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Hot atmospheric formation of carbonate accretionary lapilli at the Cretaceous-Paleogene boundary, Brazos River, Texas, from clumped isotope thermometry

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ABSTRACT

The Chicxulub impact (in the northern Yucatan Penninsula, Mexico) marks the Cretaceous-Paleogene (K-Pg) boundary and is implicated in one of the five major extinctions. Researchers have examined ejecta from the Chicxulub impact, and most recently a drill core from the crater itself, yet the processes and chemical reactions occurring in the impact vapor plume are poorly constrained. Rounded carbonate particles, identified as accretionary lapilli, have been found thousands of kilometers from the impact crater and may be a unique record of plume conditions. We present carbon ($\delta^{13}C$), oxygen ($\delta^{18}O$), and clumped (Δ_{47}) isotope ratios of lapilli from the Brazos River, Texas (USA), as well as from foraminifera and a mudstone. Unaltered lapilli $\delta^{13}C$ and $\delta^{18}O$ values covary, ranging from –9.38‰ to –2.10‰ and from –7.72‰ to –5.36‰, respectively, and they are distinct from mudstones, foraminifera, and secondarily altered lapilli in the same section. Clumped isotope temperatures [$T(\Delta_{47})$] from the lapilli range from 66 °C to 539 °C and average 155 ± 46 °C (1 standard deviation), with sedimentary and fossil carbonates recording clement, shallow ocean–like $T(\Delta_{47})$. These data are consistent with petrography and hypothesized vapor plume formation, and we argue that the $\delta^{13}C$ and $\delta^{18}O$ values result from target rock decarbonation. Atmospheric temperatures >100 °C extending >1800 km from the Chicxulub crater imply an uninhabitable zone within seconds to minutes of the impact that was 10× larger in diameter than the crater itself.

INTRODUCTION

Bolide impacts induce global-scale changes resulting in mass extinctions and other geologic catastrophes (Simonson and Glass, 2004). They rapidly introduce massive amounts of kinetic energy upon impact, the dissipation of which causes target rock devolatilization (Hörz et al., 2015), vaporization of marine and lithospheric material (Pope et al., 1997), and the formation of exotic phases and features, such as planar deformation features and tektites (e.g., Blum and Chamberlain, 1992; Schulte et al., 2010). When bolides hit sedimentary rocks, as was the case for the Chicxulub crater in present-day Yucatan, Mexico, excavated debris can contain tektites, aerosols, and lapilli that form between the time of the impact and their sedimentary deposition (Pope et al., 1999; Yancey and Guillemette, 2008). These new materials may record the conditions in the impact aftermath.

Proximal deposits from Chicxulub contain spinel spherules that often co-occur in layers with anomalous Ir concentrations (Schulte et al., 2010) and, at some localities, layers rich in accretionary lapilli. These lapilli are aggregates of carbonate and minor silicic glass hypothesized to have formed in the impact plume (Pope et al., 1999; Simonson and Glass, 2004; Yancey and Guillemette, 2008). Carbonate lapilli have been identified in Cretaceous-Paleogene (K-Pg) boundary sediments in Mexico, Belize, Texas, and the northwest Atlantic Ocean (Pope et al., 1999; Yancey and Guillemette, 2008; Schulte et al., 2009), implying formation and transport up to thousands of kilometers from the impact. Based on experiments by Agrinier et al. (2001) and the widespread distribution of micritic carbonate at the K-Pg boundary (Bralower et al., 2020), these lapilli formed via decomposition of carbonate-rich target rocks and back-reaction as

$$\begin{aligned} CaCO_3 &\rightarrow CaO[\text{or } Ca(OH)_2] + CO_2 \\ &\rightarrow CaCO_3(\text{or} + H_2O). \end{aligned} \quad (1)$$

Given the possible reaction between decomposition products and the vapor plume or end-Cretaceous atmosphere, $\delta^{13}C$ and $\delta^{18}O$ values of carbonate lapilli may constrain carbon sources and atmospheric conditions after the impact. Carbonate clumped isotope thermometry may also reveal lapilli formation temperatures or postdepositional alteration.

