

## $\delta^{44/40}\text{Ca}$ variability in modern shallow water carbonates

C. HOLMDEN<sup>1\*</sup>, D.A. PAPANASTASSIOU<sup>2</sup>,  
P. BLANCHON<sup>3</sup> AND S. EVANS<sup>4</sup>

<sup>1</sup>Saskatchewan Isotope Laboratory, University of Saskatchewan, Saskatoon, Canada S7N-5E2  
(\*correspondence: ceh933@mail.usask.ca)

<sup>2</sup>Science Division, Jet Propulsion Laboratory, M/S 183-335; California Institute of Technology<sup>3</sup>, Pasadena, CA 91109

<sup>3</sup>Instituto de Ciencias del Mar y Limnología, Apartado Postal 1152, Cancún, D.F. Mexico.

<sup>4</sup>Department of Geosciences<sup>5</sup>, Boise State University, 1910 University Drive, Boise, Idaho 83725-1535

Shallow water carbonates from Florida Bay, the Florida Reef Tract and the Mexican Caribbean fringing reef at Punta Maroma were studied to determine the range of Ca isotope variation among the cohort of modern carbonate producers, and to look for local scale Ca cycling effects. The total range of Ca isotope fractionation is 0.4‰ in carbonates from Punta Maroma, yielding a production weighted average  $\delta^{44/40}\text{Ca}$  value -1.12‰. This value compares well with bulk carbonate sediments from the Florida Reef Tract (-1.11‰) and Florida Bay, near a tidal inlet in the Florida Keys (-1.09‰). No evidence was found for the ~0.6‰ fractionation between calcite and aragonite observed in laboratory precipitation experiments.

Isotope fractionation effects are subordinate to local scale Ca cycling effects as a potential source of isotopic variability in shallow water carbonates. This is observed in the innermost restricted region of northeastern Florida Bay, where a 0.7‰ gradient of decreasing  $\delta^{44/40}\text{Ca}$  values in sediments and waters occurs between the coastal zone of Florida Bay and the southern mangrove fringe of the Florida Everglades. The reduction in  $\delta^{44/40}\text{Ca}$  values towards the Everglades in this setting is predominantly due to submarine groundwater discharge (SGD), which is characterized by low  $\delta^{44/40}\text{Ca}$  values, similar to marine limestone, and Ca concentrations that are higher than seawater. Mixing model calculations show that between 9 and 71% of the Ca in coastal waters with salinities ranging between 30 and 14 ppt, respectively, is from SGD and surface water runoff.

By analogy with Florida Bay, restricted circulation with contemporaneous oceans may have led to overprinting of ocean  $\delta^{44/40}\text{Ca}$  signatures in carbonate deposits located in near shore settings of ancient epeiric seas. If this is correct, some of the scatter in the Paleozoic portion of the Ca isotope evolution curve of Phanerozoic oceans, which is, itself, reconstructed from analyses of brachiopods collected from the deposits of epeiric seas, may be due to local Ca cycling effects.

## Diffusive fractionation of transition metals in grain boundaries

V. HOMOLOVA, E.B. WATSON AND J.B. THOMAS

Rensselaer Polytechnic Institute, 110 8<sup>th</sup> Street, Troy, NY USA (\*correspondence: homolv@rpi.edu)

Grain boundaries (GBs) provide one of the most important transport pathways in metamorphic rocks. The equilibration length scale of a particular element may be dependent upon its GB diffusivity, and inter-element differences in these quantities may lead to a diffusive fractionation of elements during metamorphism. The detector particle method is one way to study GB diffusivities and consists of juxtaposing a diffusant source with a pre-synthesized matrix “rock” containing dispersed sink phases. The diffusion profile obtained by measuring diffusant concentrations in the detector (sink) particles will reflect the GB concentration of the diffusant to an extent determined by the volume percent of sink phases ( $\text{vol}\%_{\text{sink}}$ ) and the partitioning behaviour of the diffusant between the grain boundary and the sink phase ( $K_{\text{d}}^{\text{prt/gb}}$ ). To better constrain GB diffusivities, experiments and finite difference modelling were undertaken to elucidate the relationships between  $\text{vol}\%_{\text{sink}}$ ,  $K_{\text{d}}^{\text{prt/gb}}$ , and the characteristic distance (x). Experiments involved juxtaposing a pre-synthesized quartzite matrix containing 1-3.5wt% dispersed enstatite with a source of either chromium-nickel-iron alloy, chromium oxide, or nickel metal containing 2200ppm manganese. Experiments were run in a piston cylinder apparatus at 1250°C and 1GPa for durations of 9.25-92 hours. Post-experiment analyses of the enstatite sink particles for the GB diffusants (Cr, Mn, Ni) were performed with a Cameca SX100 microprobe. In 24 hours, Cr GB diffusion length scales decrease from 0.069 to 0.019cm in experiments containing 1 to 3.5wt% sink particle, respectively, while Mn GB diffusion length scales decrease from 0.108 to 0.027cm. Due to the incompatibility of Ni in the sink particles (relative to Mn), Ni effectively experiences 0  $\text{vol}\%_{\text{sink}}$  at short diffusion distances where Mn concentrations are high. Nonetheless, Ni GB diffusion length scales decrease by ~70% (from 0.94 to 0.26cm) in experiments containing 1 and 3.5wt% sink particles, respectively. GB diffusion length scales of Cr, Mn and Ni all appear to decrease by a factor of ~4 over the range of  $\text{vol}\%_{\text{sink}}$  studied here. These results are in line with finite difference modelling which also predicts a decrease in x with a decrease in spacing of the sink particles (which is equivalent to an increase in  $\text{vol}\%_{\text{sink}}$ ). The models also predict a non-linear, inverse correlation between  $K_{\text{d}}^{\text{prt/gb}}$  and x.