COVARIANT C AND O ISOTOPE TRENDS IN ARCTIC CARBONATE CRUSTS AND ALH 84001: POTENTIAL BIOMARKER OR INDICATOR OF CRYOGENIC FORMATION ENVIRONMENT? Richard A. Socki[1], Paul B. Niles[2], Weston Blake, Jr.[3], and Richard Leveille[4]; [1]ESCG and [2]KR, Astromaterials Research and Exploration Science, NASA/Johnson Space Center, Houston, TX 77058, [3]Geological Survey of Canada, Ottawa, Ontario, K1A 0E9, Canada, [4]Planetary Exploration and Space Astronomy, Canadian Space Agency, St-Hubert, Quebec, J3Y 8Y9 Canada. (*richard.a.socki@nasa.gov*)

Introduction: This work seeks to use the chemical, isotopic, and mineralogical characteristics of secondary carbonate minerals produced during brief aqueous events to identify the conditions of the aqueous environment in which they formed. Liquid water near the surface of Mars is subject to either rapid freezing and/or evaporation. These processes are also active on Earth, and produce secondary minerals that have complex chemical, mineralogical, and isotopic textures and compositions that can include covariant relationships between $\delta^{13}C_{(VPDB)}$ and $\delta^{18}O_{(VSMOW)}$ [1-7]. The extremely well studied four billion year old carbonates preserved in martian meteorite ALH 84001 also show covariant $\delta^{13}C$ and $\delta^{18}O$ compositions [8], but these variations are manifested on a micro-scale in a single thin section while the variation observed so far in terrestrial carbonates is seen between different hand samples.

Arid and/or cold regions on the Earth have long been identified as ideal martian analogs due to the scarcity of liquid water in their environments. Secondary minerals formed in these regions typically have not undergone significant diagenesis due to the lack of liquid water and these minerals typically form rapidly in brief aqueous environments that are undergoing evaporation, freezing, or both. The result is that the characteristics of secondary minerals, formed by aqueous processes in these liquid-water-poor environments, can be dominated by poorly understood kinetic processes rather than equilibrium relationships, which are commonly used to model aqueous systems [1, 2, 9-12].

We hypothesize that the covariant $\delta^{13}C$, $\delta^{18}O$ relationships observed in arid and cryogenic terrestrial environments and in the ALH 84001 carbonates are linked by a common mechanism whose identification will provide significant insight into the geological conditions that led to the formation of the ALH 84001 carbonates. In order to test this hypothesis we are performing detailed micro-scale stable isotope analysis of arctic carbonate crusts collected on Ellesmere Island [13]. Most precipitates (Fig. 1) are located on Precambrian bedrock that has been heavily modified by glaciation. The carbonates appear as brown or white crusts, are on average 2 cm in diameter, up to 7 mm thick, and most have radiocarbon ages of less than 3000 years [13]. Some samples are closely associated with bacterial features such as filaments, and the presence of cyanobacteria, while other samples are speculated to
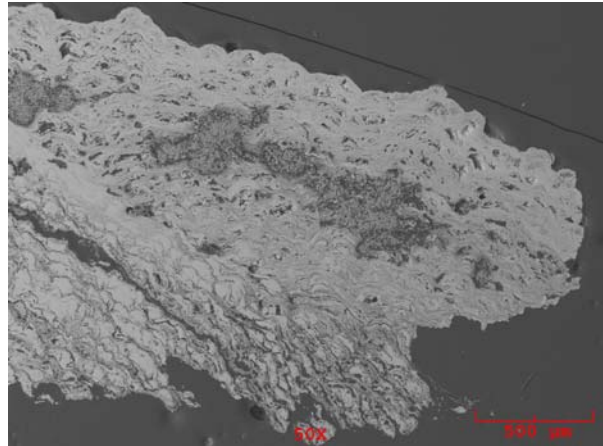

Figure 1. SEM backscatter image of arctic carbonate crust sample 2001-BS-03 from Ellesmere Island. This sample contains complex layering on a micro-scale. Chemical x-ray maps confirm that this sample is totally composed of calcium carbonate.

have formed through glacial processes related to carapace ice caps [13]. Bulk (whole crust) analyses have shown large variations between different crusts with very elevated $\delta^{13}C$ values [13]. This work looks in detail for isotopic variation within single crusts.

Methods and Results: Carbonate crusts were cross-sectioned and mounted as thick sections on 1" round glass slides using epoxy, characterized by SEM, and micro-sampled using a New Wave Micro-Mill. ~200 x ~2000 μm swaths were removed along growth planes providing approximately 5-6 samples across each individual crust. Carbonate powder collected from each sampling area were then analyzed via Thermo Gas Bench II/MAT 253 IRMS system operating in continuous flow mode.

Results are shown in Figure 2. Four different crusts have been analyzed and each shows a strong enrichment in $\delta^{13}C$ (up to ~15‰), well above the typical range for terrestrial carbonates. Three of the four samples also show a strong covariant trend, which is also strongly correlated with sampling location. The regions closest to the rock (inner portions) show the lowest $\delta^{13}C$ and $\delta^{18}O$ while the outer portions show the highest $\delta^{13}C$ and $\delta^{18}O$ values.

