

Dissociated water adsorption to stepped forsterite surfaces: Implications for planetary accretion

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The origin of water and the mechanism of its incorporation into rocky planets, such as the Earth, are perplexing and much debated questions. Presently, there are three accepted scenarios for this mechanism. These are based on whether the water was incorporated during or after accretion and the origin of the water source [1]. However, the discrepancies between geochemical and isotopic fingerprints expected for comets and asteroid water sources and those found on Earth indicate that they could not have delivered the majority of the Earth's water [1]. Water adsorption onto forsterite dust grains in the planetary nebula during accretion is one alternative scenario. Preliminary work by Stimpf *et al.* [2] and Muralidharan *et al.* [3] has demonstrated that this could be a feasible water source, estimating that a volume equivalent to 1-3 Earth oceans could be adsorbed in this way. However, these studies do not account for surface defects, such as steps. These steps may facilitate the adsorption of water by providing under-coordinated magnesium sites. Dissociated water adsorption is also not studied but would be expected to form strong interactions with the surface that could aid the retention of water during the energetic accretion processes. To continue examining this hypothesis we have performed atomistic simulations of dissociated water adsorption to stepped forsterite surfaces using the METADISE code [4]. Sites at the step edge, base and in the centre of the terrace were examined for each step. In all but one final configuration the hydroxyl group preferentially moved to coordinate with two surface magnesium atoms. The final adsorption energy is dictated by individual adsorption sites on the surface and rather than the overall stability of the surface. The energies of dissociated adsorption found on the steps examined are larger than those found by Stimpf *et al.* [2] for associative adsorption. This indicates that even on stable surfaces a water molecule could adsorb to these low coordination sites with enough energy to form strong interactions. These results strengthen the argument that adsorption to dust grains in the accretion disk could be a viable source of water for rocky planets.

[1] Drake & Righter (2002) *Nature* **416**, 39-44. [2] Stimpf *et al.* (2006) *J. Cryst. Growth* **294**, 83-95. [3] Muralidharan *et al.* (2008) *Icarus* **198**, 400-407. [4] Watson *et al.* (1996) *J. Chem. Soc. Faraday Trans.* **92**, 433-438

Dissolved atmospheric noble gases: just contamination? Yes, but with potential..

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Atmospheric noble gases enter aquatic systems by gas/water partitioning at a free (surface waters) or a closed (ground water) air/water interface. Atmospheric equilibrium concentrations are therefore a simple and well defined function of the physical conditions prevailing during gas exchange. This textbook knowledge leads to two simple conclusions: i. dissolved atmospheric noble gases in natural waters allow the reconstruction of past environmental/climate conditions, and ii. the application of dissolved atmospheric noble gases are principally constrained to the analysis of gas partitioning processes between phases.

Therefore, to further broaden and develop the application of atmospheric noble gases in environmental research one either has to deepen the understanding of physical mechanisms covering gas exchange or exciting concepts have to be carried forward to new aquatic archives.

Recently, remarkable advances were made in both areas. Lab experiments on soil columns and new physical gas exchange models significantly improved the mechanistic understanding of the gas/water partitioning in porous media and ground water. Excess air (surplus of atmospheric gases commonly observed in groundwater) was identified as a valuable proxy for the hydraulic conditions during recharge. This insight was successfully applied to reconstruct groundwater recharge in Wisconsin in response to the last glaciation [1]. The same physical concepts were used to study CH₄ driven bubble emission in the Black Sea [2], gas/water interactions in natural gas fields [3] and to quantify the efficiency of artificial aeration of lakes.

New experimental methods enable us to analyse the noble gas concentrations in the pore water of lacustrine and oceanic sediments or in very small water masses (< 1 mg). The first method allows to reconstruct former salinity and water level fluctuations in lakes [4], whereas the second method yields information of past environmental conditions from dissolved noble gas in fluid inclusion in speleothems [5].

Our presentation heads to summarize and to comment some of these recent and stimulating results and to put them in the perspective of emerging applications of dissolved atmospheric noble gases to study sedimentary basin evolution and past ocean circulation.

[1] Klump *et al.* (2008) *Geology* **36**, 395-396. [2] Holzner *et al.* (2008) *EPSL* **265**, 396-495. [3] Zhou *et al.* (2005) *GCA*, **69**, 5413-5428. [4] Brennwald *et al.* (2003) *GRL* **31**, L04202, [5] Kluge *et al.* (2008) *EPSL* **269**, 407-414.