Clumped isotopes refer to the abundance of ^{13}C-^{18}O bonds in carbonates. At lower temperatures, there is a thermodynamic preference for these heavy isotope bonds, the abundance of which is denoted by Δ_{47} (Eiler, 2007). The equilibrium temperature dependence of Δ_{47} [$T(\Delta_{47})$] has been calibrated across a wide range of temperatures (e.g., Petersen et al., 2019). However, at high temperatures, such as those encountered during impacts, this may be complicated by diffusive exchange of neighboring oxygens that can reset Δ_{47} values (Dennis and Schrag, 2010; Passey and Henkes, 2012; Stolper and Eiler, 2015; Hemingway and Henkes, 2021). Some geologic scenarios have a cooling rate that is faster than the rate of internal carbonate oxygen exchange, producing $T(\Delta_{47})$ between the peak temperature and the final ambient rock temperature. This is conceptually similar to thermochronometric closure temperatures and is relevant given the extreme heating and fast cooling following impacts. Based on model-derived rates of clumped isotope bond

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reordering lapilli formed during the impact with peak temperatures >1000 °C and rapid cooling, would yield $\Delta_{47} = 0.191‰$ (Hemingway and Henkes, 2021), representing a disordered distribution of carbonate ^{13}C and ^{18}O.

In this framework, we interpret new $\delta^{13}C$, $\delta^{18}O$, and Δ_{47} values from carbonate accretionary lapilli in basal Paleocene Kincaid Formation sediments exposed along the Brazos River, Texas (Figs. S1–S5 in the Supplemental Material[1]). The petrography of these millimeter-scale lapilli indicates very little postdepositional diagenesis, consistent with our isotope results (Fig. S6; Yancey and Guillemette, 2008). The lapilli results are complemented by isotope measurements of a Kincaid Formation mudstone and foraminifera. We hypothesize that our data are consistent with extremely warm atmospheric temperatures (>150 °C) within the vapor plume that extended thousands of kilometers from the Yucatan Peninsula. This temperature informs models of the ejecta curtain (e.g., Artemieva and Morgan, 2020) and extends the radius at which life and the hydrologic cycle would have been directly affected by the impact.

METHODS

We focused on carbonate lapilli, foraminifera, and mudstones collected from outcrops of the K-Pg boundary complex (Figs. S1–S5; Yancey, 1996; Yancey and Guillemette, 2008). Lapilli and foraminifera samples were grouped into similar size fractions for analysis (Table S1). The samples were powdered by pestle in capsules used for carbonate acid digestion. Isotope measurements were performed from 2013 to 2020 at Johns Hopkins University (JHU, Maryland), Harvard University (HU, Massachusetts), and Stony Brook University (SBU, New York). In all cases, carbonate sample powder was reacted with >104% phosphoric acid at 90 °C on custom cryogenic gas-purification systems. Devices at JHU and SBU were functionally identical; the device at HU was described by Petersen and Schrag (2014). At JHU and SBU, the evolved CO_2 was purified using cryogenic separation via a −80 °C water trap and liquid nitrogen as well as a Porapak™ He-carrier gas chromatography column (Henkes et al., 2013). Once purified, the CO_2 was analyzed on a Thermo MAT 253 mass spectrometer. The Δ_{47} values were calculated using the intensity ratios of isotopologue masses 44–49 in the sample to a reference gas. Instrumental effects on Δ_{47} were accounted for by analyzing carbonate standards and CO_2 gas equilibrated at 30 °C and 1000 °C (Dennis et al., 2011). Carbonate standard isotope values are reported in Table S2. The Δ_{47} values were calculated using equilibrated gases according to the scheme of Dennis et al. (2011) and International Union of Pure and Applied Chemistry (IUPAC) ^{13}R, ^{18}R, and ^{17}R assignments for Vienna Peedee belemnite (VPDB) and Vienna standard mean ocean water (VSMOW; Brand et al., 2010). $T(\Delta_{47})$ was calculated using equation 1 of Petersen et al. (2019), adjusted for acid fractionation temperature, as it covers a range of temperatures and uses the IUPAC correction scheme.

