

Electronic Supplement Appendix 4

Osmium Isotopes: Proof of a Pyroxenite Source? Not Quite

An astute reviewer pointed out that Kogiso et al. (2004), using Os-Sr isotopic ratios, suggested that Hawaiian lavas *require* a distinct pyroxenite source, that melts separately from peridotite. As we show in the figure below, the Kogiso et al. choice of end members was arbitrary and their solution to the problem of high $^{187}\text{Os}/^{188}\text{Os}$ is both non-unique, and at odds with trace element ratios that show no hint that $^{187}\text{Os}/^{188}\text{Os}$ ratios derive from a source distinctly rich in either or both of pyroxene and garnet.

We are skeptical of the arguments of Kogiso et al. (2004) for several reasons. 1) Kogiso et al. (2004) select a particularly low- $^{187}\text{Os}/^{188}\text{Os}$, low- $^{87}\text{Sr}/^{86}\text{Sr}$ end member to represent peridotites, but the peridotite field is quite broad, and the Hawaiian lavas considered for the present study fall within the field of peridotites (Fig ES1-A), as well as that of Baffin Island lavas, which overlap considerably with the peridotite field and likely represent peridotite partial melts themselves. 2) Hawaiian lavas with elevated $^{187}\text{Os}/^{188}\text{Os}$ show an array of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios: post-shield lavas ranging to lower $^{87}\text{Sr}/^{86}\text{Sr}$ as $^{187}\text{Os}/^{188}\text{Os}$ increases, while some shield stage lavas show either no overall change in $^{87}\text{Sr}/^{86}\text{Sr}$ or increasing $^{87}\text{Sr}/^{86}\text{Sr}$ with increased $^{187}\text{Os}/^{188}\text{Os}$, especially at Koolau. Ironically, Lassiter ascribe the high $^{187}\text{Os}/^{188}\text{Os}$, low- $^{87}\text{Sr}/^{86}\text{Sr}$ post-shield lavas to a pyroxenite-bearing source, although a study of Hawaiian pyroxenites by Sen et al. (2011) leads them to argue, convincingly to us, that selective assimilation of sulfides that occur on phase boundaries are a likely cause of increased $^{187}\text{Os}/^{188}\text{Os}$ at near constant $^{87}\text{Sr}/^{86}\text{Sr}$. 3) As we show in panel B, the few pyroxenites in the Georoc database have very high $^{87}\text{Sr}/^{86}\text{Sr}$ at just modest $^{187}\text{Os}/^{188}\text{Os}$ values, and trend towards Archean basalts, as one might expect if pyroxenites are recycled basaltic crust. These lithologies do not explain Os-Sr isotopic ratios at Koolau, or

elsewhere at Hawaii. 4) Only one pyroxenite plots close to the putative end-member of Kogiso et al. (2004) (not shown). Moreover, Continental Flood Basalts (CFBs) follow the Kogiso et al. (2004) peridotite-“pyroxenite” curve remarkably well (panel B, Fig. ES1): what these CFBs have in common is their transport through continental crust; we suspect that the odd “pyroxenite” source of Kogiso et al. (2004) serves as a proxy for a high $^{187}\text{Os}/^{188}\text{Os}$ component situated within, and common to, continental crust.

So why might $^{187}\text{Os}/^{188}\text{Os}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios both be elevated for some shield stage lavas? We are open to the idea that Koolau lavas might be affected by something pyroxenite-like, or at least lithologically different from other Hawaiian lavas, but the answer might be related to the model of Sen et al. (2011). Sen et al. (2011) do not deny that pyroxenites may be important at Hawaii, but their analysis of $^{187}\text{Os}/^{188}\text{Os}$ ratios in Hawaiian pyroxenites forces them to reject a pyroxenite source for elevated $^{187}\text{Os}/^{188}\text{Os}$ in Hawaiian lavas. They instead suggest that mantle-derived melts react with sulfides on the grain boundaries of mantle lithosphere, selectively dissolving high-Os and high- $^{187}\text{Os}/^{188}\text{Os}$ ratio sulfides that occur on grain boundaries. It would be an odd coincidence if only high $^{87}\text{Sr}/^{86}\text{Sr}$ primary mantle melts experienced such an interaction. But if the silicate host of such sulfides also had elevated $^{87}\text{Sr}/^{86}\text{Sr}$, the correlation would be explained. To illustrate the idea we show a mixing curve between a source that is a sulfide-bearing peridotite and normal peridotite which quite nicely explains Koolau compositions (see curve 2 in Figure ES1). Perhaps more interesting is the fact that that young (Cenozoic) arc lavas and some CFBs show very similar $^{187}\text{Os}/^{188}\text{Os}$ - $^{87}\text{Sr}/^{86}\text{Sr}$ values as observed at Hawaii, with high $^{187}\text{Os}/^{188}\text{Os}$ and only modest or no increases in $^{87}\text{Sr}/^{86}\text{Sr}$. Perhaps the Sen et al. (2011) model applies in many other tectonic settings than Hawaii.

