Geochemical patterns of *Spartina maritima* from Portuguese estuaries

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This study reports on the geochemistry of *Spartina maritima* (*S. m)* tissues collected from Lima, Mira, Sado and Tagus salt marshes; the discussion will focus on element distribution patterns and extent of geochemical fractionation between *S. m* tissues and their respective sedimentary substrates. Sediments from the studied estuaries display UCC type REE patterns and $^{87}Sr/^{86}Sr$ values (0.715367 – 0.725351), but have distinct total element contents due to variations on their clay / carbonate / sand / organic matter components; tissue element contents do not correlate with textures of their substrates, and the main features of different sediment normalized (*sn*) element distribution patterns of *S. m* are similar. Except for regular $Na_{S.\ m}/Na_{sed} > 1$, most element contents of *S. m* tissues are usually lower than those found in their sediment substrate (relative depletion generally increases from roots ~ leaves to stems, reaching $\sim10^{-3}$). Thus, *S. m* $_{(sn)}$ alkaline metal distribution patterns exhibit strong depletions for Li, K, Rb and Cs relative to Na; Mg and Sr are also enriched relative to Ca and Ba, with *S. m* Na/Ca (7 – 29), Mg/Ca (1.2 – 4.3), Sr/Ba (2 – 193) and $^{87}Sr/^{86}Sr$ (0.709074 – 0.709408) approaching seawater values. Transition metals *S. m* $_{(sn)}$ patterns display Mn and Cu, Zn enrichment relative to Sc, Cr, V and Co, Ni. Ag and Au are concentrated by *S. m* (up to 30×sed - Ag and 12×sed - Au) being enriched relative to Cd, Sn, Hg and As. ∑REE in *S. m* tissues are highly variable (leave/stem = 3 – 10); despite this, (and except for LREE/HREE enrichment in Lima samples), *S. m* $_{(sn)}$ REE patterns show similar shapes with relative MREE (Eu, Tb) enrichment and a Gd negative anomaly. HFSE patterns are characterized by a distinct positive Mo anomaly and augmented Mo/W, Mo/Ta, Nb/Ta (which correlate with high U/Th) in *S. m* tissues (Mo/Ta$_{S.\ m}$ = 30 – 1500; Nb/Ta$_{S.\ m}$ = 10 – 20; U/Th$_{S.\ m}$ = 0.31 – 1.40) compared to those values in their substrates. Results indicate that there is considerable geochemical fractionation between *S. m* tissues and their respective estuarine substrates. Seawater is influencial, but the main fractionation mechanisms should be related to element bioavailability for specific *S. m* metabolic processes.

Rhenium geochemical cycling: Insights from continental margins

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The accumulation of Re in sediments is due to diffusion of Re from bottom waters across the sediment-water interface to its depth of precipitation, but the controls on Re accumulation have proved elusive. Our study of pore water profiles from the Mid-Atlantic Bight (MAB, eastern margin of the USA), combined with profiles from coastal areas (Hingham and Buzzards bays, Massachusetts), suggests that: (1) the oxidation of labile organic matter in sediments is a controlling factor for the flux of Re into sediments, and (2) non-diffusive transport (irrigation) is important for Re accumulation in sediments. There is a linear relationship between organic carbon oxidation rates and pore water Re fluxes into sediments, although this relationship is lost at Hingham Bay. At the Hingham Bay site, the pore water Re flux is underestimated since non-diffusive transport (irrigation) was not included. At the site in Buzzards Bay, where non-diffusive transport is included in the modelled pore water profiles, the calculated pore water Re flux is consistent with the measured solid phase authigenic Re accumulation rate.

A compilation of data suggests authigenic solid phase Re accumulation in sediments requires a minimum organic carbon oxidation rate (> 0.4 mmol/m²/d). However, results from locations shallower than 100 m water depth are not consistent with the overall trend and may hamper the use of Re as an indicator for past changes in organic carbon oxidation rates. An oxygen penetration depth ($O_{2,\ pen}$) of ≤ 1 cm in sediments does not appear to be a criterion for Re accumulation. The Re accumulation rate varies by a factor of 20 when $O_{2,\ pen}$ ≤ 1 cm, and appreciable Re accumulation is measured in southern MAB sediments where oxygen extends 1.4 to 3 cm below the sediment-water interface.