Isotopic tracers for CO_2 produced during a planetary impact into limestone target rocks

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Terrestrial meteorite impacts have been directly linked with mass extinction events throughout Earth's history. Among these impacts, those landing in sedimentary target rocks are thought to generate large quantities of CO_2 via decarbonation. This injection of CO_2 into the atmosphere has the potential to alter the climate and threaten terrestrial habitability. The magnitude of this change depends upon the net amount of CO_2 released, which is controlled by how much CO_2 is produced by the impact, how much CO_2 is removed by back-reactions after the impact, and other post-impact CO_2 sinks. To interrogate the behavior of CO_2 release into the impact atmosphere, we present carbon ($\delta^{13}C$), oxygen ($\delta^{18}O$), and clumped (Δ_{47}) isotope results from carbonate clasts preserved within the impact breccia of the Steen River Impact Structure (SRIS) in Alberta, Canada. These clasts exhibit a ~65‰ range in $\delta^{13}C$ and a ~5‰ variation in $\delta^{18}O$. However, while $\delta^{13}C$ and $\delta^{18}O$ are positively correlated, Δ_{47} unexpectedly has a negative relationship with $\delta^{13}C$ and $\delta^{18}O$. Based on prior assumptions, there would either be (1) no relationship with carbonate Δ_{47} and the bulk ratios because Δ_{47} would be reset at extreme impact temperatures, or (2) a positive correlation with Δ_{47} and the bulk ratios, reflecting gradual Δ_{47} 'resetting.' To reconcile the SRIS results with these expectations, we conducted a series of *in vacuo* heating experiments at temperatures above calcite decomposition. As predicted by Rayleigh fractionation, these heating experiments generated depletions in $\delta^{13}C$ and $\delta^{18}O$ that increased with reaction time. Mimicking the SRIS results, these experiments also produced concomitant increases in Δ_{47}. Adapting a mechanistic model for decomposition fractionation [1], we hypothesize that these exotic isotope trends are caused by Rayleigh fractionation and a Δ_{47} kinetic isotope effect that results from the disproportionation of O to CaO and CO_2 during thermal decomposition. This high Δ_{47} CO_2 subsequently exchanges with the residual $CaCO_3$. This work highlights a potential pathway for identifying and quantifying CO_2 generation by impacts and builds on the relatively limited literature characterizing the behavior of carbonate clumped isotopes at very high geologic temperatures.

[1] Hayles & Killingsworth (2022), *Chem. Geo.* 589, 120646.