Isotopic tracers for CO₂ produced during a planetary impact into limestone target rocks

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Terrestrial meteorite impacts have been directly linked with multiple mass extinction events throughout Earth’s history. Among these impacts, those that land in sedimentary target rocks are thought to generate large quantities of CO₂ via decarbonation. This injection of CO₂ 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 CO₂ released, which is controlled by how much CO₂ is produced by the impact, how much CO₂ is removed by back-reactions after the impact, and other post-impact CO₂ sinks. To interrogate the behavior of CO₂ release into the impact atmosphere, we present carbon (δ²³C), oxygen (δ¹⁸O), and clumped (Δ⁴⁷) 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 δ¹³C and a ~5‰ variation in δ¹⁸O. However, while δ¹³C and δ¹⁸O are positively correlated, Δ⁴⁷ unexpectedly has a negative relationship with δ¹³C and δ¹⁸O. Based on prior assumptions, there would either be (1) no relationship with carbonate Δ⁴⁷ and the bulk ratios because Δ⁴⁷ would be reset at extreme impact temperatures, or (2) Δ⁴⁷ would have a positive correlation with the bulk ratios, reflecting gradual Δ⁴⁷ ‘resetting.’ To reconcile the SRIS result 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 δ¹³C and δ¹⁸O that increased with reaction time. Mimicking the SRIS results, these experiments also produced concomitant increases in Δ⁴⁷. Using an adaptation of a mechanistic model for decomposition fractionation (Hayles & Killingsworth, 2022) we hypothesize that these exotic isotope trends are caused by Rayleigh fractionation and a Δ⁴⁷ kinetic isotope effect that results from the disproportionation of O to CaO and CO₂ during thermal decomposition. This high Δ⁴⁷ CO₂ subsequently exchanges with the residual CaCO₃. This work highlights a potential pathway for identifying and quantifying CO₂ generation by impacts and builds on the relatively limited literature characterizing the behavior of carbonate clumped isotopes at very high geologic temperatures.