RESULTS

All isotope ratios are given in Table S1. Lapilli diameters range from 0.71 to 2.10 mm, and there was no relationship between lapilli size and their isotope values (Fig. S6). Given their small size, it was impossible to replicate measurements of individual samples. Instead, we measured many lapilli and focused most of our interpretations on the distribution of data. The $\delta^{13}C$ and $\delta^{18}O$ values of the lapilli ranged from −9.38‰ to −2.10‰ VPDB and from −7.72‰ to −5.36‰ VPDB, respectively. Both isotope ratios were much lower than typical end-Cretaceous limestones ($\delta^{13}C >> 1.5‰$ and $\delta^{18}O >> -2.5‰$; Veizer and Hoefs, 1976), implying a distinct, nonmarine origin (Fig. 1). Unaltered lapilli Δ_{47} ranged from 0.228‰ to 0.503‰ (Carbon Dioxide Equilibrium Scale at 90 °C [CDES90]), which correspond to temperatures from 66 °C to 539 °C, with a mean of 0.394‰ ± 0.058‰ (1 SD), equivalent to 155 ± 46 °C. Despite no relationship between $\delta^{13}C$ and $T(\Delta_{47})$ (Fig. 2A), some of the lapilli with higher $\delta^{13}C$ (>–4‰) had $T(\Delta_{47})$ >100 °C (Fig. 1). Invariant lapilli $\delta^{18}O$ values relative to $T(\Delta_{47})$, when compared with equilibrium lines of differing water $\delta^{18}O$, also indicated no secondary lapilli alteration (Fig. 2B). However, we suspect secondary alteration of RB-4a-SCBbed-3 lapilli, which appear to plot along a mixing line between average, unaltered lapilli isotope values and those for the Kincaid Formation mudstone (Fig. 1). This can also be seen in Figure 2B, where the RB-4a-SCBbed-3 lapilli plot along a line that connects the mudstone with the invariable lapilli $\delta^{18}O$ data.

Coexisting benthic foraminifera, *Lenticulina navarroensis*, appeared to retain primary shell morphology and have no visible signs of alteration (e.g., opacity, overgrowths, or dissolution). Their $\delta^{18}O$ values, −1.68‰ to −1.27‰, overlap with other *Lenticulina* spp. from the Brazos River section, and their $\delta^{13}C$ values, −0.09‰ to 0.29‰, are identical to a foraminifera average of 0‰ (Keller et al., 2009). Average $T(\Delta_{47})$ from single foraminifera measurements on larger-diameter (~>2 mm) tests at HU (Petersen and Schrag, 2014) were 17 ± 4 °C and 24 ± 2 °C,

