

The influence of diagenesis and mineralogy on Ca isotopes in Lower-Upper Triassic carbonate rocks

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The calcium cycle is linked to the carbon cycle through the weathering and burial of carbonate rocks. As a result, calcium isotope ratios ($^{44}\text{Ca}/^{40}\text{Ca}$, or $\delta^{44/40}\text{Ca}$) can help to constrain ancient carbon cycle dynamics if Ca cycle behavior can be reconstructed. However, $\delta^{44/40}\text{Ca}$ of carbonate rocks is influenced not only by seawater but also by fractionation associated with CaCO_3 precipitation and by diagenesis. We investigate the controls on carbonate $\delta^{44/40}\text{Ca}$ in Upper Permian to Upper Triassic limestones (~253 to 235 Ma) from south China and Turkey. Parallel negative $\delta^{13}\text{C}$ and $\delta^{44/40}\text{Ca}$ excursions were previously identified at the end-Permian extinction horizon. We find a second negative excursion of ~0.2‰ in both south China and Turkey within Lower Triassic strata. However, this excursion is not synchronous and $\delta^{44/40}\text{Ca}$ values are different between the two sections. The excursion cannot be interpreted as secular change in the $\delta^{44/40}\text{Ca}$ of global seawater. The [Sr] and $\delta^{44/40}\text{Ca}$ data are best described statistically by a log-linear correlation that exists also in many previously published datasets. Using a model of early marine diagenetic water-rock interaction, we illustrate that this correlation can be explained by the chemical evolution of carbonate sediment samples with a range of initial calcite-to-aragonite ratios. Although these factors strongly influence carbonate $\delta^{44/40}\text{Ca}$ values, it may still be possible to infer changes in seawater $\delta^{44/40}\text{Ca}$ from carbonate rocks after controlling for recrystallization effects.