INTRODUCTION

This thesis consists of two parts: I. Aqueous alteration of carbonaceous chondrite parent bodies—insights from carbonate clumped isotope thermometry; and II. Kinetic isotope fractionations of clumped isotopologues associated with chemical reaction—implications for carbonate clumped isotope thermometry. Both parts consider a common theme—carbonate clumped isotope thermometry, but focus on different problems. Part I centers on the application of carbonate clumped isotope to novel geoscience problems, and the development of analytical techniques to deal with particularly challenging samples; Part II attempts to develop a quantitative understanding of the physiochemical principles behind carbonate clumped isotope thermometry, particularly for carbonate systems that show signs of isotopic disequilibrium. In Part II, I use both theoretical techniques from ab initio chemical theory, transition state theory and statistical thermodynamics and experimental measurements of natural and lab-synthesized materials.

^{13}C and ^{18}O in thermodynamically equilibrated carbonate minerals preferentially group or 'clump' together into the same carbonate ion group to form $^{13}C^{18}O^{16}O^{16}O^{2-}$ as opposed to being randomly dispersed. This effect leads to abundances of $^{13}C^{18}O^{16}O^{16}O^{2-}$ higher than that expected for a random distribution of isotopes. This preferential clumping of heavy rare isotopes results from the fact that the doubly-substituted isotopologue of the carbonate ion, $^{13}C^{18}O^{16}O^{16}O^{2-}$, has a lower zero point energy than its normal and singly-substituted relatives ($^{12}C^{16}O^{16}O^{16}O^{2-}$, $^{13}C^{16}O^{16}O^{16}O^{2-}$ and $^{12}C^{18}O^{16}O^{16}O^{2-}$), and can be expressed through the equilibrium constant for the exchange reaction (Ghosh et al., 2006; Schauble et al., 2006):

$$M\,^{13}C^{16}O^{16}O^{16}O + M\,^{12}C^{18}O^{16}O^{16}O \xrightleftharpoons{K_{eq}} M\,^{13}C^{18}O^{16}O^{16}O + M\,^{12}C^{16}O^{16}O^{16}O \qquad \text{(I)}$$

The equilibrium constant, K_{eq}, for this reaction varies as a function of the temperature of carbonate growth or equilibration and forms the basis of carbonate clumped isotope thermometry (Ghosh et al., 2006; Schauble et al., 2006). This K_{eq} can be determined through the measurements of anomalous enrichment of mass 47 CO_2 (mainly $^{13}C^{18}O^{16}O$) in the CO_2 derived from phosphoric acid digestion of carbonate minerals (Ghosh et al., 2006). The mass 47 anomaly, Δ_{47}, is defined as the difference between the measured value of R^{47} (=[mass 47]/[mass 44]) and the value of R^{47} expected in that sample if its C and O isotopes are randomly distributed among all isotopologues: $\Delta_{47} = \left(\frac{R^{47}_{\text{measured}}}{R^{47}_{\text{random}}} - 1\right) \times 1000$ (Eiler and Schauble, 2004).

Unlike conventional stable isotope thermometry thermometry (e.g., the classic carbonate-water oxygen isotope thermometry), which is based on a heterogeneous thermodynamic equilibrium between two different phases (e.g., carbonate and water), the carbonate clumped-isotope thermometer is based on a homogeneous thermodynamic equilibrium that orders ^{13}C and ^{18}O into bonds with each other within the carbonate lattice (i.e., reaction I). Therefore, it is independent of the isotopic composition of any co-existing phases, and lets one determine carbonate formation temperatures based on only the isotopic compositions of carbonate minerals. This provides great advantage for quantitative estimations of carbonate formation temperatures, especially when the oxygen isotope composition of the fluid from which carbonate grew can not be reliably constrained. Furthermore, this temperature information, combined with the known temperature-dependence of carbonate-water oxygen isotope fractionation, allows one to determine the oxygen isotope compositions of waters from which these carbonates grew. Since its development (Ghosh et al., 2006; Schauble et al., 2006), carbonate clumped isotope thermometry has been successfully applied to a number of geoscience problems, e.g., to reconstruct the uplift history of the Altiplano (Ghosh et al., 2006) and the global surface temperature during the Palaeozoic era (Came et al., 2007).

In Chapter 1 and Chapter 2 I apply carbonate clumped isotope thermometry to carbonates in carbonaceous chondrites (CM chondrite, Chapter 1; CI chondrite, CR chondrite and Tagish Lake, Chapter 2), in order to estimate the temperatures of aqueous alterations on their parent bodies.

Aqueous alteration of primitive meteorites is one of the earliest and most widespread geological processes in the solar system, occurring within the first tens of million of years of solar system history and producing abundant secondary minerals (including carbonates) in the matrix of carbonaceous chondrites (Brearley, 2006). Understanding of these alteration processes, including precise reconstructions of alteration temperatures, will help us constrain the early conditions of the solar system and test models of thermal and chemical evolution of planetesimals. Previous estimates of the alteration temperatures, based on stabilities of constituent phases (e.g., tochilinite; Zolenksy, 1984) or the oxygen isotope fractionation between carbonate and phyllosilicate in the matrix (Clayton and Mayeda, 1984), are inconclusive and range from <20˚C to <300˚C for different types of carbonaceous chondrites (Keil, 2000). Both of these approaches are compromised in certain ways: the first approach provides only upper limits for the alteration temperature; the second requires the assumption that matrix carbonate and phyllosilicate reached isotopic equilibrium with one another. In contrast, carbonate clumped isotope thermometry is independent of the isotopic composition of any coexisting phases, can provide a precise determination of the carbonate precipitation temperature, and has the added benefit of constraining the oxygen isotope composition of the alteration fluid.

