N and S isotope fractionation in the terminal electron acceptors during biodegradation of BTEX compounds

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The biodegradation of BTEX compounds occurs under varying redox conditions [1]. Anaerobic processes are of particular interest as groundwater is often anaerobic as a result of initial mineralization of BTEX compounds [2]. Isotopic fractionation has been shown to occur for carbon and hydrogen isotopes of benzene during biodegradation [3] and other natural attenuation processes [4]. During the microbial reduction of the terminal electron acceptors (TEA) nitrate, and sulphate, significant isotope fractionation has also been demonstrated [5, 6]. The objective of this on-going project is to assess the extent of N and S isotope fractionation during BTEX biodegradation in laboratory studies and aquifers. Bioactivities of denitrifying and sulphate-reducing bacteria retrieved from a contaminated aquifer are respectively summarized in Table 1.

TEA	Carbon Source	Cells/mL
Nitrate	Benzene	9.16×10^4
Nitrate	Toluene	2.05×10^5
Sulphate	Benzene	1.84×10^6
Sulphate	Toluene	1.12×10^6

Table 1: Bioactivity measurements for benzene & toluene degrading bacterial cultures.

In laboratory studies with bacterial cultures growing on a mixed lactate/benzene carbon source, we observed biodegradation of benzene coupled with bacterial sulphate reduction evidenced by decreases of sulphate concentrations from 2500 to 216 mg/L accompanied by increases of $\delta^{34}S$ values from 0.4 to 12.7‰. Further laboratory experiments and groundwater investigations will reveal whether the coupling of isotopic tracers for BTEX and TEA compounds is a suitable approach for separating biodegradation within aquifers from other processes of natural attenuation [4] that affect both concentration and isotopic composition of BTEX compounds.

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Noble Gas Recycling and He-Ne-Ar Solubility in Ring Structure-Bearing Minerals

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There is increasing evidence that significant amounts of noble gases have been recycled back into the mantle. Data on the solution properties of noble gases in geologic materials remain scarce, and thus it is unclear what materials are capable of recycling noble gases and how noble gas recycling is coupled to the recycling of other volatiles.

Towards this end, we have experimentally determined He-Ne-Ar solubility in beryl and cordierite. He-Ne-Ar solubility in beryl and cordierite is very high: 7×10^{-8},1×10^{-7}, 2×10^{-8} in beryl, and 3×10^{-7}, 4×10^{-7}, and 4×10^{-7} in cordierite (list order: He-Ne-Ar, mol g^{-1} bar^{-1}) which are around 10^4 times greater than He solubility in olivine.

Experiments were conducted using an externally-heated pressure vessel (equal parts He-Ne-Ar pressure medium) and analyzed using laser-ablation, noble gas-mass spectrometry. Experiments essentially utilized a constant-source approach, where the minerals diffusivly equilibrated with the imposed fugacity of noble gases present in the pressure medium. Temperatures ranged from 750-800°C, and total pressure ranged from 1.3-1.5 kbar.

Beryl and cordierite were choosen because they possess six-member tetrahedral ring structures in their lattice, and similar lattice structures are present in commonly recycled, hydrothermal minerals (e.g. amphibole, clays, serpentine). These lattice structures are large radius and commonly unoccupied (zero-charge), suggesting they are energetically favorable locations for noble gas dissolution in minerals.

Recent He and Ne solubility determinations for amphibole also indicate that noble gas solubility is correlated with the form of the unoccupied ring structures. Interestingly, the ratio of He to Ne solubility in amphibole is greater than that determined for both beryl and cordierite. Ring structure geometry differs amongst minerals, which may explain why amphibole apparently fractionates He and Ne relative to beryl and cordierite. This suggests that ring structure-bearing minerals may have diagnostic noble gas fractionations. Comparing the expected fractionations of noble gases in subducted materials to the integrated pattern of recycled noble gases in the mantle should yield insight into viable mechanisms for noble gas recycling.

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