

Seawater $\delta^7\text{Li}$: A tracer for global CO_2 consumption by continental silicate weathering?

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Lithium isotope fractionation has been used as a proxy for silicate weathering and as a tracer in geothermal systems [1,2]. Misra & Froelich [1] recently presented the first record of Cenozoic seawater $\delta^7\text{Li}$ showing an increase of 9‰ over the last 60 Ma. This increase was attributed to increasing riverine $\delta^7\text{Li}$ values caused by a general change in continental silicate weathering behaviour.

Reactive transport modelling was performed using TOUGHREACT [3] to gain insight into the geochemical and isotopic effects of the changing weathering pattern. Simulations considered a granitic aquifer feeding a major river system. Li isotope fractionation was assumed to solely occur during Li incorporation into precipitating secondary minerals, computed using a solid solution approach [4]. Different weathering patterns were simulated by varying the contribution from weathering of unaltered granitic mineral phases (quartz, feldspars, micas), including the precipitation and dissolution of secondary minerals (kaolinite, chlorite) using a dual continuum approach.

Simulated $\delta^7\text{Li}$ values increased with an increasing contribution from weathering of primary granitic mineral phases suggesting that today's heavy riverine and seawater $\delta^7\text{Li}$ values are the result of a "weathering-limited" weathering pattern such as proposed by Misra and Froelich [1]. In contrast, our simulations suggest that low $\delta^7\text{Li}$ values inferred for the Paleocene-Eocene boundary [1] were largely inherited from weathering of previously formed secondary mineral phases associated with little or no Li isotope fractionation. Moreover, total simulated CO_2 consumption by silicate weathering reactions are positively correlated with $\delta^7\text{Li}$ values suggesting that global riverine and seawater $\delta^7\text{Li}$ values are directly linked to the total amount of global CO_2 consumption by continental silicate weathering. For a quantitative correlation, however, more experimental work is needed to better understand Li isotope fractionation processes including identifying key minerals involved and determining corresponding Li isotope fractionation factors.

[1] Misra & Froelich (2012), *Science* 335, 818-823. [2] Millot & Negrel (2007), *Chem. Geol.* 244, 664-678. [3] Xu *et al.* (2011), *Comput. & Geosci.* 37, 763-774. [4] Wanner & Sonnenthal (2013), *Chem. Geol.* 337-338, 88-98.

Noble gas partitioning in CO_2 environments: a supercritical assessment of current assumptions

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Noble gases are powerful inert tracers which can yield key information about physical processes occurring within geological systems. Currently all modelling involving binary phase noble gas partitioning are based on the determinations by Crovetto *et al.* 1982 [1] under conditions that did not require consideration of phase composition, supercriticality nor the effect of non ideality on solute noble gases. Subsequent studies have not investigated these factors; the validity of all current interpretations is based on the assumption that these variables have no effect on noble gas partitioning. However, no published study exists which substantiates this supposition. Assessing the effects these variables have on partitioning will give us a much warranted greater insight and understanding into geological systems that operate under significantly different PVTX conditions.

We present noble gas partitioning results from a supercritical CO_2 - H_2O binary phase system at elevated temperatures and pressures (50-100°C & 90-140 bar). This system was chosen due to a strong current interest in underground storage of anthropogenic CO_2 and their natural analogues for which noble gases have already proven invaluable [2,3]. Partitioning is determined using a combined experimental and numerical simulation-based approach to generate partitioning values which forms the basis of a robust model for predicting partitioning over a wide range of PT conditions. We present our methodology and results which we compare and contrast with values derived from the Crovetto *et al.* dataset. Preliminary findings suggest noble gas partitioning is demonstrably different for a supercritical CO_2 - H_2O system; overall water phase solubility is significantly reduced, especially for the heavier noble gases by up to 60%. This observed disparity appears greatest at higher pressures and lower temperatures although an observable difference is noted across the studied PT range.

[1] Crovetto *et al.* (1982) *J. Chem. Phys.* 76, 1077-1086. [2] Gilfillan *et al.* (2009) *Nature* 458 614-618. [3] Zhou *et al.* (2012) *Geochim. Cosmochim. Acta* 86 257-275.