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Ca isotope fractionation in coccolithophores

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Coccolithophores are important marine primary producers and are responsible for about half of the global carbonate export production. Since coccoliths are a significant sink of marine calcite, their Ca isotopic composition is an important factor for modeling the isotopic Ca budget of the ocean. In addition, they provide the potential to record long-term changes in the ocean chemistry, because their first occurrence dates back to the late Triassic.

Here we report results of Ca isotope analysis of several coccolithophore species grown in mono-specific cultures under controlled laboratory conditions with changing environmental parameters such as temperature, carbonate chemistry and illumination.

The investigated coccolithophores (*Emiliania huxleyi*, *Calcidiscus leptoporus, Syracosphaera pulchra*, *Umbilicosphaera foliosa* and *Helicosphaera carteri*) show a coherent temperature dependent Ca isotope fractionation, which is similar to the planktic foraminifer *Orbulina universa* [2] and in general agreement with a previously published value for cultured *E. huxleyi* at 16°C [1]. In contrast, Quaternary coccolith oozes show considerably lighter δ^{44}Ca values [3]. The origin of this discrepancy is not yet clear. It may be due to culturing artifacts, diagenetic alteration or so far unknown effects controlling Ca isotope fractionation. Since all five investigated species show a coherent behaviour, a coccolithophore-species-dependent Ca isotope fractionation appears to be rather unlikely to explain this discrepancy.

Ca isotope ratios of *E. huxleyi and C. leptoporus* cultured at different pH values appear to be insensitive to pH.

E. huxleyi cultured at different light intensities showed no variation in Ca isotopes. This indicates, that the precipitation rate, which varied with light intensity, did not play an important role for Ca isotope fractionation in coccoliths.

Our results demonstrate that the fractionation coefficient of Ca isotopes in coccolithophores is rather constant and similar to several foraminifera species, implying a rather homogeneous Ca isotope sink in the ocean.

References

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2.7.54

High precision calcium isotope abundance variations measured by the high mass resolution Finnigan Neptune

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Calcium plays a significant role in the geochemical interaction between atmosphere and oceans. Isotope abundance variations of this element enable the investigation of the mechanisms and consequences of these processes. The incorporation of calcium by marine organisms will fractionate the isotopes of calcium such that a record of ocean water pH, temperature, bioactivity and salinity may be recorded in the biominerals. However, these isotopic effects are proving to be very subtle and reliable measurements are only possible using high precision analytical techniques. In the past, double spiking and analysis by thermal ionization mass spectrometry have been employed, necessitating the addition of Ca with two isotopes greatly enriched relative to natural levels. Another very promising approach, that does not require the addition of enriched isotopes, is high mass resolution multi-collector inductively coupled plasma mass spectrometry in combination with standard-sample bracketing. The high mass resolution of the Finnigan Neptune ensures that molecular interferences are resolved from calcium isotopes measured, including ^{42}Ca, ^{43}Ca, ^{44}Ca and ^{48}Ca thus providing for a stable background and high sensitvity. The stable mass bias of the FinniganNeptune enables normalization of the measured isotope abundance ratios relative to standard reference materials. Quantitative separation of the calcium from the sample matrix was done to ensure that the measurements were independent of the sample type. In addition, thorough desolvation of the aerosol was found to have a significant effect on the stability and sensitivity of the method. Delta values with external reproducibilities better than ±0.2 ‰ (2s) were routinely measured. In this presentation we will demonstrate the robustness of the analytical technique and provide a comparison of several materials employed as calcium isotope standards.