

Submarine groundwater flux of Nd to coastal waters

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Submarine groundwater discharge (SGD) is an important source of nutrients, carbon, and metals to coastal ocean waters. Combining fluxes of SGD estimated from seepage meters and ²²²Rn measurements, as well as Cl mass balance considerations [1] with measurements of rare earth element (REE) concentrations in submarine groundwater, a simple three-box (i.e., subterranean estuary, surface estuary, coastal ocean) mass balance model is applied to investigate the cycling of REEs, and Nd in particular, within a subterranean estuary along central Florida's Atlantic coast. The mass balance model indicates that SGD represents a substantial net flux of Nd (and the other REEs) to these coastal waters. The net SGD Nd flux is ~100 mmol Nd day⁻¹, which is 7-fold larger than the effective, local river flux of Nd to these coastal waters, and more than twice the total possible river flux in the absence of Nd removal by salt-induced, colloid coagulation in the surface estuary. We suggest biogeochemical reactions occurring in the subterranean estuary act to mobilize Nd, and the other LREEs and MREEs, from sediments of the subterranean estuary to advecting groundwater, and are subsequently transported to overlying coastal waters by SGD. The subterranean estuary, however, appears to act as a sink for HREEs. The SGD fluxes of Nd documented here have important implications for resolving the oceanic 'Nd paradox', and balancing the global oceanic Nd budget, which is critical to the use of Nd isotopes in paleoceanographic studies. If this net SGD Nd flux is characteristic of carbonate coastlines, which are estimated to account for 25% to 40% of the world's coastlines, then SGD Nd fluxes along carbonate coasts alone could explain 12% to ~20% of the missing Nd flux necessary to balance the ocean Nd budget and resolve the Nd paradox.

[1] Martin *et al.* (2007) *Water Resour. Res.* **43**, W05440, doi:10.1029/2006WR005266.

Water in extreme environments: From open networks to close packing coordination

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Extreme aqueous environments are commonplace in nature, including ore deposition, volcanic eruptions, hydrothermal vents, as well as the formation and migration of petroleum and natural gas. Conditions of these systems are not readily accessible experimentally for their direct structural and thermodynamic analysis, hindering our ability to study and interpret relevant geochemical processes taking place in the Earth's crust and mantle. At normal conditions water is usually described as a fluid having a near tetrahedral distribution of neighbours in its first coordination shell resulting from a rather open hydrogen-bonded network. However, aqueous environments at extreme pressure and temperature conditions might exhibit coordination shells populated by up to twelve first nearest neighbors, which resemble those encountered in either crystalline close-packing structures or the first coordination shell of fluids interacting with spherically symmetric potentials.

Most of our current understanding of water coordination and hydrogen-bond networks has been acquired through non-polarizable water models, which are basically unable to account for charge asymmetry. In contrast, polarizable water models are inherently charge-asymmetric, as a direct response to the inhomogeneous nature of the local electric field around the water's interactions sites. This feature makes the polarizable water model powerful to gain insights into the local polarization behavior underlying the hydrogen bonding coordination over wide ranges of water environments, especially at very high temperature and pressure. In this presentation we argue about the existence of an underlying link between the magnitude of some well-defined orientational order parameters and the strength of the water polarization as represented by the magnitude of either the total or the induced average dipole moment at the prevailing state conditions. We illustrate the alleged link through isobaric-isothermal molecular dynamics simulation of a successful Gaussian Charge Polarizable water model [1, 2] over a wide range of extreme conditions, to characterize the microstructural evolution, and discuss their implications in the interpretation of structural data from neutron diffraction as well as on the modelling of extreme aqueous environments [3].

[1] Chialvo & Cummings (1998) *Fluid Phase Equilibria* **150-151**, 73–81. [2] Paricaud, Predota, Chialvo & Cummings (2005) *Journal Of Chemical Physics* **122**, 24. [3] Chialvo & Horita (2010) *Journal of Chemical Physics*. Submitted