Boron isotopic ratios from the Salar de Uyuni, Bolivian Altiplano as a paleoenvironmental indicator

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The Salar de Uyuni on the Bolivian Altiplano is the largest salt flat in the world with over half of the world's lithium reserves and extensive borate deposits. The Salar fluctuated during the Late Pleistocene from being a dry salt pan to a deep (>100 meters) lake during periods of increased precipitation/inflow. The drier periods are recorded in the sediments as evaporites whereas the wetter periods are characterized by carbonate-bearing mud.

We present new data on the boron concentrations and isotopic ratios recorded in fluids entrapped in sediment and evaporite deposits from the Salar. Boron concentrations and isotopic ratios were analyzed on over 40 samples collected from a core drilled in 1999; δ^{11}B values vary from -22‰ to -4 ‰. Present-day surface water in the Uyuni basin, including the major inputs of the Rio Desaguadero and the Rio Grande, have δ^{11}B values between -6‰ to +4‰.

The δ^{11}B of evaporites deposited >50 ka fluctuates between -20‰ and -12‰. The transition from these evaporites to lacustrine sediments deposited during the wetter climate represented by paleolakes Minchin (~46-36 ka) and Tauca (~26-15ka)[1] is associated with a sharp change of δ^{11}B from -16‰ to -4‰, followed by a gradual decline to -14‰ in the lacustrine sediments. By contrast, the two most recent halite intervals have δ^{11}B of -4‰. The low δ^{11}B values recorded in the sediments are different from those of modern river water input and thus could reflect a contribution of an unknown water source with a distinguished high B and low δ^{11}B composition. We attribute this to an unmonitored geothermal source with high B, Li, and Mg contents. The relative contribution of this source predominates over surface inflows during drier periods >50 ka. The measurement of the boron isotopic ratios in fluids entrapped in sediments and evaporites offers a new paleoenvironmental proxy for reconstructing the hydrology of the basin.

[1] Baker *et al.* (2001) *Nature* **409**, 698–701.

The kinetics of binding of aspartic acid to aqueous calcium ion by molecular dynamics

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Specific amino acids such as aspartic acid play an important role in the mechanism of action of biomineralization proteins. Much research has been performed in the last several decades on elucidating the mechanisms by which these macromolecules affect morphology, phase selection, and kinetics of biomineral growth. Affecting all of these processes is the mechanism and rate that biomineralization proteins bind to the inorganic phase of interest. The interaction of aspartic acid and aqueous calcite surfaces has been studied widely in the field of biomineralization for their abundance in natural systems.[1, 2] However, despite the abundance of research in biomineralization, meaningful kinetic data at the molecular-scale is still needed to understand reaction mechanisms. We analyzed the proposed binding mechanism of a carboxyl group of an aspartic acid to an aqueous calcium ion using molecular dynamics. Simulations were performed using the LAMMPS code using the DREIDING [3] force field for aspartic acid and a new model for aqueous calcium ions [4]. Rate expressions were computed using the reactive flux method metadynamics. The rates of attachment, detachment and binding energies of an aqueous calcium ion binding to the carboxyl of an aspartic acid have been calculated. Rate estimates were validated by estimating an equilibrium constant from the ratio of attachment to detachment rate and comparing to experimental information. This presents the first meaningful molecular level kinetic information for this system in solution.

[1] Teng *et al.* (1998) *Science* **282**, 724–727. [2] Elhadj *et al.* (2006) *Proc. Nat. Acad. Sci. U.S.A* **103**, 19237–19242. [3] Mayo, Olafson & Goddard (1990) *J. Phys. Chem.* **94**, 8897–8909. [4] Raiteri, Gale, Quigley & Rodger (in press) *J. Phys. Chem. C*.