Isotope fractionation of dissolved Silicon in groundwater – Weathering of secondary minerals.

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We investigated the isotopic composition of the dissolved Si in groundwater and the direct flux into the ocean. It appears that the Si isotope composition evolves with age and depth from positive river-like δ^{30}Si values to negative, from rivers distinct, values. For the Ganges-Brahmaputra system we found groundwater derived Si fluxes as delivered by submarine groundwater discharge (SGD) are enhancing the total Si flux into the Bay of Bengal by ~60%. Its isotope composition (mean δ^{30}Si 0.25‰) however, was found to be clearly distinct from the riverine counterpart (mean δ^{30}Si 1.3‰). The overall Si isotope composition (river + SGD) delivered into the oceans is about 0.5‰ lighter than deducted from the riverine signal alone.

We found similar fractionation trends for groundwater samples from the Navajo aquifer, Black Meza, Arizona, USA. The Si isotope composition evolves from positive to negative δ^{30}Si values of about -1.5‰. Concomitant changes in water chemistry, e.g. in pH, with depth and age, causing mineral stabilities to change significantly. Saturation index calculations show that the water saturation with respect to kaolinite changes from over-saturated to near saturation at greater depth, indicating that kaolinite is increasingly contributing to the dissolved load. With kaolinite being unstable and in fact contributing to the dissolved load, the Si sources switch from primary to secondary mineral sources and accompanied Si isotope fractionation is inactive. Moreover, the release of Si from clayey phases represents an input of previously clay-induced fractionated and isotopically light-enriched Si into the dissolved load.

Our findings represent the first systematic surveys of the Si isotope composition in groundwater and show how groundwater impacts on the riverine isotope composition and the Bay of Bengal. Our data suggest that breakdown of secondary minerals contributes significantly to continental weathering and erosion. We will discuss the implications for the global Si cycle and it's isotopic balance.

Fluid inclusions provide evidence for early oil composition prior to gas condensate migration into reservoirs

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Oil-bearing fluid inclusions can provide evidence of prior oil charge to currently gas-filled reservoirs [1]. By analysing oil released from these inclusions, oil–oil (-condensate) and oil–source correlations can be made, and the thermal maturity of the original oil charge determined [2]. These observations provide important constraints on the reservoir fill history.

Rock samples and reservoir fluids from three offshore hydrocarbon provinces from NW Australia were used. The East Spar (Barrow Sub-basin - Cretaceous) and Bayu (Bonaparte Basin - Jurassic) discoveries are gas condensate fields. In the Browse Basin, samples from six gas wells were used (Crux-1, Argus-1, North Scott Reef-1, Dinichthys-1, Titanichthys-1 and Brewster-1A); these contain gas in Triassic (Crux-1 only), Jurassic and Cretaceous reservoirs. In all cases, biomarker data shows a significant difference between included oil and recovered gas condensate, with the former derived from a less terrestrially-influenced, less oxic facies. This suggests early charge was typically from more labile, oil-prone kerogen, and that this was followed by generation at higher maturity of greater volumes of gas condensate from more terrestrial facies and reflects the mixed nature of the recognised source rocks. At East Spar and Bayu, displacement of original oil by gas condensate, with some dissolution, is inferred, although seal breach can not be excluded. The Browse Basin inclusion oils (except Crux-1) and the gas condensates have very high maturities and evidence of evaporative fractionation, suggesting burial of the reservoirs below the dew point after inclusion trapping.

[1] Lisk M., O'Brien G.W. and Eadington P.J. (2002) *AAPG Bulletin* **86**, 1531-1542. [2] George S.C., Lisk M., and Eadington P.J. (2004) Mar. Pet. Geol. **21**, 1107-1128.