

## Fe-isotopes of arc basalts indicate a variably oxidised mantle source?

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New Fe-isotope data on (> 60) primitive basalt samples from the global network of arcs is used to investigate if Fe isotopic compositions reflect differing oxidation and water content of arc sources due to tectonic factors (rate of subduction, age of subducting plate) [1]. Subduction magmas are wetter than those of from other tectonic settings [2]. Melt-inclusion studies using XANES have established good positive correlations between water content of primitive melts and their oxidation state ( $\text{Fe}^{3+}/\Sigma\text{Fe}$ ) [2]. Arc magmas have elevated  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (>0.1 to 0.5), compared to MORB (0.1-0.2) [3,4], and studies of peridotite from the sub-arc mantle [5] also reveal elevated oxidation states compared to non-arc mantle. Still, the site of oxidation of arc magmas is controversial. Redox-sensitive element ratios (V/Sc or Zn/Fe<sub>T</sub>) imply oxidation is imposed after magmas leave the mantle wedge [3,6].

Our  $\delta^{57}\text{Fe}$  data range from -0.2‰ to +0.2‰ ( $\pm 0.04$ ), with  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in the range 0.2 to 0.5.  $\delta^{57}\text{Fe}$  correlates positively with Pb- or Sr-isotope ratios and  $\text{Fe}^{3+}/\Sigma\text{Fe}$  and weakly with age of subducting crust. The trend to heavier iron is not coupled to any correlation with MgO so not driven by olivine or pyroxene crystallisation. A two-fold increase in  $\text{Fe}^{3+}/\Sigma\text{Fe}$  requires >50% olivine crystallization [3] and will only increase  $\delta^{57}\text{Fe}$  by ~0.06 ‰. As magnetite  $\Delta^{57}\text{Fe}_{\text{mag-melt}}$  values are ~+0.30 ‰, they record pre-magnetite conditions.

### Results and Conclusions

Our data may reflect differences in oxidation state of the mantle of different arcs. As  $\text{Fe}^{3+}$  mineral sites tend to have heavier Fe-isotopic compositions [7] and as  $\text{Fe}^{3+}$  is more incompatible than  $\text{Fe}^{2+}$  during mantle melting, partial melting of more a oxidized wedge will yield melts with heavier iron isotopes (as will smaller % melting) [7].

Positive correlations with Pb- and Sr-isotopes may be a measure of slab input to the wedge, and that with slab age may indicate that colder, older slab subduction delivers more oxidation capacity to that part of the mantle wedge that yields arc basalt magmas.

[1] Syracuse, *et al.* (2010) *Phys Earth & Planet. Int* **183**, 73-90. [2] Kelley & Cottrell (2009) *Science* **325**, 605–607. [3] Lee *et al.*, (2010) *Nature* **468**, 681–685. [4] Bezos & Humler (2005) *Geochim. Cosmochim. Acta* **69**, 711–725. [5] Parkinson & Arculus (1999) *Chem Geol* **160**, 409–423. [6] Lee *et al.* (2005) *J. Petrol.* **46**, 2313–2336. [7] Dauphas *et al.* (2009) *Earth & Planet. Sci Let* **288**, 255–267.

## Microbes at work: Biogeochemistry in oil sands tailings ponds

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Extraction of surface-mined oil sands ores yields bitumen for upgrading, plus tailings: a slurry of water, sand, silt, clay, unrecovered bitumen and hydrocarbon solvent. These extraction wastes are deposited into enormous tailings ponds where they de-water as the fine particles consolidate very slowly by gravity. After several years the tailings may reach >25% solids, becoming 'mature fine tailings' (MFT). Complex communities of diverse microbes have developed in the ponds (enumerated at  $10^6$  to  $10^8$  cells/ml MFT) where they anaerobically degrade labile aliphatic and aromatic hydrocarbons in the solvent (and perhaps low molecular weight components of the bitumen) to produce methane,  $\text{CO}_2$  and organic metabolites. This activity has environmental and industrial significance because it affects physical properties of the MFT through unresolved mechanisms, promoting consolidation and de-watering of the MFT ('biodensification'), and generating copious volumes of greenhouse gases, a proportion of which is emitted from the ponds through ebullition. The microbial communities determined using 454 pyrosequencing of 16S rRNA genes comprise hundreds of bacterial genera, many of which represent uncultivated taxa, but only a few methanogenic euryarchaeal lineages. Laboratory enrichment cultures derived from MFT demonstrate methanogenic degradation of short-chain (< $\text{C}_{10}$ ) and long-chain (> $\text{C}_{14}$ ) *n*-alkanes, *iso*- and *cyclo*-alkanes, mono-aromatics (BTEX) and a few polyaromatics. Biodegradation is also observed under sulfate-reducing conditions by amending MFT with sulfate; the community structure shifts in response to C source and electron acceptor availability. However, often the communities are reluctant to 'go to work', sometimes with lag times of 1–2 years in laboratory cultures before biodegradation is apparent. Pure cultures isolated from enrichment cultures are now being studied to infer their roles in situ. Sequencing of functional gene families associated with anaerobic hydrocarbon activation is contributing to understanding biogeochemical potential in the tailings ponds, and full community metagenomic sequencing has provided additional context. Results from this work are contributing to models for predicting the consequences of microbial activity in situ and providing guidance for tailings management and reclamation strategies.