Testing the effect of crystal growth rate on foraminiferal calcite microchemistry using Sr/Ca of individual day/night bands

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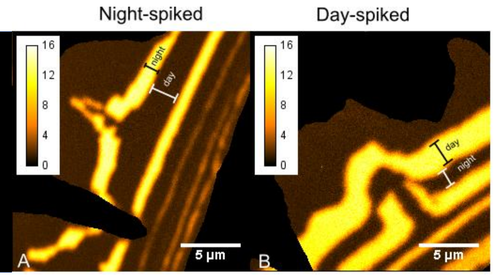
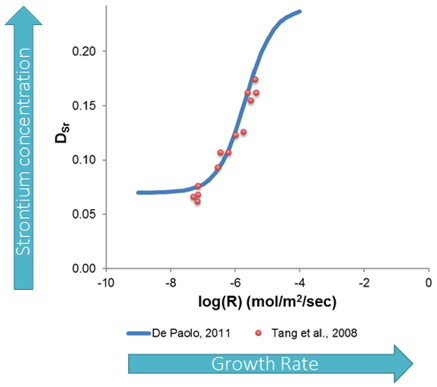
Can Kinetics Explain Geochemical Banding Within Single Foraminifera?

Banding: Many geochemical paleoproxies vary systematically on a diel cycle within single foraminifera, even when cultured at constant temperature and seawater chemistry.

→ Can complicate proxy interpretation
→ Rich source of new information about biomineralization and possibly climate
→ **Need to understand mechanism to use this information**

Growth rates in the cultured foraminifera *Orbulina universa* are higher during the day than during the night as recorded wthin test wall (right). Bright colors show location of ^{43}Ca day or night label. NanoSIMS image.





- Sr/Ca increase with growth rate for inorganic calcite (left)
- If mineral growth kinetics controls banding, then **Sr should be higher during the day than during the night** (up to 10%)
- Possibility to use Sr/Ca as an idicator or correction for kinetic effects?
- Previous experiments don't see signal. **Can we exclude kinetics or is signal obscured by analytical uncertainty?**

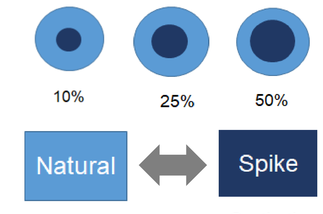
How to Measure Composition of Micrometer Scale Bands with Precision of Solution-Based Methods?

- Adapt Isotope dilution to occur within living cultured foraminifera (Gagnon et al., 2012)
- Mixed isotope spike (Ca-Sr-Mg) labels either day or night portion of test
- Culture *O. universa* foraminifera at constant T and carbonate chemistry
- Use isotope labels to unmix composition of bulk sample after growth
- Measure isotope ratios of ¼ of a single foraminifera test using Element HR-ICP-MS and micro-FAST syringe driven sample introduction system
- Compare with NanoSIMS and ToF-SIMS analysis of skeletal banding for growth rate

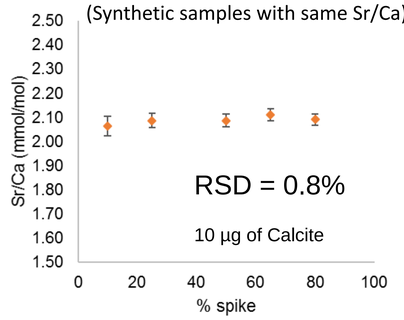
Foraminifera collected by blue-water diving

Mixed-Spike Method Can Measure Sr/Ca of Labeled Calcite in Single Foraminifera at High Precision

Precision Test Using Synthetic Samples

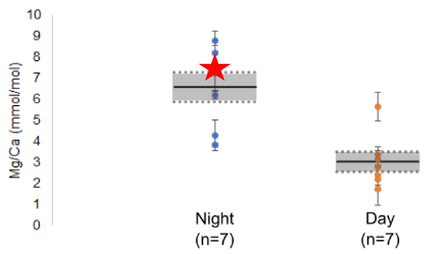


Sr/Ca of Unmixed Natural Endmember
(Synthetic samples with same Sr/Ca)



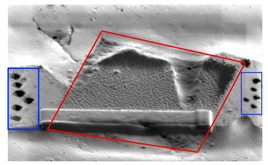
Mixed-Spike Method Recovers Same Mg/Ca as Independent NanoSIMS Measurements

Mg/Ca of Day and Night Bands



Multi-Spike Method. 14 cultured *O. universa* labeled during day or night

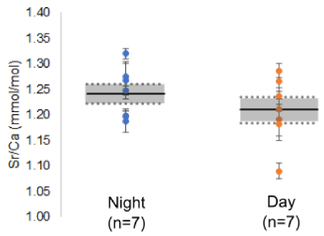
Red star is sample analyzed by both methods. Statistically identical: 7.2 ± 0.1 mmol/mol



Burn marks from calibrated NanoSIMS spots (1 µm) shown near image site.

