

## Chondritic initial $^{187}\text{Os}/^{188}\text{Os}$ in Paleoproterozoic shale (seawater) and onset of oxidative weathering

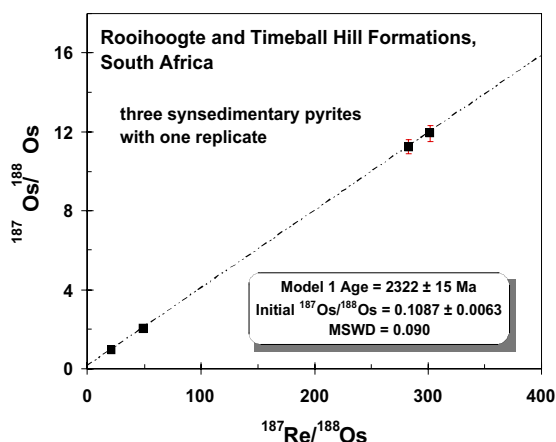
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Re-Os data from synsedimentary or early diagenetic pyrite in highly carbonaceous marine shales of the Rooihooigte and Timeball Hill Formations, South Africa, yield an isochron age of  $2322 \pm 15$  Ma and chondritic initial  $^{187}\text{Os}/^{188}\text{Os}$  of  $0.1087 \pm 0.0063$  (Hannah *et al.*, submitted). Highly negative  $\delta^{34}\text{S}$  values and lack of evidence for mass independent fractionation of sulfur in these same pyrite samples indicate that the atmospheric  $\text{O}_2$  level was higher than  $10^{-5}$  present atmospheric level (Bekker *et al.*, submitted).

Assuming the initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio reflects seawater composition at the time of deposition, the surprising chondritic value indicates minimal riverine input of radiogenic  $^{187}\text{Os}$  to early Paleoproterozoic oceans. The rise of  $^{187}\text{Os}$  in seawater with increasing atmospheric  $\text{pO}_2$  depends on: (1) increasing mobility of Re and Os in increasingly oxidizing surface environments; (2) increasing concentrations of Re and Os in seawater and therefore, in marine sediments; (3) accumulation of  $^{187}\text{Os}$  over time in increasingly Re-rich marine sediments; and (4) uplift, exposure, and oxidative weathering of  $^{187}\text{Os}$ -rich carbonaceous shales, the dominant source of  $^{187}\text{Os}$  in the weathering environment. Thus, there is a time lag of yet unknown length between the rise of atmospheric oxygen and the rise of  $^{187}\text{Os}$  in seawater.



### References

- Bekker, A., Holland, H.D., Wan, P.-L., Rumble, D. III, Stein, H.J., Hannah, J.L., Coetzee, L.L., and Beukes, N.J., (submitted).  
Hannah, J.L., Stein, H.J., Bekker, A., Markey, R.J., and Holland, H.D., (submitted).

## Slab-melting for high-Mg andesite magma formation in the Setouchi volcanic belt, SW Japan: Contribution from hafnium isotope geochemistry

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High-Mg andesites (HMA) and associated basalts in the Setouchi volcanic belt, SW Japan were analyzed for Hf isotopic compositions in order to examine whether fluid or melt from the subducted slab act as metasomatic agents during HMA magma genesis. Hf is a high-field-strength elements that may not be readily transported by aqueous fluids, in contrast to large-ion-lithophile elements and their isotopes (e.g., Sr, Nd, Pb), which are preferentially partitioned into aqueous fluids. Hf isotopes in combination with Sr-Nd-Pb isotopes should thus provide strong constraints for the identification of slab-derived components and their metasomatic agents for subduction related magmatism.

Setouchi HMAs and basalts have lower  $^{176}\text{Hf}/^{177}\text{Hf}$  ( $\epsilon_{\text{Hf}} < +10.8$ ) than MORBs and Izu-Bonin-Mariana arc basalts ( $> +13$ ). Hf isotopes are well correlated with Sr and Nd isotopes. HMAs from Shodo-shima Island demonstrate little variation in  $^{176}\text{Hf}/^{177}\text{Hf}$  and have lower  $^{176}\text{Hf}/^{177}\text{Hf}$  than associated basalts. These isotopic observations suggest that (1) subducted sediments significantly contributed to Setouchi magma genesis, (2) the source of the HMAs was more affected by subducted sediments than that of the basalts, and (3) sediment-melt is more likely than fluids as a metasomatic agent, as demonstrated by the coupled behavior of Hf and Nd isotopes.

Hf isotope ratios correlate well with La/Nb and La/Sm ratios: La/Nb ratios of Setouchi HMAs and basalts are lower than those of Izu-Bonin-Mariana basalts. Elevated La/Nb ratios of the latter can be explained by fluidal overprint from subducted oceanic crust. By contrast, the relatively low La/Nb of Setouchi HMAs and basalts, coupled with enriched Hf isotopes, again indicate a subducted sediment-melt contribution to the source region of the Setouchi HMAs and basalts.

A possible mechanism for HMA formation, involving melting of subducted sediments and altered oceanic crust, and subsequent melt-mantle interaction, was examined through geochemical modelling of dehydration, partial melting and melt-solid interactions. The modelling results demonstrate that the reaction products possess major and incompatible trace element compositions, as well as Sr-Nd-Pb-Hf isotope ratios, that are close to those of the undifferentiated HMAs and basalts.