In-situ LA-ICPMS analysis of a giant spicule of a deep sea sponge

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Sponges are simple and the evolutionary oldest animals that appeared approximately 800 Million years ago. We have determined 37 trace element concentrations in a giant spicule, Q-B, of a deep sea sponge (*Monorhaphis intermedia* [Hexactinellida]) using LA-ICPMS. The spicule was collected from China East Sea and provided by the Institute of Oceanography (Quingdao). It is about 110 cm long and has a diameter of 7 mm in maximum. Scanning electron microscopic inspection of cross sections reveals their lamellar organization. A complete series of LA-ICPMS analyses could be performed on the same spicule within µm areas. The detection limits range between 0.3 and 10 ng/g.

The results demonstrate that most trace elements are uniformly distributed from the axial canal to the surface of the spicule. It is of prime interest that the giant spicules are composed to over 99.5 % of pure silica. Na = 1500 µg/g and Ca = 200 µg/g are the most abundant trace elements in Q-B, whereas the 35 remaining elements contribute only unimportantly to the inorganic composition in bio-silica. This implies that the quality of bio-silica in the spicule is in the range of quartz grade. The impact of this finding becomes even more meaningful in comparison with the element composition of seawater. Referring to natural seawater Na and Cl are dominant with 32.4 and 58.5 % (solid material), respectively. Ca contributes with 1.2 % and Si with only 0.006%. Amazingly, the LA-ICPMS data demonstrate that sponges produce almost pure bio-silica in an aqueous environment, which contains only trace levels of Si. These results can be explained by the ability of sponges to produce amorphous quartz glass as the material to construct their bio-silica skeleton by the enzyme silicatein.

Rare earth element cycling in a subterranean estuary

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Johannesson and Burdige [1] suggested that submarine groundwater discharge (SGD) represents a substantial source of Nd to the oceans that may be sufficient to resolve the ocean "Nd paradox" [2, 3]. In order to test this hypothesis, rare earth element (REE) concentrations were measured in SGD samples collected beneath a coastal lagoon on Florida's Atlantic coast. Shale (PAAS)-normalized REE patterns for SGD samples exhibit substantial enrichments in the heavy REEs compared to the light LREEs. SGD from piezometers located 10 m and 22.5 m from shore exhibit REE patterns that are similar to the patterns of the overlying lagoon water. Neodymium concentrations of the SGD samples range from 230 to 2400 pmol/kg (mean = 507 pmol/kg); open ocean seawater Nd ~20 pmol/kg. Similarities between SGD and lagoon water Nd concentrations and REE patterns suggests that recirculation of lagoon water and subsequent SGD exerts a strong control on Nd concentrations in the lagoon [4]. Elevated Nd concentrations in deep groundwater are consistent with recirculated, marine SGD is a net source of REEs within subterranean estuaries. Our preliminary results underscore the importance of recirculated, marine SGD to the lagoon waters, and further supports that SGD may contribute substantial fluxes of Nd to the coastal oceans.

[1] Johannesson & Burdige (2007) *Earth Planet. Sci. Lett.* **253**, 129. [2] Jeandel *et al.* (1995) *Geochim. Cosmochim. Acta* **59**, 535. [3] Goldstein & Hemming (2003) *Treatise on Geochemistry*, **6**, 453. [4] Martin *et al.* (2007) *Water Resour. Res.* **43**, W05440, doi:10.1029/2006WR005266.