

What can Ca and Mg isotopes in formation brines tell us about the depositional and diagenetic history of buried marine carbonates?

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Proximal-distal gradients in sedimentary $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values have been reported in a sequence of Late Ordovician burrow-mottled carbonates in the Williston Basin, an intracratonic epeiric marine basin in North America. The dolomite gradient is interpreted to reflect two superimposed dolomitization events: (1) brine reflux dolomitization during early diagenesis, and (2) thermal circulation of deep fluids during burial diagenesis. These hot burial fluids are interpreted to have passed upwards through the network of burrows, partially re-dolomitizing the early diagenetic dolomite in the direction of ascending fluid flow.

The studied carbonates have remained buried since deposition. Brines collected from the deepest carbonates have geochemical signatures of evaporatively concentrated seawater, which raises the question, are these remnants of the fluid that ascended and re-dolomitized the burrows? To address this, we measured brine $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values to determine whether isotopic equilibrium or disequilibrium exists between the brines and the dolomite aquifer material.

Brines from four production wells near to, or in the same wells sampled for dolomite, were collected and measured. Brine $\delta^{26}\text{Mg}$ values were compared to dolomite $\delta^{26}\text{Mg}$ values, yielding $\Delta^{26}\text{Mg}_{\text{dol-brine}} = -1.05 \pm 0.13\text{‰}$. Brine and dolomite $\delta^{44}\text{Ca}$ values were also compared, yielding $\Delta^{44}\text{Ca}_{\text{dol-brine}} = -0.44 \pm 0.08\text{‰}$. The value of $\Delta^{44}\text{Ca}_{\text{dol-brine}}$ matches a previously proposed field estimate equilibrium Ca isotope fractionation factor for dolomite of $-0.41 \pm 0.17\text{‰}$ [1], indicating that brine and dolomite are in Ca isotope equilibrium in the studied carbonate aquifer. Substituting the value of $\Delta^{26}\text{Mg}_{\text{dol-brine}}$ into the dolomite paleotemperature equation yields 114°C. This is slightly cooler than formation waters in the basin today at these depths (~142°C) but agree with the warmer temperatures deduced from clumped isotope analyses of the dolomites ($92 \pm 9^\circ\text{C}$) [2]. These data suggest that present-day Red River brines may be remnants of the ascending fluids that re-dolomitized the early diagenetic dolomite.

[1] Holmden, Kimmig & Nadeau (2024) *GCA* 151–168.

[2] Kimmig, Nadeau & Holmden (2021) *GCA* 198–225.