Divalent cation incorporation into Alcyonarian spicules (Octocorallia)

I. TAUBNER[1]*, F. BÖHM[1], A. EISENHAUER[1], D. GARBE-SCHÖNBERG[2] AND J. EREZ[3]

[1]Leibniz Institute of Marine Sciences, IFM-GEOMAR, Kiel, Germany (*correspondence: itaubner@ifm-geomar.de) (fboehm@ifm-geomar.de, aeisenhauer@ifm-geomar.de)
[2]Institute of Geosciences, Christian-Albrechts-Universität, Kiel, Germany (dgs@gpi.uni-kiel.de)
[3]Institute of Earth Sciences, The Hebrew University of Jerusalem, Israel (erez@vms.huji.ac.il)

A better understanding of biocalcification mechanisms improves the interpretation of environmental proxies. Here a new model organism *Parerythiopodium fulvum,* building high magnesian calcite spicules (~13mol% $MgCO_3$), was grown under controlled laboratory conditions in natural seawater at (i) a temperature range from 19 to 32°C at constant pH; and (ii) a pH range from 7.6 to 8.5 at constant temperature and dissolved inorganic carbon concentration. Results indicate that trace element ratios and Ca isotope fractionation are controlled by more than one environmental parameter.

The temperature response of Mg/Ca in *P. fulvum* is significant (1.0±0.1mmol/mol/°C), but less sensitive than inorganically precipitated Mg-calcites [1]. Additionally, the Mg content of the calcite is lower than for inorganic marine cements [2]. While the weak temperature dependency of Sr/Ca in *P. fulvum* (-0.012±0.003mmol/mol/°C) agrees well with experimental data of inorganic calcites, precipitated at rates typically known for corals ($\log(R)=4\mu mol/m^2/h$), the strontium distribution coefficient is slightly higher ($D_{Sr,\ P.fulvum}$~0.3 compared to $D_{Sr,\ inorg.}$<0.2 [3]).

The pH exerts an even stronger control on metal partitioning, with 6.1±0.5 and 0.22±0.04mmol/mol/pH-unit for Mg/Ca and Sr/Ca, respectively. So far no other studies have been conducted in this field.

Although being a high Mg-calcite, the $\delta^{44/40}$Ca of *P. fulvum* (0.79±0.05‰ relative to NIST SRM 915a) is identical within error with mean value measured for *Acropora* sp. (0.81±0.05‰, [4]), an aragonitic scleractinian coral, but shows no significant temperature dependency. On the other hand $\delta^{44/40}$Ca demonstrates a weak dependence on pH (-0.18±0.14‰/pH-unit).

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Early differentiation of the lunar magma ocean – New Lu-Hf isotope results from Apollo 17

D.J. TAYLOR*, K.D. MCKEEGAN, T.M. HARRISON AND E.D. YOUNG

Department of Earth and Space Sciences & Institute of Geophyscis and Planetary Physics, UCLA, Los Angeles, CA, USA 90095 (*correspondence: dtaylor@ess.ucla.edu)

The current paradigm for the early silicate differentation of the Moon holds that the outer few hundred km of the Moon was completely molten due to the high temperatures associated with its formation in a giant impact event [1]. Over time this vast silicate ocean cooled and crystallized, forming a layered cumulate mantle topped by a bouyant plagioclase crust, with an incompatible-trace-element-enriched (ITE) layer (KREEP) sandwiched in between. Despite nearly 40 years of investigation, the timescale for the silicate differentation of the Moon is not agreed upon. Model ages for crystallization of the lunar magma ocean (LMO) range from as late as 4.352 Ga [2] to as early as 4.505 Ga [3] and a recent ion probe U-Pb date of a lunar zircon [4] provides a younger age limit of 4.417±0.006 Ga.

Our approach has been to undertake coupled Lu-Hf/U-Pb analyses of individual lunar zircons since zircons effectively freeze-in the Hf isotopic compositions of their source magmas thus constraining the timescale of Lu/Hf fractionation accompanying silicate differentiation. Highly non-radiogenic Hf in zircons from Apollo 14 confirm that they have sampled the KREEP source region and indicate a separation age of 4.478±0.046 Ga (~90 Ma after CAIs) of the KREEP source [5]. As the last region of the LMO to crystallize, this formation age of KREEP provides a robust constraint for the differentation age of the Moon.

We have extended this approach to zircons isolated from Apollo 17. Breccia 72275 appears to sample a different KREEP reservoir from Apollo 14 and provides evidence for geographic compositional variation of KREEP [6]. The 72275 zircons also show negative ε_{Hf} (ranging from -2 to -4), adding to the emerging picture of early differentiation of KREEP on a global scale.

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