We thus maintain that whatever the nature of the isotopic heterogeneities at Hawaii, the isotopically contrasting materials are probably thoroughly admixed, or are at least not highly different from one another in mineralogy. We test this idea in panel C of Figure ES1, where $^{187}\text{Os}/^{188}\text{Os}$ ratios clearly do not vary with trace element ratios that would be strongly fractionated by a source rich in either of both of pyroxene and garnet (e.g., Sc/Mn, where Sc is highly compatible in both pyroxene and garnet relative to olivine, whereas Mn is more nearly equally compatible; see main text for citations to trace element partitioning studies). And while high $^{187}\text{Os}/^{188}\text{Os}$ lavas may have high Al_2O_3 (Lassiter et al. 2000), none are enriched in Al_2O_3 relative to MgO , i.e., the observed Al_2O_3 enrichments are driven by fractionation, not source characteristics (Fig ES1 D). The only compelling trace element pattern is that $^{187}\text{Os}/^{188}\text{Os}$ decreases with increasing Os (or increasing Ir; elevated $^{187}\text{Os}/^{188}\text{Os}$ is also restricted to low Ni and Cr, both of which are rich in peridotites). The strong binary-mixing signature implied by $^{187}\text{Os}/^{188}\text{Os}$ vs. $1/\text{Os}$ correlations, and the occurrence of elevated $^{187}\text{Os}/^{188}\text{Os}$ at arcs and CFBs, often without elevated $^{87}\text{Sr}/^{86}\text{Sr}$, indicate that high $^{187}\text{Os}/^{188}\text{Os}$ ratios are probably a shallow-level mixing/assimilation phenomena and are quite likely not part of the convective mantle.

References Cited

- Kogiso, T., Hirschmann, M.M., and Reiners, P.W. (2004) Length scales of mantle heterogeneities and their relationship to ocean island basalt geochemistry. *Geochimica et Cosmochimica Acta*, 68, 345-360.
- Lassiter, J.C., Hauri, E.H., Reiners, P.W., and Garcia, M.O. (2000) Generation of Hawaiian post-erosional lavas by melting of a mixed lherzolite/pyroxenite source. *Earth and Planetary Science Letters*, 178, 269-284.
- Sen, I.S., Bizimis, M., Sen, G., and Huang, S. (2011) A radiogenic Os component in the oceanic lithosphere? Constraints from Hawaiian pyroxenite xenoliths. *Geochimica et Cosmochimica Acta*, 75, 4899-4916.

