediments contain sufficient OM to fuel microbial respiration [2, 3]. Here we employ reactive transport modeling to simulate transport of DOM in aquifers from the Murshidabad district of West Bengal, India. The goal was to assess the possibility that OM originating in surface ponds could be transported to depth in the local sediments where As is chiefly being mobilized (i.e., ~ 30 m below ground surface). A one-dimensional advective-dispersive transport code was linked to the generalized, two-layer surface complexation model (SCM) for Fe(III) oxides/oxyhydroxides to evaluate DOM transport within local sediments. We present the results of different scenarios that include variable aquifer heterogeneity, DOM lability, and different potential surface water sources (i.e., river Bhagirathi and constructed perennial ponds). The model runs indicate that transport of pond-derived and river-derived DOM to depths in the underlying aquifer where As mobilization is greatest is unlikely to be significant over time scales consistent with the estimated ages of groundwater at these depths (e.g., ~ 50 years). Instead, DOM from surface waters would require at least 1000 years to reach the top of the As affected aquifers in Murshidabad. Results of the modelling support an *in situ*, sediment source for the DOM.

[1] Reich (2011) *Nature* **478**, 437-438. [2] Harvey et al. (2002), *Science* **298**, 1602-1606. [3] McArthur et al. (2004) *Appl. Geochem.* **19**, 1255-1293.

A triple-proxy approach to reconstructing seawater $\delta^{18}\text{O}$

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Reconstructing changes in the oxygen isotopic composition of seawater ($\delta^{18}\text{O}_{\text{seawater}}$) through geologic times is a high-value target as this proxy informs us on the evolution of Earth's cryosphere (waxing and waning of ice sheets), changes in ocean currents (with subtle differences in $\delta^{18}\text{O}_{\text{seawater}}$) and salinity effects related to the amount of evaporation of surface waters (the lighter ^{16}O isotope being preferentially fractionated in the water-vapor phase during evaporation). Unfortunately, geologic samples of biogenic marine calcite ($\delta^{18}\text{O}_{\text{calcite}}$) record the combined effects of changes in $\delta^{18}\text{O}_{\text{seawater}}$ and changing water temperature. For instance, a phase of expanded high-latitude ice sheets during a glaciation will result in heavier $\delta^{18}\text{O}_{\text{seawater}}$ (due to ^{16}O preferentially stored in the continental ice) but would also be associated with a global cooling of the ocean, thus further increasing the $\delta^{18}\text{O}_{\text{calcite}}$ values. This makes assessing the relative impact of each mechanism on $\delta^{18}\text{O}_{\text{calcite}}$ difficult, and hinders quantitative assessments of changes in $\delta^{18}\text{O}_{\text{seawater}}$.

The paleoceanography community has tried to come around this limitation by pairing $\delta^{18}\text{O}_{\text{calcite}}$ with other temperature proxies independent of $\delta^{18}\text{O}_{\text{seawater}}$. One of the most successful proxies to date is the Mg/Ca ratio of benthic foraminifers. Foraminiferal Mg/Ca ratio has been shown to be temperature dependent for many species, and the Mg/Ca ratio of seawater is thought to be conservative on the timescale of 1 million years. However, on timescales greater than a million year the Mg/Ca ratio of seawater is likely to change, implying that this proxy is a good proxy for relative temperature changes, but that it cannot unambiguously resolve absolute seawater temperatures for periods older than the Pleistocene. Furthermore, the concentration of carbonate ions seem to impact Mg/Ca intake in benthic foraminifers, and thus changes in carbonate ion concentrations in the ocean could impact on the temperature estimates from foraminiferal Mg/Ca.

This review talk will highlight how adding a third, novel proxy (clumped isotopes) could resolve some of the issues at hand. The "Clumped isotope paleothermometer" is based on thermodynamics, and thus is independent of $\delta^{18}\text{O}_{\text{seawater}}$. Calibrations have shown that clumped isotopes are independent of nearly all changes in ocean chemistry, though some exceptions occur (for instance, in hypersaline conditions). Clumped isotopes suffer from their own set of limitations, notably because the measurements require a significant amount of time and sample material (up to 25 mg if three replicates are made). However, we will show through some preliminary data what strategies can be put in place to overcome this limitation, and how a "triple-proxy" approach based on high-resolution $\delta^{18}\text{O}_{\text{calcite}}$ measurements, medium resolution foraminiferal Mg/Ca measurements and low-resolution clumped isotope measurements could help resolve some of the issues currently faced by the paleoclimate community.