

CARBONATE CLUMPED ISOTOPE THERMOMETRY:
APPLICATION TO CARBONACEOUS CHONDRITES
&
EFFECTS OF KINETIC ISOTOPE FRACTIONATION

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ABSTRACT

‘Clumped isotope’ thermometry of carbonates in the carbonaceous chondrites (CM, CI, CR and Tagish Lake) demonstrates that aqueous alteration of their parent bodies occurred from -31 to 71°C and involved reaction with fluids having $\delta^{18}\text{O}_{\text{VSMOW}}$ values of -29.7‰ to 11.8‰ and $\delta^{17}\text{O}_{\text{VSMOW}}$ of -14.9‰ to 7.6‰. Estimated carbonate formation temperatures decrease in the order: calcite > dolomite > breunnerite. Based on independent constraints on the ages of these carbonates and models of the evolution of the oxygen isotope compositions of parent body waters, I estimate that carbonate precipitation during aqueous alteration of the carbonaceous chondrite parent bodies started within 1-2 million years after the accretion of those parent bodies, and that the alteration temperatures decreased from 34°C to 18°C in the first ~4 million years and further to -20°C after a total of ~6.5 million years. Our results provide the first direct measurements of the low-temperature cooling histories of C1 and C2 carbonaceous chondrite parent bodies. Within the CM chondrite group itself, I observe a negative correlation between the $\delta^{13}\text{C}$ values of CM carbonates and the $\delta^{18}\text{O}$ of their formation waters, suggesting formation and escape of ^{13}C -depleted CH_4 during aqueous alteration on the CM chondrite parent bodies.

I apply ab initio transition state and statistical thermodynamics theory to study the kinetic isotope fractionations of clumped isotopologues (i.e., multiply-substituted isotopologues; I also consider singly-substituted isotopologues) associated with phosphoric acid digestion of carbonate minerals and with the degassing of CO_2 from aqueous solutions. Assuming that H_2CO_3 is the reaction intermediate during phosphoric acid digestion of carbonate minerals, I predict at 25°C that CO_2 derived from acid

digestion of carbonate minerals will be 10.72‰ and 0.220‰ higher, respectively, in $^{18}\text{O}/^{16}\text{O}$ ratios and $^{13}\text{C}-^{18}\text{O}$ clumped isotope anomaly than the reactant carbonate. These predicted kinetic isotope fractionations associated with phosphoric acid digestion and their temperature dependences (for both oxygen isotope and clumped isotopologues) compare favorably with independent experimental constraints for phosphoric acid digestion of calcite. I evaluate the effect of carbonate cation compositions on phosphoric acid digestion fractionations using cluster models in which disproportionating H_2CO_3 interacts with adjacent cations. These cluster models underestimate the magnitude of isotope fractionations, but do successfully reproduce the general trend of variations and temperature dependences of oxygen isotope acid digestion fractionations among different carbonate minerals (suggesting I have correctly identified the basic mechanism responsible for a dependence on cation chemistry, but not the exact structural model for cation— H_2CO_3 clusters). I further integrate our acid digestion fractionation model with previous theoretical evaluations of abundances of $^{13}\text{C}-^{18}\text{O}$ bonds in carbonate minerals, and predict the relationship between Δ_{47} values for CO_2 extracted from carbonate minerals and the growth temperatures of those carbonates, including witherite, calcite, aragonite, dolomite and magnesite. I observe reasonable agreement between these predictions and available experimental determinations (e.g., difference of less than 0.05‰ over 0–50°C, for calcite).

Kinetic isotope fractionation associated with HCO_3^- dehydration and HCO_3^- dehydroxylation reactions (the two pathways of CO_2 degassing from aqueous solutions) are estimated with ab initio transition state theory calculations. Coupled with models of isotopic fractionations accompanying carbonate precipitation, I predict that kinetic

isotope fractionation associated with CO₂ degassing reactions will increase the δ¹³C and δ¹⁸O but decrease the relative proportion of ¹³C-¹⁸O bonds in carbonate minerals that precipitate from degassing solutions. Furthermore, these kinetic isotope effects are correlated with each other. For example, I predict the ¹³C/¹²C ratio of carbonate increases by 1.1-3.2‰ and its Δ₄₇ value decreases by 0.017-0.026‰ for every 1‰ kinetic enrichment in its ¹⁸O/¹⁶O at 25°C, with the exact values depending on the pathway for CO₂ degassing (i.e., HCO₃⁻ dehydration vs. HCO₃⁻ dehydroxylation) and on the amount of carbonate formation that accompanies CO₂ degassing. These predictions compare favorably with the experimental constraints from laboratory synthesized cryogenic carbonates and speleothem-like carbonates and with the isotopic compositions of natural modern speleothems.

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