Noble gases from the Precambrian Shield of Canada

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An increased recognition of the role of subsurface microbes in the production and alteration of oil and gas deposits has sparked heated debate about the volume and extent of life in the deep subsurface. The deep terrestrial biosphere in the tectonically quiescent Precambrian Shields of Canada, Scandinavia and South Africa are dominated by radiogenic noble gases and crustal-derived carbon sources. These radiogenic gases have been used previously to calculate long residence times on the order of 10–25 million years for the deepest high-salinity fracture waters [1]. Correlations of increasing salinity with highly altered hydrogen and oxygen isotope signatures for the waters, together with increasing concentrations of radiogenic noble gases, suggest that ground waters were subject to extensive water–rock reactions over geological time in hydrogeologically isolated fracture networks [2].

We have performed noble gas analyses on 6 samples from a mine site in Ontario (ON). Results show highly radiogenic noble gas ratios for He, Ne and Ar, analogous to the anomalously high Ne signatures recently described for fracture waters in South African gold mines [3]. ^{3}He/^{4}He in these samples are <0.02Ra. We have found very high ^{40}Ar/^{36}Ar ratios (up to 44,000) the highest observed in crustal fluids and the first documented ^{129}Xe excess (~1%) that cannot be attributed to a mantle component. Elemental ratios suggest solubility controlled gas/groundwater phase partition processes have operated but Kr and Xe enrichment suggest input from sediment and / or sediment derived porewater. This sediment contribution is also required to explain the ^{129}Xe excesses. ^{129}Xe is the decay product of ^{129}I with $t_{1/2}$ = 15.7Ma implying significant closed system fluid evolution, consistent with the hydrogeologically isolated nature of the fractures.

[1] Lippmann *et al.* (2003) *GCA* **67,** 4597-4619. [2] Sherwood Lollar *et al.* (2008) *GCA* **72,** 4778-4795. [3] Lippmann *et al.* (2011) *Chem. Geol.,* In press.

Hydrothermal alteration of diatomite for the fixation of heavy metal ions

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The application of alterated diatomite as a hierarchically structured material for ion fixation from aqeuous solutions is based on macropores (~100 nm) from the intricate silica structure of diatomite, micropores (~0.3-0.4 nm) from neoformed zeolites and highly active surface sites from amorphous precursor phases. Such kind of materials can be obtained by hydrothermal synthesis.

A stock solution was prepared by dissolving 1 g of gibbsite (γ–Al(OH)$_3$) in 0.5 L of 1 M KOH and subsequent filtration (0.45 μm). 0.025 L of the stock solution reacted with 0.5 g diatomite (”Thiele”) in a Teflon coated autoclave at 50 to 150°C. After distinct reaction times from 6 up to 1500 h reaction products were separated from the solutions by filtration. Solutions were analysed for composition and solids for composition and structure. Ion fixation capacities of the reaction products were studied in aqueous solutions containing 0.5 mM of Cu^{2+}, Pb^{2+} and Zn^{2+} at pH 5.1 and 25°C for 72 h.

Initially, the diatoms are converted partly into spherical amorphous nanoparticles (20-200 nm). After 24 to 192 h mainly merlinoite and minor amounts of chabazite were formed. Proportions depend on temperature and reaction time. At a reaction time between 96 and 192 h a quasi steady state was reached with $\approx$ 30 wt.% amorphous phase, $\approx$ 60 wt.% merlinoite and 10 wt.% accessory phases (relictic quartz, mica as well as newly formed chabazite). The heavy metal ion fixation capacity of the pristine diatomite is low. Interestingly, the reaction product containing the amorphous precursor phase non-selectively reduced $\geq$ 99 % of the primarily dissolved heavy metals (specific surface area = 38 m^2/g). The final reaction products (15 m^2/g) reduced heavy metal concentrations less efficiently (~ 90 %), but selectively. Challenging tasks for the ongoing study are to tailor the reaction products with regard to metal fixation and hierarchical pore structures for waste and drinking water purification.