

Melting and refertilization in peridotites: What happens to Os?

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Most peridotites, be they from massifs, xenoliths or the ocean floor, are more refractory than estimates of the Earth's primitive mantle (i. e., they have lower Al_2O_3 and CaO). Suites of peridotites commonly form linear arrays on plots of MgO vs. Al_2O_3 or CaO , which are often interpreted as melt depletion trends. However, it has been appreciated for some time [e.g. 1] that some (many?) of these trends may also reflect melt refertilization. This point was recently brought home when it was recognized that lherzolite from its type locality in the Pyrenees is the product of refertilization of harzburgite [2]. How melt refertilization affects the Re-Os isotope system in peridotites depends on the timing of refertilization relative to melt depletion. We argue here that most refertilization observed in peridotite suites is a product of adiabatic melting processes – i. e., the refertilizing melts originate from deeper in a rising melt column and infiltrate overlying harzburgite. We term this process auto-refertilization [3]. Auto-refertilization increases Re/Os ratios in harzburgites, but because the process occurs nearly coincident with melt depletion, it will not change $^{187}\text{Os}/^{188}\text{Os}$ at the time of the event. With time, the resulting refertilized peridotites will form linear trends on Al_2O_3 vs. $^{187}\text{Os}/^{188}\text{Os}$ or Re-Os isochrons. The resulting ages will reflect the time of partial melting/refertilization. By contrast, refertilization of ancient harzburgites occurring significantly after melt depletion will produce strongly curved arrays on Al_2O_3 vs. $^{187}\text{Os}/^{188}\text{Os}$ plots [4]. Some lherzolitic xenoliths from the Kaapvaal Craton show such a trend [5]. In the absence of fugitive sulfide melts in the upper mantle, for which we argue there is little evidence, Os isotopes in whole rock peridotites may often be faithful recorders of melting episodes in the upper mantle.

[1] Elthon, 1992, *J. Geophys. Res.* **97**: 9015-9025. [2] Le Roux *et al.*, 2007, *EPSL* **259**: 599-612. [3] Rudnick and Walker, 2009, *Lithos* **112**: 1083-1095. [4] Reisberg and Lorand, 1995, *Nature* **376**: 159-162. [5] Simon *et al.*, 2007, *J. Petrol.* **48**: 589-625.

Isotopic and geochemical tracers for evaluating the environmental impact of the Tennessee Valley Authority coal ash spill in Kingston, TN

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Systematic monitoring of the environmental impacts of the largest coal ash spill in US history at the Tennessee Valley Authority (TVA) coal-burning power plant in Kingston, TN has revealed that interaction of the coal combustion products (CCPs) with natural waters mobilizes leachable coal ash contaminants (LCACs) such as boron, arsenic, selenium, strontium, and barium [1]. We have monitored the quality of water and sediments in downstream segments of the Emory and Clinch Rivers near the spill site, which revealed several distinctive patterns (1) surface waters in areas of restricted water exchange show high LCACs levels (e.g. As: 9- 95 $\mu\text{g/L}$). Removal of ash from this area and diversion of surface water has led to a reduction of the LCACs concentrations with time; (2) downstream Emory and Clinch Rivers show low LCACs concentrations below the EPA maximum contaminant level (As=10 $\mu\text{g/L}$), but with levels (e.g. As ~ 4 $\mu\text{g/L}$) above the baseline of the upstream rivers; and (3) pore water extracted from bottom sediments of the downstream Emory and Clinch Rivers with significantly high LCACs levels (e.g. As 9-285 $\mu\text{g/L}$). Our field and leaching experiments data show that boron is one of the sensitive indicators for CCP contaminants' leaching, with boron content up to 1276 $\mu\text{g/L}$ in pore water relative to the upstream river water (6 to 9 $\mu\text{g/L}$) and $\delta^{11}\text{B}$ values of -12‰ and -16‰ (relative to NIST951). This isotopic composition is significantly different from that of meteoric boron. Overall, we show that while significant dilution reduces the LCACs' impact in the Emory and Clinch Rivers, leaching continues to occur at the bottom sediments and mobilizes LCACs to the underlying pore water.

[1] Ruhl, *et al.* (2009) *Env. Sci. Tech* **43**, 6326–6333.