

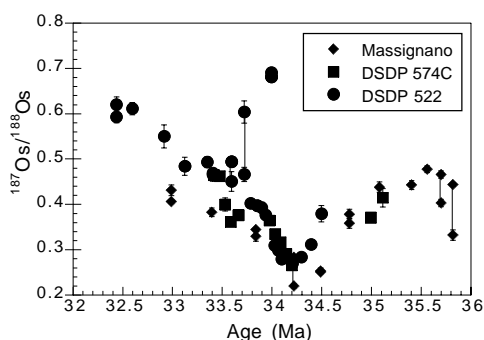
## The marine Os isotope record of the Eocene-Oligocene transition

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Osmium isotope analyses of bulk sediment samples from the South Atlantic (DSDP 522), Equatorial Pacific (DSDP 574C) and the Italian Apennines (Massignano) are used to construct a composite record of seawater <sup>187</sup>Os/<sup>188</sup>Os variations across the Eocene-Oligocene (E-O) transition. Between 34 and 34.5 Ma all three records display a pronounced excursion to very low <sup>187</sup>Os/<sup>188</sup>Os (0.29 to 0.26) from higher late Eocene <sup>187</sup>Os/<sup>188</sup>Os ratios (0.4 to 0.45). Following the local minimum <sup>187</sup>Os/<sup>188</sup>Os rises rapidly to approximately 0.6 by 32.5 Ma. Both the late Eocene <sup>187</sup>Os/<sup>188</sup>Os excursion and the asymmetry about this minimum are also apparent LL44-GPC3 record of Pegrarn and Turekian (1999).



We contend that these data reflect large changes in the <sup>187</sup>Os/<sup>188</sup>Os of seawater across the E-O transition. Direct comparison of the Os isotope record to benthic foram oxygen isotope variations, a proxy record of ice volume change, shows that rising <sup>187</sup>Os/<sup>188</sup>Os is correlated with the growth and decay of the first major Antarctic ice sheet. This coupling provides evidence of glacially enhanced continental weathering that is globally significant. A large excursion to low seawater <sup>187</sup>Os/<sup>188</sup>Os precedes major Antarctic ice sheet formation. If this excursion is not the result of increased influx of cosmic dust, then the Os isotope record suggests that dramatic shifts in global weathering patterns may have played a primary causative role in the first major Antarctic glaciation.

Pegrarn, W.J., and Turekian, K.K., 1999, *Geochim. Cosmochim. Acta.* 63, 4053-4058.

## A Chlorine Isotope Effect for Biochlorination

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Recent studies have identified several chlorinated organic compounds (COCs) accumulating in marine animals, which may be derived from natural or anthropogenic sources (Vetter *et al.*, 2001). To determine whether isotope ratios could be used to identify different sources, we investigated the chlorine isotope effect for biochlorination. We chlorinated 1,3,5-trimethylbenzene (TMB) and 3,5-dimethylphenol (DMP) with a chloroperoxidase isolated from the fungus *Caldoromyces fumago*. Each experiment was performed in triplicate in solutions of H<sub>2</sub>O<sub>2</sub> and excess KCl with a known chlorine isotopic composition (-1.4‰). Extraction and analysis by gas chromatography revealed that the DMP was trichlorinated (~75%) and dichlorinated (~25 %). The TMB was almost fully dichlorinated (90%) with traces of the mono- and trichlorinated isomers. Bulk δ<sup>37</sup>Cl values of the extracts were -12.06 ± 0.18 ‰ and -11.08 ± 0.08 ‰ for the TMB and DMP halogenated products, respectively, and indicate that chlorine isotopes may be useful in identifying natural versus anthropogenic sources of COCs. For example, natural COCs synthesized by this enzymatic pathway will have δ<sup>37</sup>Cl values that are approximately -13 to -9‰ assuming a δ<sup>37</sup>Cl of natural Cl from -2 to 1‰ (Jendrzejewski *et al.*, 2001). These products should be easily distinguished from anthropogenic COCs with δ<sup>37</sup>Cl values of -5.10 to +1.22 ‰ (Drenzek *et al.*, 2002).

### References

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 Jendrzejewski, N., Eggenkamp, H., and Coleman, M. (2001). *Appl. Geochem.* 16, 1021-1031.  
 Vetter, W., Heibl, J., and Oldham, N.J. (2001). *Env. Sci. and Tech.* 35, 4157-4162.