Microbially mediated chromate reduction in alkaline soils

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Over the last century vast quantities of chromium ore processing residue (COPR) were produced and many millions of tonnes have been dumped in and around urban areas. Very few legacy COPR disposal sites are engineered to prevent off-site migration of contaminated leachates and these leachates commonly contain problematic Cr(VI) concentrations and at pH 10-12 are very alkaline. Chromium is very soluble and mobile in the Cr(VI) oxidation state as chromate, but when it is reduced to Cr(III), insoluble Cr-hydroxides are formed that remove Cr from solution. Thus the *in situ* reduction of Cr(VI) to Cr(III) within contaminated ground has been proposed as a treatment strategy for COPR leachate.

The behaviour of chromate was investigated in two alkaline soil-water systems affected by leachate from COPR at a waste site in the North of England [1]. Acetate was added to two leachate affected closed soil-water systems; one had a pH of 7.7, the other 9.3. Cr(VI) reduction occurred in both systems as part of a cascade of microbially mediated terminal electron-accepting processes, occurring between nitrate and iron reduction. Nitrate, Cr(VI) and iron reduction were inhibited in experiments that had been sterilised by heat treatment. Nitrate reduction rates were similar in both pH systems but Cr(VI) and subsequently iron reduction took longer to start and were slower in the more alkaline system. At the time point when Cr(VI) reduction was essentially complete, the microbial populations in both systems showed an increase in species closely related to β-proteobacteria that are capable of nitrate reduction.

[1] Stewart (2007) *Geomicrobiol. J.* **24**, 655-669.

Ar solubility in mantle phases (revisited)

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Interpretation of isotopic data of natural samples depends on understanding the behaviour of parent and daughter in the system being studied. Information on the parent-daughter behaviour often comes from experimental work, for example simulating melting conditions (as best we can) in the laboratory to determine parent-daughter distribution when mantle is melted. However, information on relative parent-daughter behaviour can also be derived from the natural system itself: radiogenic isotope ratios melt residues suggest the daughter is less compatible than the parent. However, a re-examination of data is required when experimental data conflicts with behaviour predicted from the natural world.

Recent experimental data [1] suggest that Ar is compatible, i.e. Ar remains in the residue after melting. This is difficult to reconcile with the noble gas distribution in the Earth [2]. For example, $^{4}He/^{40}Ar$ of the bulk mantle is independently constrained from estimates of (U+Th)/K. Volatiles trapped in basaltic glasses are consistent with the calculated $^{4}He/^{40}Ar$ production ratio, suggesting that He and Ar behave similarly during mantle melting. And yet, incontrovertible experimental evidence demonstrates that He is incompatible. And therefore so must Ar be incompatible.

Confirmation of experimental data is paramount. Experiments are underway that will conclusively demonstrate whether Ar is indeed compatible. Ar is dissolved into olivine, and the diffusion profile is measured using an excimer laser. Given the possibilty of extremely slow diffusion of Ar in olivine, long (600h) experimental runs are required to produce a diffusion profile sufficiently deep (c. 100 nm; fig) to interrogate by laser.
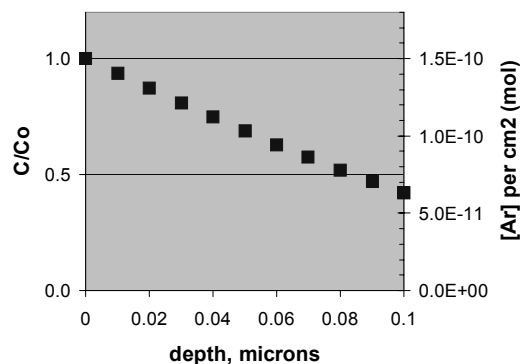
Figure 1: Depth profile predicted for these experiments. Given a detection limit of c. $5e^{-14}$ mol of Ar and ablation depths of c. 10nm, a 100nm deep profile is readily analysed.

[1] Watson *et al.* (2007) Nature **449**, 299-304 [2] Ballentine *Nature N+V* **449**, 294-296.