

Contrasting silicon and magnesium isotope fractionation with clay mineralogy in volcanic soil weathering sequences, Guadeloupe

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The weathering of continental silicate rocks influences global climate by consuming atmospheric CO₂. Magnesium and Si stable isotopes are used as weathering proxies in soils and rivers, but the impact of the mineralogy of secondary phases on isotope fractionation remains unexplored so far. Here, we investigate variations in δ²⁶Mg vs. DSM-3 and δ³⁰Si vs. NBS28 in bulk soils and clay fractions relative to their parental andesite in two soil weathering sequences (Guadeloupe) that were formed in contrasting climatic conditions. The Western slope of La Soufrière volcano (dry conditions) presents a soil sequence Andosol - Cambisol - Vertisol with formation of smectite, whereas the Eastern slope (high rainfall) presents Andosol - Nitisol - Ferralsol with formation of kaolinite.

For Mg isotopes, clay fractions (δ²⁶Mg -0.41 to -0.10‰) were isotopically heavier than the andesite (δ²⁶Mg -0.47‰), supporting a preferential incorporation of heavy Mg isotopes in secondary Mg-bearing clay minerals. The clay fractions on the Eastern slope were progressively heavier with increasing weathering degree, -in contrast to the Western slope where clay fractions were progressively lighter with increasing weathering degree and with increasing exchangeable Mg associated with smectite. For Si isotopes, clay fractions were lighter than the parental material, and progressively lighter with increasing weathering degree. More importantly, larger Si isotope fractionation was associated with the formation of kaolinite (δ³⁰Si -1.95 to -1.32‰) than with the formation of smectite (δ³⁰Si -1.05 to -0.94‰) relative to the parental andesite (δ³⁰Si -0.37‰). Our results highlight that a similar parental andesite exposed to different climatic conditions can generate contrasting Mg and Si isotope fractionations in secondary phases, which offers great potential for paleo-reconstruction of soil environments.

Impact of reductants on the optical properties of Humic Substances (HS)

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Our previous results have shown that the reduction with sodium borohydride of Suwannee River humic and fulvic acids, a commercial lignin, and a series of solid phase C18 extracts from fresh, estuarine, coastal and offshore waters of the middle Atlantic bight produces a preferential loss of long wavelength (visible) absorption and enhanced, blue-shifted emission [1]. These results are consistent with and interpreted within a previously proposed charge transfer model [2, 3]. Here we extend this work to other reducing agents (such as cyanoborohydride and sodium dithionite) and other humic substances (from aquatic and soil environments) to investigate the impact of other reductants on the optical properties of humic substances and attempt to assess the relative importance of quinones and ketones to the optical properties of these materials. Preliminary results indicate that a) borohydride reduces all HS examined independent of their source as determined by UV/Vis and fluorescence; b) cyanoborohydride did not reduce any of the HS examined to a significant extent; c) dithionite appears to reduce HS but to a much smaller extent than borohydride. Ongoing work aims to extend this work to more HS and model quinones/ketones and to quantify the loss of absorption with respect to dithionite consumed.

[1] Ma *et al.* (2010) *Environ. Sci. Technol.* **44**, 5395-5402.
[2] Del Vecchio and Blough (2004) *Environ. Sci. Technol.* **38**,
3885-3891. [3] Boyle *et al.* (2009) *Environ. Sci. Technol.* **43**,
2262-2268.