

Deep fracture fluids isolated in the crust since the Precambrian

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Water bearing macrosystems that have been isolated from the surface and preserved on geological timescales (>10Ma) are seemingly rare. Nevertheless, the unique insight they provide into the evolution of chemolithotrophic life makes these systems important areas of study. The Witwatersrand Basin in the South African Precambrian Crystalline Shield provides the case type [1,2]. Here, we have determined the noble gas concentration and isotopic composition of 6 gas samples, co-produced with water, from deep exploratory boreholes in a producing mine in the Timmins region of the Canadian Precambrian Crystalline Shield.

We show that ^{124,126,128}Xe excesses in the Timmins mine fluids can be linked to Xe isotope changes in the ancient atmosphere [3] and can be used to calculate a minimum mean residence time for this fluid of ~1.5Ga. We also resolve in all samples a clear ¹²⁹Xe signal in excess of atmospheric values. Mass fractionation and U fission can be excluded as sources of ¹²⁹Xe, and a mantle source is unlikely. We postulate ¹²⁹Xe is sourced in carbon rich metamorphic material of sedimentary origin and extracted by fluid migration processes at ~2.64Ga. Neon isotopic compositions are similar to the Witwatersrand study and are used to validate the closed system assumption for the radiogenic noble gases [1]. Closed system radiogenic noble gas residence times are 1142±64.5, 1655±789, 1498±784, 1610±825Ma for ⁴He, ²¹Ne, ⁴⁰Ar, ¹³⁶Xe respectively. Combined together, these complementary strands of evidence lend further support to the hypothesis that ancient pockets of water can survive the crustal fracturing process and remain in the crust for billions of years [4].

[1] Lippmann-Pipke *et al* (2011) *Chem. Geol.* **283**, 287-296.
[2] Lin *et al* (2006) *Science* **314**, 479-482. [3] Pujol, M. *et al*, (2011). *Earth Planet. Sci. Lett.* **308**, 298-306. [4] Holland *et al*, (2013) *Nature*, *in press*.

Influence of different organic carbon substrates on denitrification rates in riparian sediment

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Nitrate (NO₃⁻) is an ubiquitous groundwater contaminant in agricultural and wastewater discharge areas [1]. The prediction of microbially mediated NO₃⁻ removal in subsurface environments requires an understanding of the rates at which electron donors are utilized by denitrifying microbes [2]. This study focuses specifically on the following organic carbon compounds as electron donors: glucose, acetate, adenine, cysteine and fulvic acid. Six triplicate series of flow through reactors (FTRs) containing 35cm³ of natural, organic-poor, riparian sediment were supplied for 10 weeks with solutions containing nitrate and the individual carbon compounds, along with a no-carbon added control. The organic carbon compounds were selected to yield a range of Gibbs Free Energy (ΔG) values when their oxidation is coupled to denitrification. The initial flow rate of the FTRs was 1 ml h⁻¹. Once steady NO₃⁻ concentrations were reached in the outflow, the flow rate was increased to 2 ml h⁻¹ and, subsequently, 4 ml h⁻¹. Maximum potential denitrification rates (R_{max}) measured for the different carbon substrates spanned an order of magnitude, ranging from 0 to 91nmol cm⁻³ h⁻¹. Fulvic acid did not induce denitrification, while acetate yielded the highest rate. The outflow solutions for FTRs supplied with adenine and cysteine contained ammonia and sulfate, respectively. These results are consistent with the structure of the organic components of adenine, containing an amine, and cysteine, containing a thiol group. R_{max} values for the studied carbon substrates are relatively low compared to those in the literature for similar experiments, which have values ranging from 98 to 933 nmol cm⁻³ h⁻¹ [3]. Most likely, the low rates reflect a low abundance of denitrifying organisms in the riparian sediment used.

[1] Xue *et al* (2009) *Water Research* **43** 1159-1170.
[2] Thullner *et al* (2007) *Geomicrobiol. J.* **24** 139-155.
[3] Laverman *et al* (2006) *FEMS Microbiol Ecol* **58** 179-192