Calcium Isotope Variations of Phanerozoic Seawater

FLORIAN BÖHM[1], ANTON EISENHAUER[1]

[1]GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany
fboehm@geomar.de, aeisenhauer@geomar.de

Fossil records of well-preserved brachiopods and belemnites indicate that the $\delta^{44/40}$Ca of Phanerozoic seawater varied on 100 Ma timescales (Farkas et al. 2007, GCA 71, 5117-5134). On the other hand, Precambrian marine bulk carbonate sediments show no long-term calcium isotope trends, indicative of a largely invariant $\delta^{44/40}$Ca of the input to the oceans on these timescales (Blättler & Higgins 2017, EPSL 479, 241-251). Similarly, our compilation of published Ordovician to Neogene marine bulk carbonate data shows a narrow $\delta^{44/40}$Ca range (-1.3 to -1.1 ‰ SW), in agreement with the upper continental crust composition (-1.2 ‰, Wang et al., 2019, GCA 259, 37-52).

We amended the fossil record of Farkas et al. (2007) with Jurassic-Cretaceous records (Blättler et al. 2012, Geol. 40; Brazier et al. 2015, EPSL 411; Gussone & Friedrich 2018, Chem. Geol. 488). The resulting record starts with a long Silurian to Devonian interval (470 to 350 Ma) with $\delta^{44/40}$Ca values 0.5 ‰ lower than the modern ocean. During the Carboniferous (350 to 310 Ma) $\delta^{44/40}$Ca increased to nearly modern values that prevailed during the early Permian and then dropped to a plateau, 0.4 ‰ lighter than modern values, lasting from the late Permian until the Jurassic (260 to 170 Ma). During the Late Jurassic $\delta^{44/40}$Ca increased to reach modern values in the Early Cretaceous.

With the likely invariable isotopic composition of the calcium input to the oceans, the observed long-term marine $\delta^{44/40}$Ca trends are best explained by variable isotope fractionation during calcium carbonate precipitation. The fractionation variability can partly be explained by a change from calcite to aragonite seas during the Carboniferous (Farkas et al. 2007). However, this explanation is at odds with the subsequent return of $\delta^{44/40}$Ca to lower values during the late Permian while the aragonite seas continued until the early Jurassic.

We find a strong correlation ($r^2 = 0.55$) between the Silurian to Middle Jurassic part of the fossil $\delta^{44/40}$Ca record and global mean seawater temperature (Song et al. 2019, JES 30). The magnitude of the slope (-0.02 ‰/°C) is in good agreement with the well-known temperature sensitivity of $\delta^{44/40}$Ca in $CaCO_3$ precipitation (Gussone et al. 2005, GCA 69). The negative sign indicates that temperature-dependent fractionation of the $CaCO_3$ output from the oceans is controlling seawater composition, while temperature has only a minor influence on the proxy recorders. The correlation breaks down during the Late Jurassic, possibly due to the increasing importance of calcareous micro-plankton at this time.