

## Biogeochemical redox reactions controlling $^{99}\text{Tc}$ solubility

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Technetium-99 ( $^{99}\text{Tc}$ ), a long-lived fission-product of nuclear fuels reprocessing, is of environmental concern at a number of locations world-wide. Exhibiting an intermediate redox potential, Tc is highly mobile in its anionic, oxidized state, pertechnetate,  $[\text{Tc}(\text{VII})\text{O}_4^-]$ . In its reduced state, Tc can form a relatively immobile, poorly soluble oxyhydroxide precipitate  $[\text{Tc}(\text{IV})\text{O}_2 \cdot n\text{H}_2\text{O}]$ . To predict its environmental behavior, we sought to understand the biogeochemical parameters governing the solubility and reactivity of Tc – complex functions of redox reaction pathways, mineralogic environment, and aqueous geochemistry.

Pertechnetate can be rapidly reduced by Fe(II) associated with sediments, clays, and biomagnetite. In some cases, a portion of the resultant  $\text{Tc}(\text{IV})\text{O}_2$  can be resistant to oxidation by molecular oxygen ( $\text{O}_2$ ), possibly due to redox buffering by Fe(II) or to physical protection offered by resulting Fe(III) solids. In an Oak Ridge saprolite, for example, non-oxidizable  $\text{Tc}(\text{IV})$  was associated with Fe(III) oxides within intra-grain domains of 100- $\mu\text{m}$  Fe-micas.

In general, direct enzymatic reduction of Tc is slower than Tc reduction by mineral-associated Fe(II). However, the rate of direct enzymatic reduction depends on the nature of the microorganism and electron donor. The re-oxidation of biogenic  $\text{Tc}(\text{IV})\text{O}_2$  can be faster than re-oxidation of  $\text{Tc}(\text{IV})$  resulting from reduction by Fe(II). In addition, ligands, such as bicarbonate and lactate, can maintain biogenic  $\text{Tc}(\text{IV})$  in a soluble state via complexation mechanisms [1], and such ligands appear to be more effective as  $\text{Tc}(\text{IV})$  complexants when  $\text{Tc}(\text{VII})\text{O}_4^-$  is reduced enzymatically than by sediment-associated Fe(II) [2, 3].

[1] Wildung *et al.* (2000) *Appl. Environ. Microbiol.* **66** (6) 2451-2460. [2] Fredrickson *et al.* (2004) *Geochim. Cosmochim. Acta* **68** (15) 3171-3187. [3] Wildung *et al.* (2004) *FEMS Microbiol. Ecol.* **49**, 151-162.

## Li and Mg isotopes in the mantle: Heterogeneity or diffusion?

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Fingerprinting material returned by subduction to the mantle is a key to our understanding the dynamics of the Earth's interior. Lithium (Li) isotopes should provide a valuable system for tracing crustal recycling, because subducted material has a distinctive heavy isotopic signature due to low temperature processes. However, recent studies have identified that Li isotopes fractionate during high temperature diffusive processes. This means that the interpretation of Li isotope ratios in MORB or OIB is not unequivocal. Coupled use of Li with Mg isotopes can be used to resolve this ambiguity. The vast Mg reservoir of the mantle is highly unlikely to be affected by the recycling of low-Mg crustal material. However, it has been shown that Mg isotopes can be diffusively fractionated at magmatic temperatures. Therefore Mg isotopes can in principle be used to fingerprint the role of diffusive fractionation which should have collateral effects on Li isotopes. Conversely, by illustrating an absence of diffusive fractionation in Mg isotopes, it should be possible to attribute Li isotopic variability to crustal recycling.

To establish a baseline mantle reference, we have analysed Li and Mg isotope ratios for over 40 whole-rock peridotites xenoliths, massif peridotites and abyssal peridotites from several global localities, in addition to a suite of EPR MORB glass. The  $\delta^{26}\text{Mg}$  of the peridotites (-0.36 to +0.06‰) shows a similar, but slightly heavier, range to that of MORB (-0.39 to -0.10‰). This variability is implausibly recycling; rather the primary cause of variation is likely to be diffusion. This implies that the high variability in  $\delta^7\text{Li}$  in peridotites (-4.0 to +8.0‰ compared to MORB (+3.9 to 4.7‰)) may also be primarily due to diffusional fractionation.

Peridotites show a positive co-variation between Li and Mg isotopes, suggesting that both systems are undergoing fractionation due to the same processes. This may indicate that both isotopic systems are being primarily affected by diffusive processes. Ultimately this leads to the conclusion that Mg isotope variations can be used to monitor Li isotope variations to reveal crustal recycling.