# Evaluating the leverage to alter seawater chemistry: The effects of diagenesis and dolomitization on Ca and Mg isotopes in shallow marine carbonates

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Metal isotopes have potential as geochemical proxies to reveal fundamental aspects of the Earth system over a range of time scales. Development of these novel tools in carbonates requires a firm understanding of isotopic effects associated with precipitation and diagenesis. To this end, the current study reports the measured Ca, Mg, O, and C isotopic and elemental compositions of an alternating sequence of shallow water marine limestones and dolostones from Ocean Drilling Project Leg 194, Site 1196 on the Southern Marion Platform (21˚0.371'S, 152˚51.512'E; 304 m water depth).

The Ca isotopic composition ($\delta^{44}$Ca, SRM-915a) of limestones and dolostones from 1196A range from 0.6–1.3‰ (*n*=12), exhibiting no significant correlations with lithology, depth, or age. Magnesium isotopic compositions ($\delta^{26}$Mg, DSM-3) of limestones (-3.6±0.25‰) are distinct compared to dolostones (-2.7±0.1‰). The average limestone $\delta^{13}$C (1.96±0.31‰, PDB) is slightly higher than that of dolostones (1.68±0.57‰), while the limestone (-1.22±0.94‰, PDB) and dolostone (2.72±1.07‰) $\delta^{18}$O values are distinctly different. Finally, the molar ratios of Sr and Na to (Mg+Ca) are measureably different in limestones (1.7 and 10.8 mmol:mol, respectively) and dolostones (0.2 and 2.9 mmol:mol). Both the limestones and dolostones form coherent trends in isotope-isotope space that are interpreted as diagenetic trends.

From a global cycling perspective, the $\delta^{44}$Ca of shallow water carbonates are significantly higher than the mean carbonate measured to date (~0.6‰), bulk nannofossil ooze, and modern coral. This suggests there is some leverage for altering seawater isotopic composition by varying the $\delta^{44}$Ca of the output flux. Interestingly, diagenesis appears to enhance the leverage for $\delta^{44}$Ca, an effect that is likely most significant in open systems. Dolostone $\delta^{26}$Mg suggests a fractionation factor of ~2‰ associated with dolomitization, broadly consistent with estimates of Mg isotope fractionation factors from deep-sea pore fluid profiles. Non-steady state removal of dolomite should, therefore, drive seawater $\delta^{26}$Mg to higher values.