

COVARIANT C AND O ISOTOPE TRENDS IN SOME TERRESTRIAL CARBONATES AND ALH 84001: POSSIBLE LINKAGE THROUGH SIMILAR FORMATION PROCESSES. Kathryn E. Volk¹, Paul B. Niles², Richard A. Socki^{2,3}, ¹Northern Illinois University Department of Geology and Environmental Geosciences, DeKalb, IL 60115 (kvolk@niu.edu), ²Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, TX 77058, ³ESCG, (paul.b.niles@nasa.gov, richard.a.socki@nasa.gov)

Introduction: Carbonate minerals found on the surface of Mars and in martian meteorites indicate that liquid water has played a significant role in the planet's history [1-5]. These findings have raised questions regarding the history of the martian hydrosphere and atmosphere as well as the possibility of life. Of particular interest are the 3.9 Ga carbonates found in the ancient martian meteorite ALH 84001 [6]. Ancient Mars may have resembled the extreme environments we see today where any liquid water only exists in brief aqueous events and is subject to fast freezing and/or high evaporation [4,7]. Considering the current inaccessibility to Mars, terrestrial analogs are valuable tools for understanding formation mechanisms of carbonates on Mars. To find suitable analogs we must look for environments on Earth that resemble potential martian environments.

Carbonates in ALH 84001 exhibit a covariant isotope trend: $\delta^{18}\text{O}$ values range from -10 to +25‰ (VSMOW) and $\delta^{13}\text{C}$ values range from +30‰ to +64‰ (VPDB) [8,9,10]. A similar covariant trend was observed by Knauth et al. [9] in a collection of bulk samples of terrestrial carbonates formed in subaerial environments from Sunset Crater, Arizona, USA.

Sunset Crater is a dry environment with relatively high evaporation and brief periods of precipitation. This environment resembles Mars and may make Sunset Crater a good analog to martian carbonates [7,9].

In this study we sought to identify discrete micro-scale isotopic variation within the carbonate crusts in Sunset Crater to see if they resembled the micro-scale isotope variation found in ALH 84001 carbonates. Sunset Crater carbonate formation may be used as a martian analog and ultimately provide insight into carbonate formation in ALH 84001.

Methods: Three samples were analyzed from subaerial basalt pinnacles near Sunset Crater, Arizona (4, 8, 10). The carbonates grew attached to the underside of basalt pinnacle overhangs and were never exposed to the soil [9]. Chunks of basalt with carbonate coating were broken from the rock and mounted in epoxy. The epoxy was then cut with an Isomet lapping saw into thick sections providing slices of rock with a basaltic interior and a carbonate ring around the edge 100 to 350 μm wide [Fig. 1]. Carbonate material was removed from the thick sections using a NewWave Technology Micromill. The carbonate rims were drilled 1 to 7 times at separate points from a single

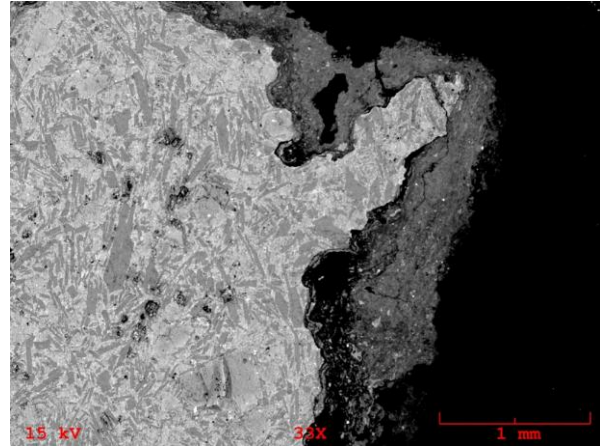


Figure 1. SEM Backscatter image of Sunset Crater rock. The carbonate appears as darker material around the basaltic interior.

crust and 300 $\mu\text{g} \pm 100\mu\text{g}$ of sample was collected each time.

Backscatter images were obtained from samples at 15kV and 50x using the 5910LV JEOL SEM at Johnson Space Center. EDS was conducted on select spots of some samples. The chemical composition of the Sunset Crater samples was confirmed to be entirely CaCO_3 . The powdered carbonate samples were reacted with 100% phosphoric acid at 72°C and analyzed for C and O isotope composition via Thermo Gas Bench II/MAT 253 IRMS system operating in continuous flow mode.

The data were corrected using 2 standards: NBS-18, and NBS-19. Uncertainties are reported in 2σ . The uncertainty includes reproducibility of the standards, standard deviation within each analysis, and reproducibility of reference gas injections. The reproducibility of standards was our largest source of error at 0.3‰ for $\delta^{13}\text{C}$ and 0.2‰ for $\delta^{18}\text{O}$.

