Global variations in H_2O/Ce: Relationships to arc magma geochemistry & slab surface temperatures

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We have compiled a dataset of 114 primitive arc magma compositions from melt inclusion and whole rock analyses to compare volatile contents, slab tracers, and calculated subduction component compositions between 18 subduction zone segments spanning the global range in slab thermal structure [1]. The average primitive magma H_2O content in our dataset is 3.3 ±1.2 wt.% (1 s.d.) for melts erupted within 50 km of the volcanic front. Although there is a wide range of volatile contents in magmas within individual arcs, the highest values occur in magmas erupted from vents along the volcanic front, where the subducting slab is located 104 ±29 km (avg. ±1 s.d.) beneath the surface. This observation, coupled with positive correlations between H_2O, Cl, S, and B contents and predictions from geodynamic models, provides strong evidence for the active supply of subduction-related components from the slab beneath volcanic arcs. Furthermore, calculated subduction component compositions become increasingly solute-rich in arcs with hotter slabs (lower thermal parameter), suggesting that fluids/melts of differing compositions are added beneath different arcs.

We have also calculated slab fluid temperatures for 51 volcanoes in 10 subduction zones [2] using the newly developed H_2O/Ce thermometer. The temperatures, adjusted to *h*, the vertical depth to the slab beneath the volcanic arc, range from ~730 to 900°C, and agree well (within 30°C on average for each arc) with sub-arc slab surface temperatures predicted by recent thermal models. The coherence between slab model and surface observation implies predominantly vertical transport of fluids within the mantle wedge. Slab surface temperatures are well reconciled with the thermal parameter (the product of slab age and vertical descent rate) and *h*. Arcs with shallow *h* (80 to 90 km) yield a larger range in slab surface temperature (up to ~200°C between volcanoes) and more variable magma compositions than arcs with greater *h* (120 to 180 km). This diversity is consistent with coupling of the subducting slab and mantle wedge, and subsequent rapid slab heating, at ~80 km. Slab surface temperatures warmer than the H_2O-saturated solidus implicate ubiquitous melting at the slab surface. Our results imply that melts or solute-rich fluids, and not H_2O-rich fluids, are thus the agents of mass transport to the mantle wedge.

[1] Ruscitto *et al.* (2012) *Geochem., Geophys., Geosys.*, in press. [2] Cooper *et al.* (2012) *Geochem., Geophys., Geosys.*, in press.

Leak fluid chemistry control on ^{90}Sr sorption mechanism in sediments

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Strontium-90 is present in contaminated land at nuclear sites around the world and is also an important component of nuclear waste inventories. The mobility of ^{90}Sr in the subsurface is often controlled either by adsorption to sediment particle surfaces or incorporation reactions into secondary mineral precipitates. Here, we present an overview of a multidisciplinary study examining the behaviour of ^{90}Sr in West Cumbrian unconsolidated aquifer sediments under a range of groundwater compositions relevant to contaminated land scenarios.

Batch experiments have been used to test the influence of pH and ionic strength (IS) on the degree of adsorption to sediments. In other experiments hyperalkaline cement waters were used to investigate the effect of mineral alteration and secondary mineral precipitation on ^{90}Sr sorption. Experiments containing 20 ppm Sr^{2+} (spiked with ^{90}Sr tracer) were sampled from 2 days up to one year. Change in Sr speciation within sediments was determined using X-ray absorption spectroscopy and sequential extraction techniques. Mineral precipitates were characterised using SEM, microprobe and TEM techniques.

pH titration experiments showed the optimum pH for maximum ^{90}Sr sorption was between pH 6-8, and in experiments using low IS groundwaters ~99% of ^{90}Sr was removed from solution at circumneutral pH. In experiments with higher IS artificial waste tank leachate at pH 11 only ~80% of ^{90}Sr was removed, suggesting that higher concentration of ions in solution inhibited ^{90}Sr sorption. When both Na^+ and Ca^{2+} solutions were used as competing ions, sorption decreased markedly in experiments when IS was greater than 5 mmol L^{-1}, closely matching model fits to the data. Sr K-edge EXAFS analysis of sediment samples revealed Sr-O bond distances at 2.60 Å, indicating outer-sphere sorption. Sequential extractions found 70-85% of ^{90}Sr remained exchangeable after one year.

In contrast, experiments using high pH young cement water, found sorption to be >99% despite the extremely high IS, suggesting another mechanism of Sr removal predominated. Sequential extractions on a sediment sample aged at 70°C for a year, found that 25±6 % of ^{90}Sr was residual. Sr K-edge EXAFS analysis of a 70°C aged sample contained evidence for an additional Sr-O-Si(Al) bond distance at 3.45 Å consistent with Sr incorporation in a neoformed silicate mineral. XRD and electron microscopy analysis indicate that the neoformed mineral could be chabazite, a zeolite mineral.

These results indicate that at contaminated nuclear sites, ^{90}Sr in the environment will predominantly sorb at circumneutral pH, but can be remobilised if affected by higher IS solutions. In a high pH cementitious repository, alkali alteration of silicate minerals could provide a sink for ^{90}Sr, however even after alteration much of the ^{90}Sr may remain exchangeable with other ions in solution.