

A revised estimate of the $\delta^{44/42}\text{Ca}$ of continental runoff

E. T. TIPPER¹, A. GALY¹, M. J. BICKLE¹, D. CALMELS²,
J. GAILLARDET²

¹Department of Earth Sciences, University of Cambridge,
Cambridge, CB2 3EQ, UK, (ett20@esc.cam.ac.uk)

²Institut de Physique du Globe de Paris 4, Place Jussieu
75252 Paris cedex 05

Ca isotope ratios have the potential to trace biogeochemical processes at the surface of the Earth.

Analysis of river water, limestone and travertine from the high altitude, negligible vegetation setting of the Southern Tibetan Plateau demonstrates that Ca isotope ratios are fractionated during weathering. Dissolved Ca in the two rivers studied is derived primarily by limestone dissolution. $\delta^{44/42}\text{Ca}$ in the rivers averages 0.43‰ and is statistically distinct from limestone at 0.31‰.

Ca isotope ratios in limestone dominated rivers from the Jura mountains in E. France are also fractionated during limestone weathering with $\delta^{44/42}\text{Ca}$ in the rivers enriched in the heavy isotopes of Ca by up to 0.5‰ compared to average limestone. The range in $\delta^{44/42}\text{Ca}$ in these small rivers from the Tibetan Plateau and France is 0.43‰, equivalent to the entire range in $\delta^{44/42}\text{Ca}$ recorded in marine carbonate over the last 80m.y (e.g. [1]).

The significance of focussing on rivers draining limestone is that at a global scale, 67% of riverine Ca is derived from carbonate weathering and therefore the average riverine $\delta^{44/42}\text{Ca}$ is anticipated to be strongly influenced by the $\delta^{44/42}\text{Ca}$ of limestone. However, all the limestone dominated rivers measured so far are heavier than limestone.

At a global scale, there are two mechanisms which may enrich dissolved Ca in heavy isotopes, secondary carbonate deposition and preferential uptake of light Ca by the biosphere [2]. In the Tibetan rivers, precipitation of isotopically light travertine with a $\delta^{44/42}\text{Ca}$ of 0.21‰ enriches solute Ca in heavy isotopes, consistent with previous explanations of non conservative behaviour of Ca in Himalayan rivers [3]. It is not yet possible to evaluate the relative importance of carbonate precipitation or biomass to the $\delta^{44/42}\text{Ca}$ of global rivers and to do so will require a systematic survey of $\delta^{44/42}\text{Ca}$ in global rivers.

References

- [1] C. L. De La Rocha, D. J. DePaolo, Isotopic evidence for variations in the marine calcium cycle over the Cenozoic, *Science* **289** (2000) 1176–1178.
- [2] A.-D. Schmitt, F. Chabaux, P. Stille, The calcium riverine and hydrothermal isotopic fluxes and the oceanic calcium mass balance, *Earth and Planet. Sci. Lett.* **213** (3-4) (2003) 503–518.
- [2] E. T. Tipper, A. Galy, M. J. Bickle, Riverine evidence for a fractionated reservoir of Ca and Mg on the continents: Implications for the oceanic Ca cycle, *Earth and Planet. Sci. Lett.* (In press).