APPLICATION OF CLUMPED ISOTOPES IN CARBONATES AS AN INDICATOR OF LIFE AND HABITABILITY. N. P. Levitt,[1,2] C. M. Johnson,[1,2] J. M. Eiler,[2,3] B. L. Beard,[1,2] and H. Xu,[1,2] [1]University of Wisconsin – Madison, Madison, Wisconsin, [2]NASA Astrobiology Institute, [3]California Institute of Technology, Pasadena, California.

Introduction: The study of "clumped isotopes" involves quantification of the preferential bonding between rare stable isotopes (e.g., ^{13}C to ^{18}O) in multiply substituted isotopologues as compared to stochastic bonding predicted for that chemical compound or mineral lattice. Chemical bonds involving isotopes of higher relative atomic mass are stronger due to reduced bond vibration frequencies and therefore, zero-point energy [1]. This stability promotes concentration of isotopes of higher relative atomic mass in the more stable bonding environment during a phase transformation. Because clumped isotopes are defined by two or more isotopes of an element of relatively high mass bonded together, thermodynamic stability is significantly increased by bond vibration frequency reductions generally twice (or more) as large as found in singly substituted isotopologues.

Potential Biosignature: Non-equilibrium fractionation of oxygen and carbon isotopes associated with biomineralization has been studied for decades. Early investigators studying isotopic fractionation involving carbonates quickly recognized biogenic non-equilibrium fractionation or so called "vital effects". These isotopic signatures preserved in carbonates have the potential to serve as a robust biomarker if fully understood and characterized. Clumped isotope analysis has opened a new dimension of forensics that can be used in tadem with traditional isotope geochemistry. Some studies of clumped isotopes in biogenic carbonate material have revealed fractionation and ^{13}C-^{18}O bonding relationships that do not seem to be consistent with many inorganically precipitated carbonates or theoretical calculations [1]. These special cases need to be explored more fully. However, if clumped isotopes do indeed have minimal "vital effects", they serve an equally important role when comparing to traditional O and C isotopes (e.g., $\delta^{13}C$, $\delta^{18}O$) where the fluid composition can be independently calculated, thus providing a reference frame to identifying potential "vital effects" from $\delta^{13}C$ and $\delta^{18}O$ values.

Precipitation Rate Investigation: We report on new experimental studies where calcite has been synthetically formed using chemostat synthesis whereby seed crystals are used to constrain mineralogy and precipitate rate. This method is also used to maintain constant solution conditions such as saturation index and pH. This approach has provided new insights into fractionations associated with CO_2 degassing utilized in previous synthetic carbonate precipitation experiments and is also utilized to directly explore the relation between precipitation rate and ^{13}C-^{18}O bond ordering in dissolved inorganic carbon (DIC) versus solid carbonate.

Recent developments in the understanding of H_2O-CO_2-carbonate system equilibrium and kinetic fractionations associated with carbonate precipitation requires a critical reassessment of ^{13}C-^{18}O bond formation in carbonates and their relationship to the DIC system [2].

Early Biosphere Conditions: Clumped isotopes can be used to investigate environmental conditions of the early Earth biosphere [3]. Understanding the origin and early evolution of life on Earth is one of the fundamental cornerstones of astrobiology research, and provides the most reliable basis for understanding the potential of life outside of Earth. However, rocks with the potential to record chemical signatures of early life biologic systems and ancient environments are extremely rare. Accordingly, the records that do remain after eons of weathering, erosion, and alteration must be interrogated with the best technology and methods available to decipher the most information possible [3, 4].

We also report on a preliminary study of clumped isotopes to infer temperature and $\delta^{18}O$ value of Neoarchean microbial habitats recorded in the well-documented Campbellrand-Malmani carbonate platform of the Neoarchean (2.68-2.50 Ga) Kaapvaal Craton, South Africa. This transgressive sequence preserves the least altered late Archean rocks known to exist, with a maximum metamorphic temperature of ~130°C [5].

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