Based on carbonate clumped isotope thermometry, I estimate that the aqueous alteration temperatures on parent bodies of the carbonaceous chondrites ranged from -31˚C to 70˚C and decreased during the course of aqueous alteration. I further estimate the oxygen isotopic compositions of the alteration fluid and interpret them in the context of aqueous alteration models (Clayton and Mayeda, 1999). I observe a negative correlation between $\delta^{13}C_{PDB}$ values of CM carbonates and the $\delta^{18}O$ of their formation water, and suggest this as evidence of formation and escape of ^{13}C-depleted CH_4 during aqueous alteration on the CM chondrite parent bodies. CI chondrites and Tagish Lake contain several generations of distinct carbonate phases (e.g., calcite, dolomite and breunnerite) that grew at different times. I use techniques of stepped acid digestion to separately determine the clumped isotope formation temperatures of these different carbonates, thereby constraining the thermal evolution of carbonaceous chondrite parent bodies. These results provide the first direct experimental constraints on the low-temperature thermal evolution histories of C1 and C2 carbonaceous chondrite parent bodies.

In Chapters 3 and 4, I employ ab initio transition state statistical thermodynamic theory to study kinetic fractionations of clumped isotopologues associated with two chemical reactions, i.e., the phosphoric acid digestion of carbonate mineral and the degassing of CO_2 from aqueous solutions.

Phosphoric acid digestion has been adopted as a routine analytical technique for oxygen- and carbon-isotope measurements of carbonate minerals since 1950, and was recently extended for use as a method for carbonate ‘clumped isotope’ analysis. The CO_2 derived from phosphoric acid digestion differs significantly in its oxygen isotope composition and clumped isotope composition from reactant carbonate, by an amount that varies with the temperature of digestion and carbonate chemistry. However, so far a quantitative understanding of this fractionation process has been missing. Based on structural arguments, I assume H_2CO_3 as the intermediate during phosphoric acid digestion of carbonate minerals and predict from ab initio transitions state theory the kinetic isotope fractionations between the product CO_2 and reactant carbonate. For example, at 25˚C we predict that CO_2 derived from acid digestion of carbonate minerals will be 10.72‰ and 0.220‰ higher, respectively, in $^{18}O/^{16}O$ ratios and ^{13}C-^{18}O clumped isotope anomaly than the reactant carbonate. The predicted kinetic isotope fractionations associated with phosphoric acid digestion and their temperature dependence (for both oxygen isotope and clumped isotopologues) agree reasonably well with independent experimental constraints for phosphoric acid digestion of calcite, including my new experimental data for fractionations of ^{13}C-^{18}O bonds (the measured change in Δ_{47}=0.23‰) during phosphoric acid digestion of calcite at 25°C. 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 ^{13}C-^{18}O clumping effects in carbonate minerals, and predict the temperature calibration relationship for different carbonate clumped isotope thermometers (witherite, calcite, aragonite, dolomite and magnesite). I observe reasonable agreement between these predictions and the available experimental determinations (e.g., difference of less than 0.05‰ over 0-50°C, for calcite).

CO_2 degassing from aqueous solution occurs in most aqueous environments that contain dissolved inorganic carbon, and is involved in a number of important geologic processes, including speleothem deposition, cryogenic carbonate formation, air-sea CO_2 exchange, etc. Significant kinetic fractionations accompany this process, influencing the isotopic compositions of both the degassed CO_2 and the carbonate minerals that might grow from degassing solutions. In Chapter 4, I focus on quantitatively understanding the influence of these kinetic fractionations on the clumped isotope anomaly in the carbonate minerals grown from degassing solutions, e.g., speleothems. I estimate the kinetic isotope fractionation factors associated with HCO_3^- dehydration and dehydroxylation reactions in aqueous solution (the two pathways of CO_2 degassing), using first principle transition state theory calculations. Combining these predicted isotope fractionation factors with models of isotopic fractionations accompanying carbonate formation, I predict kinetic isotope fractionation associated with CO_2 degassing reactions will increase the δ^{13}C and δ^{18}O but decrease the relative proportion of ^{13}C-^{18}O bonds in the carbonate precipitating from the degassing solution. Furthermore, these kinetic isotope effects are correlated with each other. I test these predictions against the experimental measurements of the lab-synthesized cryogenic carbonates and the available isotopic data of both natural modern speleothems and speleothem-like carbonates synthesized in the laboratory, and observe reasonable agreement. I also predict, based on the ab initio calculations, that CO_2 degassed from aqueous solution will be depleted in the ^{13}C-^{18}O clumped isotope distribution relative to that expected from thermodynamic equilibrium, an effect that might therefore explain the low Δ_{47} observed in terrestrial respiration CO_2 and human breath.

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