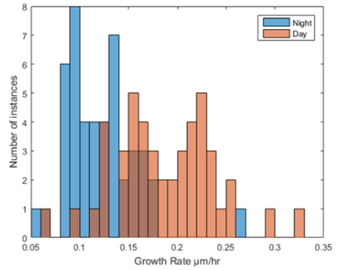
Surprise Result: Sr/Ca Lower in Fast Growing Day Bands

Sr/Ca of Day and Night Bands Mixed Spike



Mean Sr/Ca of day calcite 2.6 % lower than night calcite across 14 cultured *O. universa* (day and night different at 85 % LOC)

Growth Rate of Day and Night Bands SIMS



Mean growth rate of day calcite faster and roughly double night calcite

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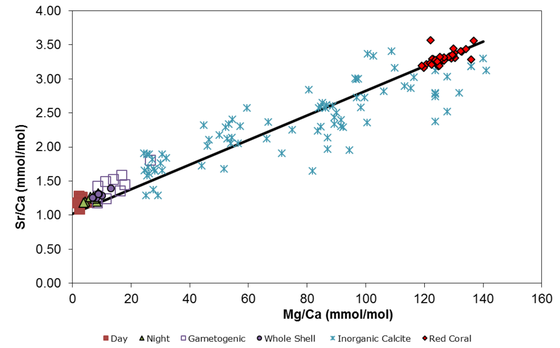
Mineralogical Line: Biomineral and Inorganic High-Mg Calcite Consistently Follows a Single Mg/Ca to Sr/Ca Relationship

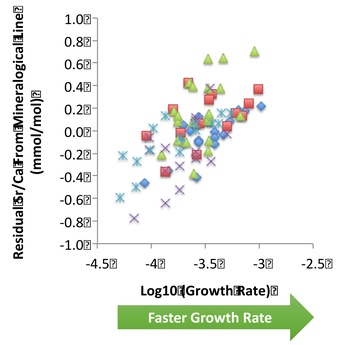


Recognized in biominerals by Carpenter & Lohmann (1992)

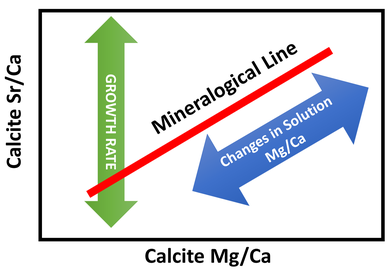
Applied to foraminifera by D. Evans et al. (2015)

Present in Inorganic Calcite (Mucci & Morse, 1983); Foraminifera (Lea et al., 1999); Calcitic corals (Vielzeuf et al., 2008), etc.

Our Reanalysis of Inorganic Data: Additional Kinetic Effect

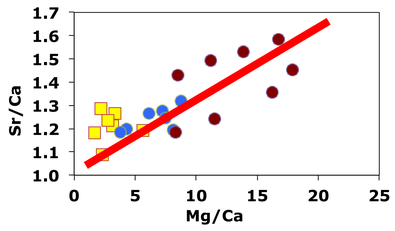


Increasing growth rate moves calcite off mineralogical line to higher Sr/Ca for inorganic calcite (Mucci & Morse, 1983)

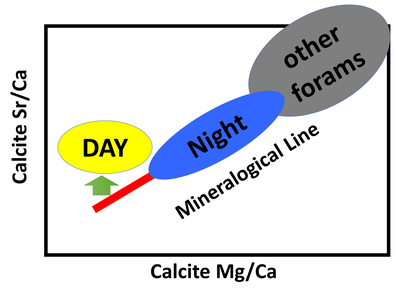


Model explaining combined impact of kinetics and solution composition on calcite grown from seawater solutions

Day Sr/Ca in *O. universa* Consistent with Faster Kinetics and Movement on Mineralogical Line



Patterns in Mg/Ca and Sr/Ca of Day and Night bands determined using mixed spike method on cultured *O. universa* consistent with movement along mineralogical line and kinetics



→ Analysis of cultured forams: T moves along mineralogical line and pH moves off line consistent with kinetic effect.