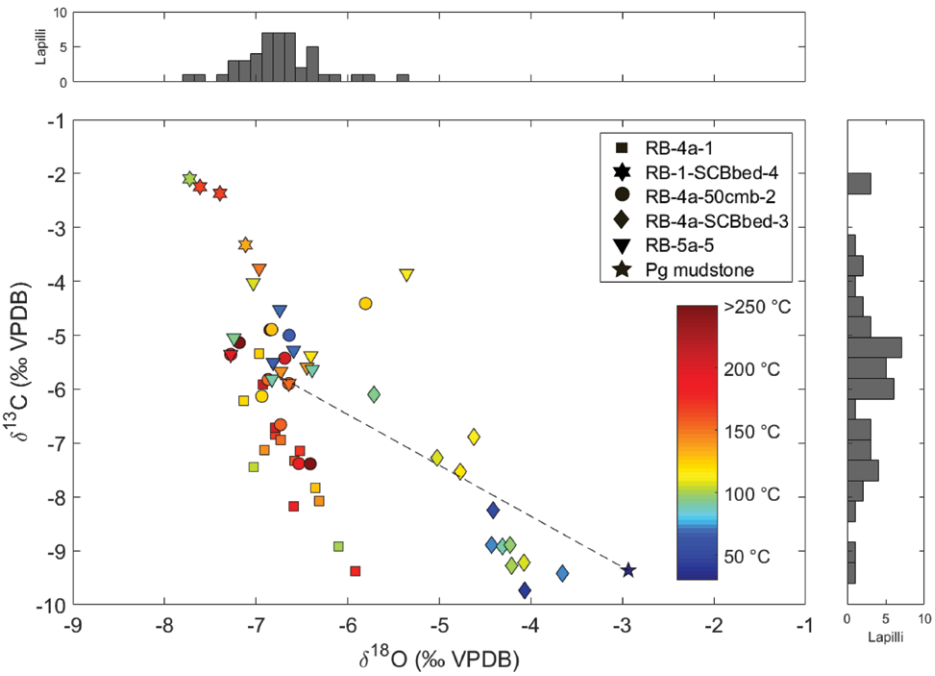

Figure 1. $\delta^{13}C$ and $\delta^{18}O$ values of carbonate lapilli from the Cretaceous-Paleogene (K-Pg) boundary at the Brazos River, Texas, USA. Symbols indicate different sections (e.g., RB-4) from Yancey (1996) and specific lithologies (e.g., "SCB" or spherulitic conglomerate bed). Symbol color indicates clumped isotope temperature, $T(\Delta_{47})$ (Table S1 [see footnote 1]). Temperatures >200 °C or <30 °C are deepest shades of red and blue, respectively. Dashed line indicates diagenesis of RB-4a-SCBbed-3 with average unaltered lapilli and mudstone as end-member isotope ratios. These data were not used in interpretations of lapilli formation. Axial histograms are for unaltered lapilli data only. VPDB—Vienna Peedee belemnite.

[1]Supplemental Material. The Rayleigh model methodology, Figures S1–S6, and Tables S1 and S2. Please visit https://doi.org/10.1130/GEOL.S.19175879 to access the supplemental material, and contact editing@geosociety.org with any questions.

