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Origin and significance of Ca isotope gradients in epeiric marine carbonates

CHRIS HOLMDEN[1], SARA R KIMMIG[2] AND MATTHEW D NADEAU[3]

[1]University of Saskatchewan
[2]Karlsruhe Institute of Technology
[3]Princeton University

Presenting Author: chris.holmden@usask.ca

Numerical models have been developed to simulate the effects of fluid- and sediment-buffered diagenesis on Ca isotope compositions of bulk carbonate sediment and other carbonate geochemical parameters. Modeling can reveal snapshots of original carbonate $d^{44}Ca$ values and contemporaneous seawater $d^{44}Ca$ values from altered carbonate sediments. In this talk, we will show that the same information can be extracted from altered carbonate rocks without models if the deposits are sampled laterally in a sequence stratigraphic framework at the platform or basin scale, establishing an alternative approach to paleoenvironmental reconstruction. Ca isotope data for Late Ordovician (Katian Stage) carbonates are presented from the Williston Basin, North America. Here we show that a single lithostratigraphic unit, the burrow mottled 'C' member carbonate of the Red River Formation records individual proximal-to-distal gradients in matrix limestone and burrow dolomite $d^{44}Ca$ values between the center and the edges of the basin. The gradient in the matrix limestone reflects changing fluid- to sediment-buffered diagenetic conditions between the shallow and deep-water carbonate deposits of the basin. Two dolomitizing events formed the gradient in dolomite $d^{44}Ca$ values. The sediment-buffered end of the limestone gradient preserves the $d^{44}Ca$ value of the original calcite carbonate mud (~ –1.28 ±0.10‰). The fluid-buffered end of the gradient records the $d^{44}Ca$ value of contemporaneous seawater (–0.47 ±0.10‰). Despite its diagenetic origin, the magnitude of the limestone gradient conserves the local value of D_{sed} (–0.81 ±0.20), which is consistent with primary calcite precipitation in a 'calcite sea'. Using these data and literature data on Ca isotope compositions in stratigraphically equivalent dolomites from the Great Basin, we build the case for circulation restriction and local Ca cycling in Paleozoic epeiric seas, with seawater in the submerged regions of the continents up to 0.4‰ higher than the contemporaneous oceans.