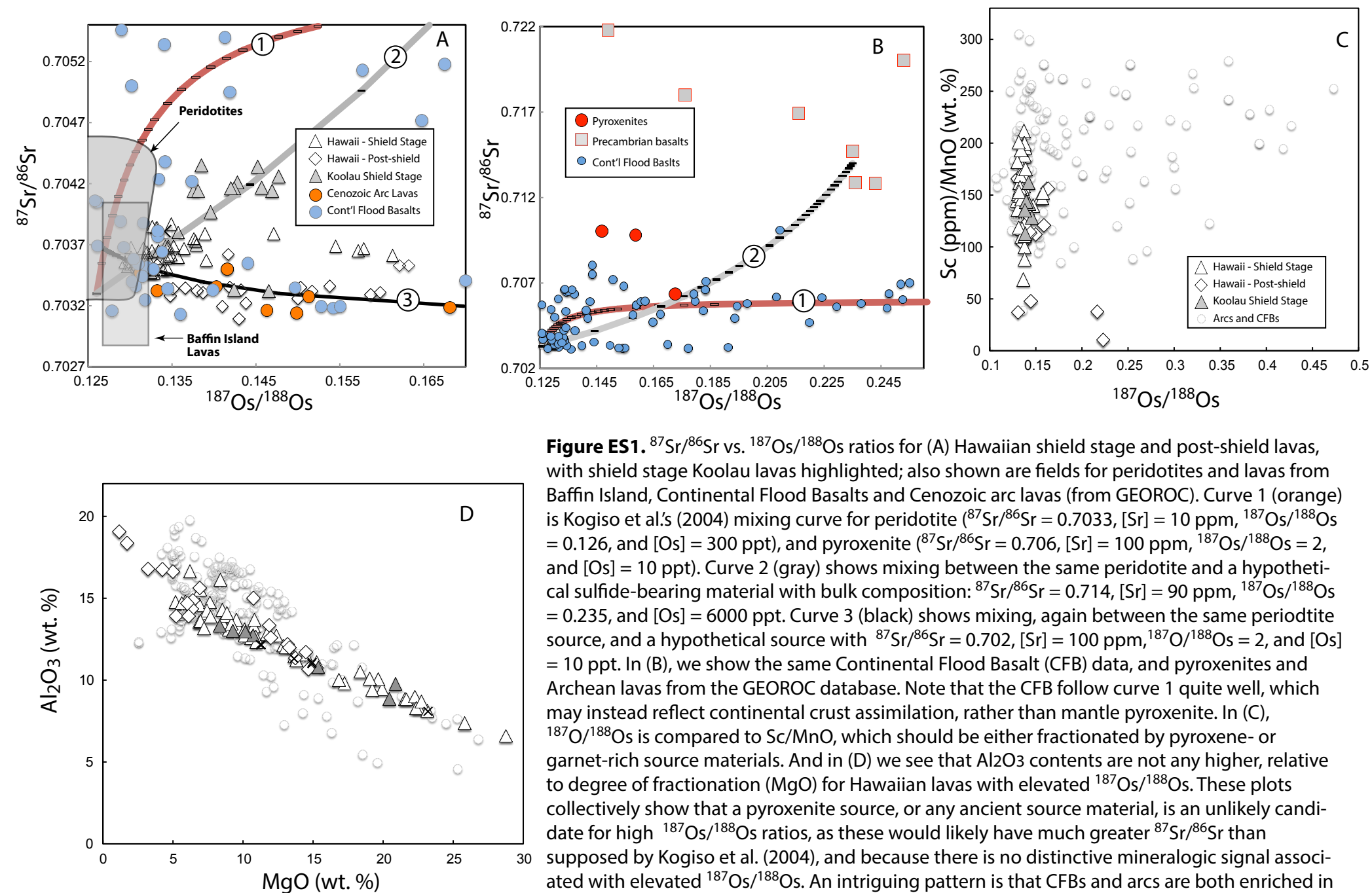


Figure ES1. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ ratios for (A) Hawaiian shield stage and post-shield lavas, with shield stage Koolau lavas highlighted; also shown are fields for peridotites and lavas from Baffin Island, Continental Flood Basalts and Cenozoic arc lavas (from GEOROC). Curve 1 (orange) is Kogiso et al.'s (2004) mixing curve for peridotite ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7033$, $[\text{Sr}] = 10$ ppm, $^{187}\text{Os}/^{188}\text{Os} = 0.126$, and $[\text{Os}] = 300$ ppt), and pyroxenite ($^{87}\text{Sr}/^{86}\text{Sr} = 0.706$, $[\text{Sr}] = 100$ ppm, $^{187}\text{Os}/^{188}\text{Os} = 2$, and $[\text{Os}] = 10$ ppt). Curve 2 (gray) shows mixing between the same peridotite and a hypothetical sulfide-bearing material with bulk composition: $^{87}\text{Sr}/^{86}\text{Sr} = 0.714$, $[\text{Sr}] = 90$ ppm, $^{187}\text{Os}/^{188}\text{Os} = 0.235$, and $[\text{Os}] = 6000$ ppt. Curve 3 (black) shows mixing, again between the same peridotite source, and a hypothetical source with $^{87}\text{Sr}/^{86}\text{Sr} = 0.702$, $[\text{Sr}] = 100$ ppm, $^{187}\text{Os}/^{188}\text{Os} = 2$, and $[\text{Os}] = 10$ ppt. In (B), we show the same Continental Flood Basalt (CFB) data, and pyroxenites and Archean lavas from the GEOROC database. Note that the CFB follow curve 1 quite well, which may instead reflect continental crust assimilation, rather than mantle pyroxenite. In (C), $^{187}\text{Os}/^{188}\text{Os}$ is compared to Sc/MnO, which should be either fractionated by pyroxene- or garnet-rich source materials. And in (D) we see that Al_2O_3 contents are not any higher, relative to degree of fractionation (MgO) for Hawaiian lavas with elevated $^{187}\text{Os}/^{188}\text{Os}$. These plots collectively show that a pyroxenite source, or any ancient source material, is an unlikely candidate for high $^{187}\text{Os}/^{188}\text{Os}$ ratios, as these would likely have much greater $^{87}\text{Sr}/^{86}\text{Sr}$ than supposed by Kogiso et al. (2004), and because there is no distinctive mineralogic signal associated with elevated $^{187}\text{Os}/^{188}\text{Os}$. An intriguing pattern is that CFBs and arcs are both enriched in $^{187}\text{Os}/^{188}\text{Os}$ with CFBs ranging to higher $^{87}\text{Sr}/^{86}\text{Sr}$; and Hawaiian lavas share a muted arc-like $^{187}\text{Os}/^{186}\text{Os}$ enrichment. These patterns point to a shallow source for high $^{187}\text{Os}/^{188}\text{Os}$, one that may be driven by assimilation/mixing processes, with a crustal influence for CFBs (and so their elevated $^{87}\text{Sr}/^{86}\text{Sr}$), and less, or no such influence for oceanic islands and arcs.