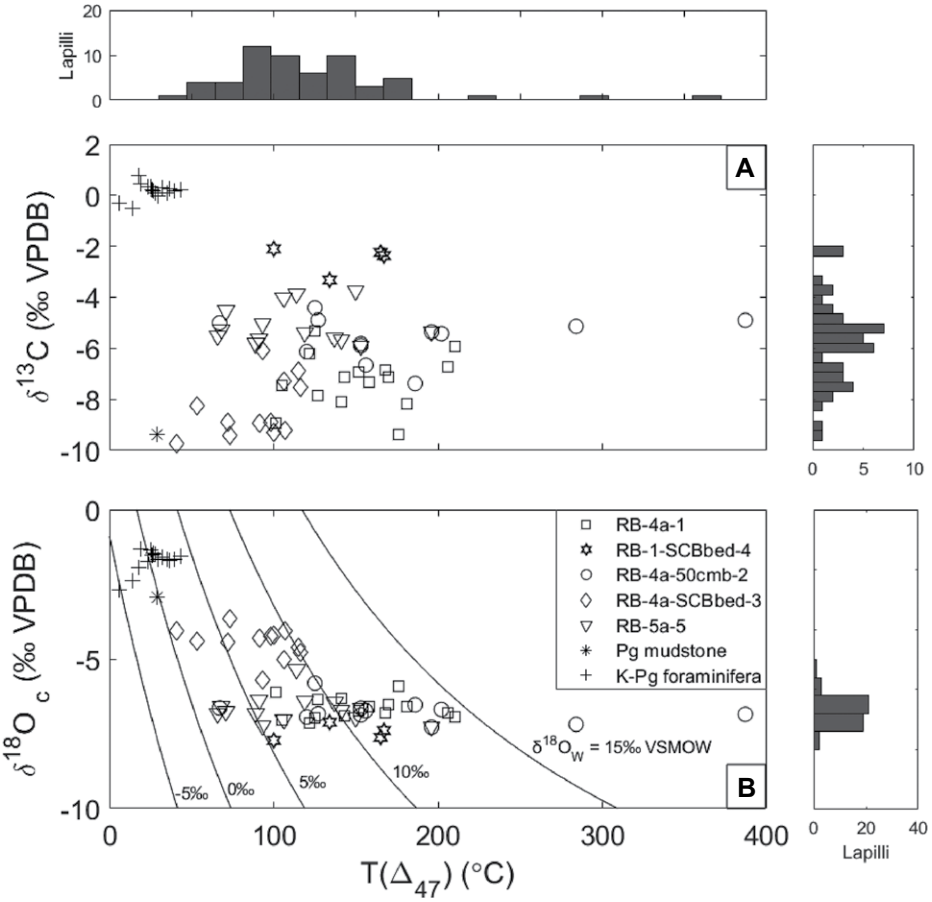

Figure 2. $\delta^{13}C$, $\delta^{18}O$, and clumped isotope temperature, $T(\Delta_{47})$, from lapilli, Kincaid Formation mudstone, and foraminifera from the Cretaceous-Paleogene (K-Pg) boundary, Brazos River, Texas, USA. (A) There is no correlation ($r^2 = 0.22$) between $T(\Delta_{47})$ and $\delta^{13}C$. (B) Solid lines are constant $\delta^{18}O$ of possible diagenetic fluids based on the carbonate-water equilibrium relationship of O'Neil et al. (1969). Data plotting along these curves would indicate alteration via secondary processes, as RB-4a-SCBbed-3 data demonstrate. VPDB—Vienna Peedee belemnite; VSMOW—Vienna standard mean ocean water.

which we consider to represent the latest Cretaceous shallow seawater temperatures. Smaller tests (<1 mm) analyzed at SBU were considerably warmer, possibly altered, and overlapped with mudstone $T(\Delta_{47})$.

DISCUSSION

Our isotope results are consistent with the conclusions of Yancey and Guillemette (2008), who interpreted that Brazos River carbonate accretionary lapilli formed in the vapor plume or ejecta cloud. This formation model suggests that the Chicxulub impactor devolatilized an ~3-km-thick succession of limestones and evaporites that overlaid a metamorphic basement (Hildebrand et al., 1991), producing an estimated 350–3500 Gt of CO_2 (Pierazzo et al., 1998). The decarbonization products back-reacted as shown in Equation 1, a mechanism which has been hypothesized for other impacts (Martinez et al., 1994; Hörz et al., 2015). Yancey and Guillemette (2008) identified the decarbonation-recarbonation mechanism by observing a uniform size (1–4 μm) in the lapilli nucleation points. Lapilli $T(\Delta_{47}) >> 150$ °C further support a hot plume origin, but we must consider alternative hypotheses given their enigmatic nature.

One hypothesis for their formation is they are pedogenic features. However, the bounding Kincaid Formation sandstones and conglomerates contain fining-upward and hummocky, cross-stratified bed forms inconsistent with pedogenesis (Figs. S2–S5; Yancey, 1996). High temperatures are conceivable if the carbonates were derived from diagenetic alteration of silicic glass during deep sedimentary burial, but distinct contacts between silicates and carbonates rule out carbonate replacement of silicic glass (Fig. S6; Yancey and Guillemette, 2008). Additionally, diagenesis could change the lapilli $\delta^{18}O$ by oxygen exchange with pore water. Except for RB-4a-SCBbed-3, in which partial alteration seems to have taken place alongside mudstone cementation (Fig. 1), lapilli have relatively uniform $\delta^{18}O$ values that do not covary with $T(\Delta_{47})$ (Fig. 2B). Such covariation is a feature of early marine carbonate diagenesis (Ryb and Eiler, 2018), and its absence strengthens our interpretation that the $T(\Delta_{47})$ values of four of five Brazos River samples are unrelated to their depositional environment. Finally, we cannot exclude the possibility that organic matter oxidation contributed to the lapilli isotopic values. However, based on $\delta^{13}C$ mass balance between marine limestones (~0‰) and sedimentary organic material (~–20‰), the amount of organic oxidation that would be required to achieve the lapilli $\delta^{13}C$ values far exceeds the organic content of Chicxulub target rocks. Measured $\delta^{13}C$ values of −9‰ to −8‰ would require >40% of lapilli carbon to be organic. Ambient ancient atmospheric CO_2 is understood to have had a steady-state $\delta^{13}C$ similar to the lapilli; however, by mass balance, we find it difficult to envision a role for pre-impact CO_2 at atmospheric mixing ratios of 350–500 ppm in the impact vapor plume with possibly thousands of gigatons of additional carbon (Beerling et al., 2002).

