Vegetation uptake controlling groundwater solute evolution on a southeast Australian granite

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Groundwater geochemical signatures are typically considered derived from rock-water dissolution and weathering interactions. However, many major ions (Ca^{2+}, K^+, HCO_3^-, Mg^{2+}, S, and Si) are essential plant nutrients, and are removed from rainfall, soil-water and groundwater, where soils are depleted in these species. This in turn affects the solute composition of infiltrating water.

Conventional methods [1] of determining relative groundwater solute contributions from specific rock weathering reactions were carried out for a pair of sub-catchments in the Dwyer Granite, southwest Victoria, Australia. This method was adapted for semi-arid, southwest Victoria by standardising all ions to rainfall Cl^- to remove the effects of evapotranspiration. While this step is commonly omitted in high rainfall, northern hemisphere studies [2], it is important for the Australian setting, where groundwater solutes are primarily derived from the concentration of rainfall by evapotranspiration [3,4].

In a few groundwater samples in the study area, enrichment with respect to rainfall of Na^{2+} and H_4SiO_4 is ascribed to plagioclase weathering, while SO_4^{2-} enrichment is ascribed to pyrite oxidation, indicating that rock weathering reactions play a role in this setting. However, in most samples, after subtracting rainfall input (as per [1]), there is wholesale depletion of all measured ions. This prevents the use of the plagioclase, biotite and k-feldspar chemical weathering reactions in the mass-balance, as these release cations (Na^{2+}, K^+, Mg^{2+} and Ca^{2+}), all of which are depleted in the groundwater with respect to rainfall.

This ion depletion is not due to mineral precipitation as neither geochemical modelling nor X-ray diffraction analyses show evidence of this occuring. Nor is it due to ion exchange as there is no balancing import of ions or significant acidification of the groundwater. Having already ruled out evapotranspiration effects through Cl^- standardisation, the depletion is instead attributed to vegetation uptake, which has been identified as a significant process elsewhere in the region [5], causing depletion of recharge solutes.

[1] Garrels and Mackenzie (1967) *Equilibrium Concepts in Natural Water Systems* **Advances in Chemistry Series**, 222-242. [2] Velbel and Price (2007) *Appl. Geochem.* **22**, 1682-1700. [3] Herczeg *et al*. (2001) *Mar. Freshwater Res*. **52**, 41-52. [4] Bennetts *et al.* (2006) *J. Hydrol.* **323**, 178-192. [5] Edwards and Webb (2009) *Hydrogeol. J.* **17**, 1359-1374.

Equilibrium Partitioning of Li between Olivine and Clinopyroxene at Mantle Conditions

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Abstract

The lithium isotope system holds great allure as a tracer of recycled subducted materials in the Earth's interior, owing to the striking isotopic contrast between lithium at the Earth's surface and that in the mantle, combined with the presence of Li at measurable quantities in mantle minerals. Unfortunately, measurements of lithium isotope ratios in mantle xenoliths have proven difficult to interpret. Mantle xenolith data compiled from samples worldwide have revealed that lithium elemental and isotopic distribution between olivine and clinopyroxene is highly variable. At high temperatures such as those found in the mantle, the isotopic fractionation factor $\alpha_{ol/cpx}$ [$=(^7Li/^6Li)_{ol}/(^7Li/^6Li)_{cpx}$] is expected to approach 1, and experimental constraints on equilibrium partitioning show that the partition coefficient ($D^{Li}_{ol/cpx}$) is between 1.5-2. Many xenolith samples exhibit equilibrium behavior with respect to both isotopic fractionation and equilibrium partitioning, but some samples do not. Xenoliths with apparent $D^{Li}_{ol/cpx} < 1$ trend toward isotopically lighter Li in clinopyroxene relative to olivine, with $\Delta^7Li_{ol\text{-}cpx}$ [$=\delta^7Li_{ol} - \delta^7L_{cpx}$] ranging from 3 - 25‰. A physical process explaining this relatively extreme isotopic fractionation between co-existing mantle phases has yet to be satisfactorily demonstrated. One proposed hypothesis to explain the apparent Li isotopic disequilibrium in mantle xenoliths is that upon exhumation, closed system redistribution of Li between mantle minerals occurs as a function of cooling, meaning the partition coefficient is temperature dependent. Richter et al. (2003) have shown potential for considerable kinetic isotopic fractionation of Li during diffusion. Thus if Li is redistributed under dynamic conditions preceding or concurrent with eruption, kinetically driven isotopic fractionation might be "locked in" to the mantle minerals upon reaching closure conditions. We have conducted a series of piston cylinder experiments at 1.5 GPa and 700-1100 °C, the results of which show that $D^{Li}_{ol/cpx}$ is 2.0 ± 0.2 regardless of temperature over this range. It seems that a new explanation is needed to explain the Li signature in mantle xenoliths. Mantle olivine contains some amount of iron (~10% FeO*), and the ambient *f*O2 controls the relative amount of Fe^{+2}/Fe^{+3}. Variation in the amount of Fe^{+3} could potentially influence the incorporation of Li^+ into the octahedral site of olivine by providing a charge-balancing mechanism. This could allow for a redistribution and isotopic fractionation of Li in response to changing fO_2. Experiments at 900°C and 1.5 GPa with solid state fO_2 buffers of Re-ReO, Ni-NiO, and Mo-MoO are currently underway to determine whether oxygen fugacity plays a role in controlling Li partitioning.

[1] Richter et al. (2003) *Geochimica et Cosmochimica Acta* **67**, 20, 3905–3923.