Discussion: CO_2 degassing and biological processes are the two most likely mechanisms for creating the covariant $\delta^{13}C$ and $\delta^{18}O$ relationships in this environment. Differentiating between the different isotopic fingerprints of these two systems will aid in the inter-

pretation of large $\delta^{13}C$ variations as potential bio-markers, and be useful for interpreting $\delta^{13}C$ and $\delta^{18}O$ data from carbonates whose formation environments are unknown, i.e. carbonates in ALH 84001. Covariant C and O isotope trends in ALH 84001 show similar trends to those seen in Arctic carbonate crusts but to a greater magnitude (up to 20‰ [8]).

Blake [13] argues that some of the arctic carbonate crusts show signs of biomineralization supporting the idea that biological processes are responsible for the elevated $\delta^{13}C$ values. In this hypothesis, carbonate precipitation is strongly influenced by photosynthetic organisms that preferentially remove CO_2 enriched in ^{12}C from the fluid, leaving behind a dissolved inorganic carbon reservoir that is enriched in ^{13}C, a process that has been observed in basaltic caves in Hawaii [14]. However, this mechanism does not affect the $\delta^{18}O$ composition of the dissolved inorganic carbon reservoir. Furthermore, if the carbonates were not forming in a cryogenic environment and water was evaporating instead of freezing, one might explain covariant enrichments in $\delta^{18}O$ and $\delta^{13}C$ as caused by evaporation and photosynthesis occurring together during brief wetting periods [15].

Alternatively, the covariant relationship could be the result of inorganic CO_2 degassing during freezing. Clark and Lauriol [1] and Socki et al [16] have performed laboratory experiments demonstrating the existence of a large kinetic fractionation factor associated with CO_2 degassing during the freezing of water. As a solution freezes, it removes H_2O from the system and concentrates the solutes in the remaining liquid; this drives CO_2 out of the solution with progressive freezing. Thus, the large carbon isotope enrichments may be caused by a kinetically enhanced preference for $^{12}CO_2$ to be outgassed from the freezing solution over

$^{13}CO_2$. Clark and Lauriol [1] also showed that the $\delta^{18}O$ composition of the carbonate would become kinetically enriched as the degassed CO_2 would preferentially remove ^{16}O from the system creating a covariance between the $\delta^{13}C$ and $\delta^{18}O$ compositions.

Summary: We use chemical, isotopic, and mineralogical characteristics of terrestrial secondary carbonates produced during brief aqueous events to identify the conditions of the environment in which they formed as analogs for martian near surface processes. The covariant C and O micro-scale isotope trends in the arctic carbonate crusts mimic, to a lesser extent, those seen in ALH 84001. These samples are the best terrestrial analogs for the isotopic composition of the ALH 84001 carbonates discovered so far, and this indicates that the arctic carbonate crusts may have shared a similar formation environment to ALH 84001 carbonates.

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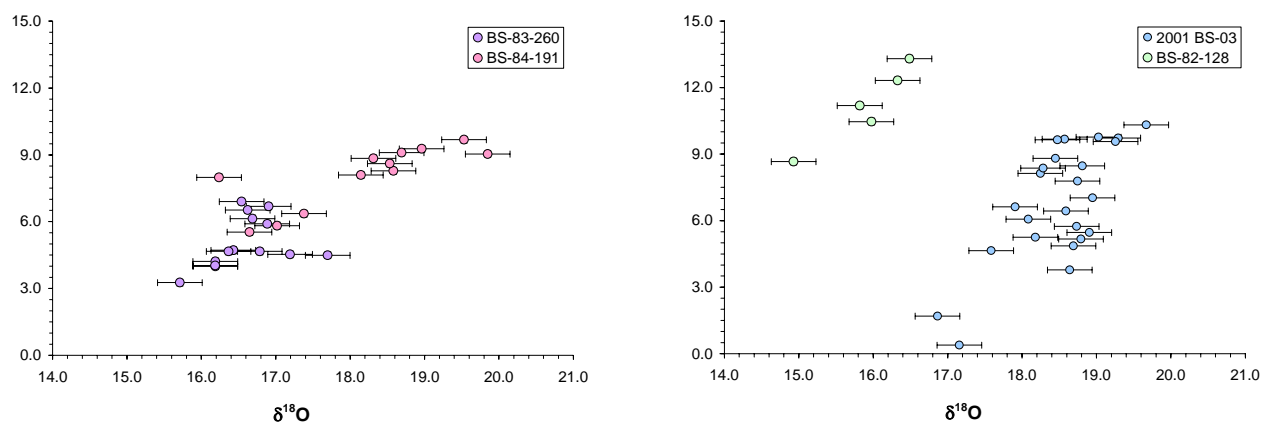Contribution 71 from the Cape Herschel Project, GSC.

Figure 2. Carbon and Oxygen crossplot displaying analysis of micro-drilled samples from 4 different arctic carbonate crusts from Ellesmere Island. The $\delta^{13}C$ values of all of these samples are elevated compared to typical terrestrial carbonates, which usually have $\delta^{13}C < 0‰$. The isotope values are also very strongly spatially correlated with the lowest $\delta^{13}C$ and $\delta^{18}O$ values corresponding to the innermost portions of the carbonate crust.