Having addressed these alternatives, we can evaluate decarbonation and back-reaction as a lapilli formation mechanism (Yancey and Guillemette, 2008; Bralower et al., 2020). Target rock decarbonation is a compelling driver for the isotope trends (Figs. 1 and 2) because it would convert two thirds of the oxygen to CO_2. We take the apparent covariance between unaltered lapilli $\delta^{13}C$ and $\delta^{18}O$, which does not seem to depend on $T(\Delta_{47})$, as evidence for this process (Fig. 1). There are no obvious end members with high $\delta^{13}C$ and low $\delta^{18}O$, and vice versa, that could relate to mixing, and carbonation kinetic isotope effects are poorly known at elevated temperatures (Fléhoc et al., 2006). Instead, we posit that Rayleigh distillation of ^{13}C and ^{18}O from the Chicxulub carbonates sufficiently explains the observed trends.

The evolution of $\delta^{13}C$ and $\delta^{18}O$ during decarbonation can be modeled assuming Rayleigh fractionation:

$$\delta_f - \delta_i = 1000[F^{(\alpha CO_2-carb^{-1})} - 1], \qquad (2)$$

where δ_f and δ_i are the final and initial carbonate isotope values, respectively, $\alpha_{CO2\text{-}carb}$ is the temperature-dependent fractionation between CO_2 and calcite, and F is the mole fraction of carbon (F_C) or oxygen (F_O) that remains (Baumgartner and Valley, 2001). We assume a constant offset between the target rock δ value and resulting CO_2 (Scheele and Hoefs, 1992; Rosenbaum, 1994; model described in section S1 of the Supplemental Material). Carbon loss by decarbonation can yield $F_C = 0$ when all C in the initial carbonate is converted to CO_2. Oxygen loss, however, is typically limited to $F_O = 0.33$ by stoichiometry with residual CaO. $F_O < 0.33$ would require isotopic disequilibrium between the carbonates and other associated O-bearing materials. Low F_O values are improbable in most geologic settings, but not inconceivable during impact heating.

