

Spontaneous D-H exchange between water ice and Complex Organic Molecules (COMs) in protostellar environments

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Multiply deuterated isotopologues of methanol have been detected in gas-phase in the protostar IRAS16293-2422 [1]. In this source, there is significantly more CH₂DOH than CH₃OD. The origin of this selective deuteration is not understood. Gas-phase chemistry modeling does not account for this multiplydeuteration [2], therefore cold atoms reactions onto the surface of the grains have been favoured thanks to experimental simulations [3, 4]. In this work, we test experimentally the hypothesis of spontaneous exchange between hydrogen and deuterium atoms in interstellar ice analogs composed of CD₃OD and H₂O. Thin films of intimate H₂O:CD₃OD ice mixtures, condensed at low temperature (<110 K), are monitored by Fourier transform infrared (FTIR) spectroscopy up to the complete evaporation of CD₃OD (~ 170 K). Rapid hydrogen/deuterium (H/D) exchange is observed, at 120 K and above, through the growth of the ν_{OD} stretching mode of HDO at ~ 2425 cm⁻¹. It is also shown that H/D exchange occurs i) on the hydroxyl functional group of methanol, i.e. through hydrogen bonds, and ii) before the completion of crystallization. The present results suggest that the much lower abundance of CH₃OD compared to CH₂DOH in IRAS16293-2422 could reflect H/D exchanges in water ice prior or during the grain mantle evaporation. This solid-state depletion mechanism, so far neglected in the astronomical literature, is expected to affect other deuterated molecules with hydrogen bonds, i.e. containing -OH, -NH- or -NH₂ functional groups [5]. This mechanism is expected to occur at any step of stellar evolution, as long as icy grains are expected to experience sublimation-condensation cycles. It is also suspected to occur in the solar nebula, and should be taken into account for interpreting the D/H ratio in organic compounds and water molecules, in comets and meteorites.

[1] Parise *et al.* (2004) *A&A* **416**, 159. [2] Garrod *et al.* (2006) *Faraday Discuss.* **133** 51. [3] Nagaoka *et al.* (2005) *ApJ* **624**, L29. [4] Watanabe & Kouchi (2002) *ApJ* **571**, L173. [5] Ratajczak *et al.* (in press) *A&A*.

Carbonate veins as recorder of seawater-crust interaction

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Seawater circulation within mid-ocean ridge flanks plays a major role in global chemical budgets of crust-seawater interaction with particular importance of the ocean crust as a sink for CO₂. We have analysed carbonate veins in basement rocks of twenty-three drill cores from the North Atlantic and the Pacific. The average proportion of carbonate veins and vugs in the upper 600-700 m oceanic crust is on the order of 2-4 vol.% which is equivalent to a global CO₂ uptake of 1-2·10¹² mol/yr. Our data are intermediate between earlier estimates based mainly on investigations of drill cores from >110 Myrs old ocean crust [1, 2] and for < 7Ma sedimented ridge flanks [3, 4].

Analyses of trace elements across single veins reveal strong, often complex compositional zonations e.g. for Y and the rare earth elements (REE). In some veins, REE concentrations increase towards the contact to the host basalt and approach values similar to MORB, whereas the vein centres show distinctly lower values and seawater-like Y/Ho ratios. The Y/Ho ratios of the carbonate veins (~40-100) encompass the complete range between average MORB (~51) and seawater (~88), indicating highly variable extents of basement-seawater exchange, during carbonate vein formation. The REE spectra also define two distinct groups, one with a pronounced negative Ce anomaly and one without anomaly. Negative Ce anomalies are exclusively observed in carbonates from veins with excess ⁸⁷Sr/⁸⁶Sr (i.e., above that of contemporaneous seawater), consistent with open circulation by oxic seawater. In contrast, all sites where low ⁸⁷Sr/⁸⁶Sr ratios indicate exchange with basement show no Ce depletion, suggesting suboxic to anoxic conditions and hydrothermal uptake of Sr and REE from the basalt. We conclude that REE concentrations and Y/Ho ratios of carbonate veins are highly sensitive indicators for the extent of seawater-basement interaction during vein formation.

[1] Staudigel *et al.* (1989) *Geochim. Cosmochim. Acta* **53**, 3091-3094. [2] Alt & Teagle (1999) *Geochim. Cosmochim. Acta* **63** (10), 1527-1535. [3] Bach *et al.* (2003) *G³* **4**, 10.1029/2002GC000419. [4] Sansone *et al.* (1998) *Geochim. Cosmochim. Acta* **62** (13), 2247-2252.