2.7.P07

Species dependent fractionation of silicon isotopes by present-day demosponges

P.Z.VROON[1], C.J. BEETS[1], D.H. SOENARJO[1], R.W.M. VAN SOEST[2], S.R. TROELSTRA[1], J. SCHWIETERS[3], J.C. VAN BELLE[1] AND B. VAN DER WAGT[1]

[1] Faculteit Aard- en Levenswetenschappen, De Boelelaan 1085, 1081 HV Amsterdam, The Netherlands (vrop@geo.vu.nl; beec@geo.vu.nl; soed@geo.vu.nl; tros@geo.vu.nl; belj@geo.vu.nl; wagb@geo.vu.nl)

[2] The Zoological Museum of Amsterdam, Mauritskade 61, 1092 AD Amsterdam, The Netherlands (Soest@bio.uva.nl)

[3] ThermoFinniganMAT, Barkhausenstrasse 2, 28197 Brem-en, Germany (JSchwieters@ThermoFinniganMAT.de)

The silicon biogeochemical cycle is a central issue in climate studies since diatoms (phytoplankton with an opal skeleton) transport large quantities of carbon between surface- and deep ocean waters. A relatively new tool has been the deployment of silicon isotopes to study this biogeochemical cycle. The variations of the silicon isotopic composition of seawater through geological time could yield information on the (paleo-)activity of diatoms in removing carbon from surface waters and on the extent of weathering on the continents. So far, only limited data are available for the fractionation factors between dissolved silica in seawater and biogenic opal. De La Rocha et al. (1997) showed that the fractionation factor between dissolved silica and diatom opal is not species dependent. However, this has not been shown for other opal incorporating life such as sponges and radiolarians. Here we report the first systematic study of silicon isotope fractionation between opal of three demosponge species (*Petrosia hoeksemai*, *Clathria thalysias basilana* and *Stylissa carteri*) and seawater from the Speramonde Shelf, Sulawesi, East Indonesia.

The demosponges of this study display a range of δ^{30}Si between -2.0 and +0.5‰. This range largely overlaps with previous published data, but extends the range to heavier values. The three species show different δ^{30}Si averages: *P. Hoeksemai*: -0.02 ±0.14‰; *S. Cateri*: -0.20±0.27‰ and *C. Basilana* -1.28±0.26‰. The results from the studied demosponges suggest that fractionation factors are species dependent, since the sponges display systematic differences at a single locality. We did not observe correlations between δ^{30}Si, opal content and water depth. Sponges are probably dissolved silica limited and not food limited in their growth. Consequently, different biological mechanisms for the uptake of dissolved silica and the conversion to sponge opal could be the reason for the different fractionation factors for each species.

Reference

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2.7.P08

Calcium isotope variations in Devonian brachiopods

F. BÖHM[1], R. VAN GELDERN[2], N. GUSSONE[1] AND A. EISENHAUER[1]

[1] IFM-GEOMAR, Wischhofstr. 1-3, 24148 Kiel, Germany (fboehm@ifm-geomar.de)

[2] Institut f. Geologie u. Mineralogie, Universität Erlangen, Schlossgarten 5, 91054 Erlangen, Germany

We investigated ^{44}Ca/^{40}Ca ratios of Devonian brachiopod shells (Lochkovian to Famennian) collected at various locations in Russia (coll. E.A. Yolkin), USA (coll. J. Day), Spain (coll. F. Alvarez), China (coll. X.P. Ma), Morocco, Belgium and Germany. We used samples previously analyzed for δ^{18}O, δ^{13}C, ^{87}Sr/^{86}Sr and trace element contents, and checked for possible diagenetic alteration [1].

Modern brachiopod shells have $\delta^{44/40}$Ca values in good agreement with other modern biogenic calcite shells [2] and show no indication of vital effects. We find the average Devonian brachiopod $\delta^{44/40}$Ca to be about 0.7 ‰ lower than its modern counterpart. This value is well below the Neogene $\delta^{44/40}$Ca minimum [3], which provides further evidence for long-term variations of seawater $\delta^{44/40}$Ca throughout earth history. The $\delta^{44/40}$Ca is relatively stable during most of the Lower to Middle Devonian, shows a possible maximum during the Givetian-Frasnian and a short negative excursion at the Frasnian-Famennian (FF) boundary.

Comparison of our $\delta^{44/40}$Ca and δ^{18}O records excludes temperature as a controlling factor of the calcium isotope variations. We can further exclude any significant influence of radiogenic ^{40}Ca (a daughter product of ^{40}K decay) on the $\delta^{44/40}$Ca record. Fractionation corrected ^{40}Ca/^{44}Ca ratios of Devonian and modern marine carbonates are identical within error (±0.002‰). There is no measurable variation in the radiogenic Ca content during the Devonian. This is in contrast to the behaviour of radiogenic strontium, which shows considerable variations throughout earth history.

Several factors may have contributed to the observed $\delta^{44/40}$Ca variations during the Devonian and the Devonian-Recent offset. The coincidence of the negative $\delta^{44/40}$Ca excursion with the mass extinction at the FF boundary points to an influence of carbonate production and burial on the marine calcium isotope record. Further possible factors include weathering on the continents and on exposed shelfs, possibly related to sea-level variations and/or climatic changes and the spreading of vascular land plants during the Middle and Late Devonian.

References

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