Reverse weathering in the Okavango Delta, northern Botswana

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Introduction

Reverse weathering was first proposed to balance elemental budgets in the oceans [1]. The suggestion was thermodynamically possible, but lacked direct observational evidence. Recent field and lab incubations unambiguously show rapid formation of authigenic clay minerals is plausible under certain conditions [2,3]. We present direct and indirect evidence for mineral authigenesis in the Okavango Delta, a shallow, freshwater, tropical wetland bounded by the southern extension of the East African rift valley. Water and sediment samples were collected after peak flood in 2011 along a hydrological gradient from riverine to seasonal floodplain. The watershed hydrodynamics and biogeochemical processing regulate elemental cycling and maintain the Delta as a freshwater system [4].

Evidence for new mineral formation

Direct evidence for rapid mineral authigenesis comes from microscopic, spectroscopic and geochemical analysis of floodplain sediments. Special attention is paid to biogenic silica particles that are known to provide viable substrates for clay precipitation.

Indirect evidence comes from downstream changes in dissolved element concentrations and Ge/Si ratios. PCA of elemental concentrations assessed by ICP-AES or -MS indicates a strong hydro-chemical concentration gradient. Boron acts conservatively and is interpreted as representing the expected enrichment (~12x inflowing concentration) if evapotranspiration was the only process occurring. Other elements show lesser or even negative enrichment (4 – 0.1x inflowing concentrations), suggesting biotic or abiotic removal. A simple mixing model suggests that for many elements involved in clay authigenesis (e.g. Fe, Mn, Mg, K) biotic uptake cannot explain the relative lack of enrichment.

The ratio of Ge to Si (Ge/Si, μmol/mol) is commonly used as a tracer of critical zone weathering processes. A downstream decrease in Ge/Si from ~1 to ~0.2 is interpreted here in terms of in-stream processing. Uptake of Ge relative to Si during biological production is poorly defined but thought to be either unbiased or slightly negative [5]. The observed decrease in Ge/Si ratios must therefore be explained by preferential abiotic Ge removal.

We suggest rapid formation of new mineral phases in floodplain sediments is an important process. Our results show biotic and abiotic processes control element cycling in the Delta and highlight the possibility of reverse weathering in freshwater systems.

References

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Nitrate (δ^{15}N) isotopic distribution in Antarctic Sea Ice,

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The only study reporting nitrogen isotopic composition (δ^{15}N vs. Air N_2) in Antarctic Sea Ice pointed out an isotopic distribution for particulate nitrogen (PN) significantly different from the marine counterpart[1-2], respectively 2 to 41‰ vs. -6 ot 6‰. Antarctic sediments from the last ice age are characterized by heavier PN δ^{15}N (including diatom bound nitrogen)[3]. Since an equatorward sea ice expansion is expected during glacial periods, the potentially higher contribution of sea ice PN in glacial sediment may explain or accentuate such variation.

We have measured δ^{15}N of nitrate in Antarctic Sea Ice, as a first step toward developing a mechanistic understanding of the processes driving such isotopic difference (sea ice vs. marine realm). The nitrate δ^{15}N was measured in the brine network both in spring and summer Antarctic pack ice, respectively, in the Bellinghausen Sea (SIMBA, October 2007) and Weddell Sea (ISPOL, December 2005).

The δ^{15}N range for nitrate measured so far, 2.7 to 13.2‰, falls in the range of previously measured values. The mean δ^{15}N (± 1sd) is heavier in summer (9.4 ± 2.8‰) than in spring (4.1 ± 1.2‰), in agreement with the seasonal nitrate depletion together with a preferential assimilation of light nitrate into organic matter. An unexpected outcome is that some samples show a δ^{15}N lower than that of lower circumpolar deep water which is typically 4.7-4.8‰ [2], implying processes in addition of nitrate assimilation. Possible nitrogen source to the nitrate pool include the organic matter and ammonium (NH_4) inside the brine network[4], the nitrification of which could yield low δ^{15}N nitrate. Indeed, nitrification has been observed to occur in Antarctic Sea Ice[5], implying a regeneration of nitrate inside the brine network. Presumably, the generation of low δ^{15}N nitrate also causes the ammonium pool to be elevated in δ^{15}N, an inference that we will test with measurements. The implication for the δ^{15}N of sea ice PN will then be investigated.

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