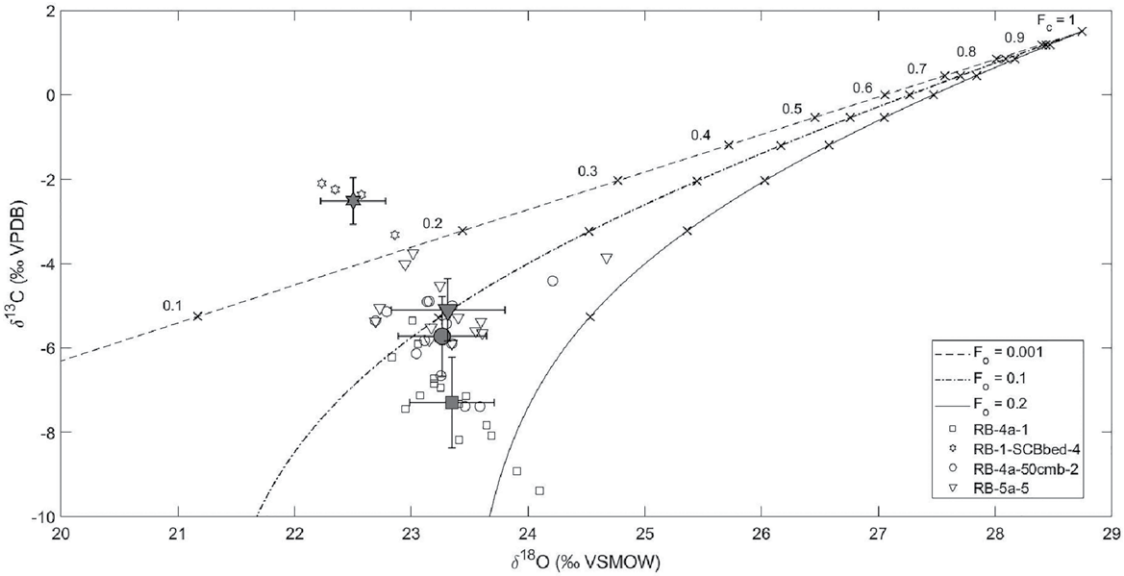

Figure 3. Lapilli δ^{13}C and δ^{18}O plotted with three Rayleigh trends (Equation 2) that represent fractionation during impact decarbonation. Average values for lapilli are plotted in light gray. Error bars are 1σ standard deviation. Extent of the reaction (f_C) is plotted along each Rayleigh curve to show the extent of decarbonation from Equation 1. F_O—mole fraction of oxygen; VPDB—Vienna Peedee belemnite; VSMOW—Vienna standard mean ocean water.

In Figure 3, we show solutions for δ^{13}C and δ^{18}O values for Equation 2 starting from a Late Cretaceous shelf carbonate with $\delta^{13}C = 1.5‰$ and $\delta^{18}O = -1.5‰$ (Fouke et al., 2002). The Rayleigh curves show that δ^{13}C and δ^{18}O pathways are dependent on F_O. These curves do not exactly predict the covariance in δ^{13}C and δ^{18}O, but it is possible that this is due to C or O isotope variation in the source rock or the modeled reaction extent. Average lapilli values are consistent with F_C of ~0.1–0.15. Such low F_C values suggest that impact decarbonation was perhaps not complete (i.e., inferred $F_C \neq 0$), involved multiple C and O sources even if dominated by limestone-derived CO_2, or may have not yielded volatiles in the manner assumed by existing models (Pierazzo et al., 1998). In this way, molecular and isotope studies of impact products, such as lapilli and aromatic hydrocarbons (Lyons et al., 2020), help to refine budgets of climate-impacting materials from the Chicxulub impact and other similar events.

The combination of isotope thermometry with prior petrographic analysis provides an opportunity to evaluate existing models for the Chicxulub vapor plume. Ejecta speed estimates from Artemieva and Morgan (2020) conservatively suggest that lapilli $T(\Delta_{47})$ values reflect atmospheric conditions within 30 min of impact. While we hypothesize that ~150 °C is a reasonable accretionary lapilli formation temperature within the plume (Equation 1), it is possible that lapilli $T(\Delta_{47})$ alternatively reflect heating from atmospheric reentry. Lapilli heating upon reentry, however, would be sufficient to activate clumped isotope bond reordering, resetting $T(\Delta_{47})$ to >>150 °C. Instead, our interpretation is the following: as the plume expanded thousands of kilometers from the crater, so too did these lethal air temperatures. A direct comparison with modeled temperatures from Artemieva and Morgan (2020) demonstrates the possible ubiquity of elevated air temperatures at Earth's surface, though this depends on the timing and altitude of lapilli formation. If the lapilli formed within 10 min of impact, then these hot conditions could have extended hundreds of kilometers into the atmosphere and across Earth's surface. This thermal pulse would have stressed regional terrestrial flora and fauna and likely spawned massive wildfires, further adding to the total impact CO_2 emissions (Beerling et al., 2002; Lyons et al., 2020).

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