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

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The Mg/Ca paleotemperature proxy in planktic foraminifera is one of the most widely-used proxies for sea surface temperature. However, this ratio is not constant throughout the test, varying systematically by several fold independent of temperature between faster and slower growing diurnal bands. This phenomenon has yet to be explained mechanistically, however, changing calcification rates may be a contributing factor. Observing the relationship between calcification rate and trace metal incorporation for multiple proxies at the scale of this banding will allow us to better understand the contribution of kinetic effects to heterogeneity. In this study, we examine Me/Ca ratios on a diurnal cycle in Orbulina universa, utilizing a novel approach based on multiple isotopic spikes that allows us to measure Sr/Ca, Li/Ca and Mg/Ca with the precision of isotope dilution while still maintaining the time resolution of microanalytical techniques. Using independently measured growth rates derived from NanoSIMS measurements of diurnal Mg/Ca heterogeneity, we examine the effect of crystal growth rate on foraminiferal Sr/Ca and Li/Ca. We observe that Sr/Ca ratios in foraminifera are ~3% higher during the night than during the day, which initially appears opposite to the expected signal based on growth rate. However, we also observe a positive correlation between Sr and Mg in foraminiferal calcite, which falls on the same mineralogical line as the Sr/Ca and Mg/Ca of other biogenic and inorganic calcites. We attribute offsets in calcite composition from this mineralogical relationship to kinetics. Interpreted within that framework, day Sr/Ca ratios appear more affected by kinetics than night Sr/Ca ratios, which is consistent with observed calcification rates. The difference between any given data point and the mineralogical line can be explained by kinetic processes, and correlates with oceanographic properties in cultured foraminifera, which could help separate temperature from growth rate effects in the paleorecord.