

CARBONATE CLUMPED ISOTOPE THERMOMETRY:
APPLICATION TO CARBONAECOUS 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 on 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 $\delta^{13}\text{C}_{\text{PDB}}$ 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

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