Li isotope variations in the upper mantle

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A large proportion of the mantle is likely to have been re-enriched by recycled oceanic lithosphere, such as envisioned by the marble cake mantle. Yet definitive evidence for such recycled material, despite the host of distinctive geochemical signatures it is expected to impart, remains elusive. Partly as a consequence, alternative theories have become popular in which subducted slabs form a deep, hidden reservoir and are largely removed from our mantle sample.

A novel means to address this issue is the use Li isotopes. Alteration of the oceanic lithosphere both increases its Li concentration and $^{7}Li/^{6}Li$. Mixing of this material back into the upper mantle should therefore elevate its $^{7}Li/^{6}Li$ and generate Li isotope heterogeneity on a small scale. New Plasma Induced Multi-collector Mass Spectrometers (PIMMS) dramatically improve the reproducibility of Li isotope measurements. Analyses with the Finnigan Neptune allow us to determine natural variations in $^{7}Li/^{6}Li$ of less than 0.5 per mil, using rapid sample-standard bracketing. Using this enhanced analytical capability, we have begun to investigate $^{7}Li/^{6}Li$ variations in well characterised basaltic glasses from the East Pacific Rise (10.5 and 11.5°N). Initial results show a significant spread in $^{7}Li/^{6}Li$ of ~1.5 per mil. The Li isotope variation correlates with $^{87}Sr/^{86}Sr$ and La/Sm, but not [Li] or MgO, suggesting it is a primary signature. It thus appears that a definitive signature of recycled material in the upper mantle has been gleaned.

Lipid biomarkers as a tool for the analysis of anaerobic methanotrophy in marine environments

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Downcore lipid analysis of gas hydrate-bearing sediments at Hydrate Ridge and methane-rich sediments from the Håkon Mosby Mud Volcano (HMMV) show elevated concentrations and high numbers of diverse membrane lipids (biomarkers) of archaeal and bacterial origin. Structural and carbon isotopic analyses demonstrate the presence of a consortium of archaea and sulfate-reducing bacteria oxidizing methane under anoxic conditions. Concentrations of relevant biomarkers are clearly enriched at locations with elevated methane seepage and decreased at locations with lower methane outflow. The enrichment of consortium-specific biomarkers is directly translated into their isotopically light carbon isotopic signature. Concentrations and carbon isotopes are in good agreement with rate measurements and rRNA analyses and thus help identifying the methane oxidation zones *in situ*. Whereas high methane oxidation rates at Hydrate Ridge can be found throughout the core, methane oxidation at HMMV takes place only in a restricted zone right below the sediment surface. Small increments may, however, indicate a second *hot spot* of anaerobic methanotrophy or, on the other hand, active methanogenesis in deeper layers. Among the specific biomarkers, isoprenoids (crocetane, pentamethylicosenes) and glycerolethers (archaeol, hydroxyarchaeol) are identifiable as markers of the archaeal partner belonging to the *Methanosarcinales* group. The most dominant biomarkers of bacterial origin are monoalkylglycerolethers containing hexadecyl carbon chains and the fatty acids cis11-$C_{16:1}$ and $\Delta C_{17:0}$. These biomarkers can be attributed to the syntrophic bacterial partner closely related to the *Desulfosarcina-Desulfococcus* group.