Results: We report $\delta^{13}\text{C}$ range of +1.8 to +12.7‰, and $\delta^{18}\text{O}$ range of +21.5 to +29.0‰ for Sunset Crater samples. There is a significant enrichment in ^{13}C compared to most terrestrial carbonates.

Our method of micro-drilling removed discrete micro-samples rather than the average bulk sample as had been done in previous studies [9]. This demonstrated heterogeneity within the crust and identified covariant trends from each sample [Fig 2].

Discussion: CO_2 degassing and photosynthesis are causes for ^{13}C enrichment. During evaporation CO_2 degassing and carbonate precipitation can occur [12].

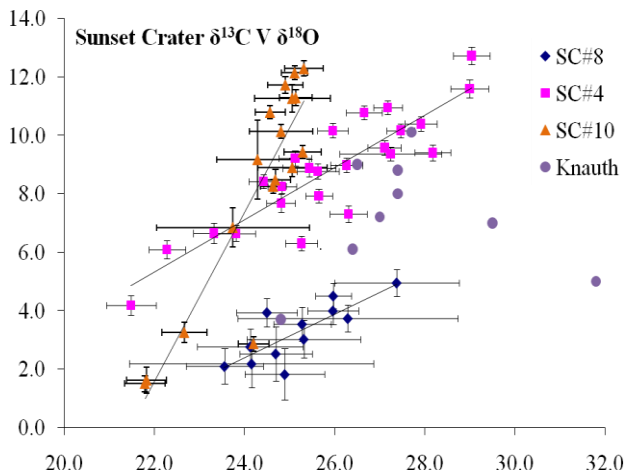


Figure 2. All data (4, 8, 10) from Sunset Crater, Arizona plus previous data by Knauth et al. [9]. Our data shows a distinct and persistent covariant enrichment trend. The large uncertainties are due to small sample sizes.

This process can also result in simultaneous smaller enrichment of ^{18}O as demonstrated by Mickler et. al. [13]. Alternatively, photosynthesis selectively removes ^{12}C resulting in enrichment of ^{13}C in the dissolved CO_2 reservoir. Thus, while CO_2 degassing can affect both C and O isotopes, photosynthesis by itself will only alter C isotopes.

If photosynthesis is the source of the C enrichments observed in our samples, then evaporation must also be happening in parallel to explain the O enrichment trends. However this scenario would not explain covariance as there is no reason to believe that the amount of evaporation should be related to the amount of photosynthesis. On the other hand, evaporation concentrates dissolved CO_2 in the remaining fluid, inducing both CO_2 degassing and carbonate precipitation resulting in simultaneous enrichment of both isotopes [12].

Our micro-sampling of the Sunset Crater carbonates revealed significant covariant trends from each sample location. This suggests that the processes of O and C isotope enrichment are linked together which is more consistent with the coupled mechanisms of evaporation and degassing rather than the independent mechanisms of photosynthesis and evaporation. This conclusion is also supported by Leveille et. al. [12] who found no significant correlation between oxygen and carbon isotopic compositions of carbonates enriched by photosynthesis and evaporation in Hawaiian caves. Furthermore the carbonate crusts formed exclusively on the underside of overhangs where water dripped off the basalt pinnacles, which is not a favorable environment for photosynthesis.

Previously, Knauth et al. [9] had analyzed bulk carbonates from Sunset Crater and favored a photosynthe-

sis-evaporation origin for the isotopic enrichments observed in the carbonates. They argued that degassing was unlikely on the basalt pinnacles due to the lack of sufficient CO_2 in the fluids. If Sunset crater rainwater contained a typical dissolved bicarbonate composition of 4 mg/L then it would take only 8 cm of water per year to precipitate a 100 μm thick crust with a 1.4 g/cm^3 density.

The isotope enrichment ranges in ALH 84001 carbonates are significantly more extensive than isotope ranges in these terrestrial analogs: $\sim 30\%$ for $\delta^{13}\text{C}$ and $\sim 30\%$ for $\delta^{18}\text{O}$ [14, 15]. Despite this, the positive covariant trend in Sunset Crater is similar to that observed in ALH 84001. The covariant trend observed in the Sunset crater carbonates exists on a micro-scale and is best explained by a coupled evaporation/degassing mechanism. Thus it may be possible that the ALH 84001 covariant isotope enrichment trends may be a result of extreme evaporation and CO_2 degassing operating under much lower atmospheric pressure [16].

Conclusion: We found substantial covariant micro-scale variations of C and O isotopes of terrestrial carbonates at Sunset Crater, AZ. The isotopic variation found in the Sunset Crater carbonates has a similar covariant relationship to the isotope variation found in the martian ALH 84001 carbonates with a smaller magnitude. The positive covariant enrichment trend observed in Sunset Crater is most likely a result of coupled evaporation and abiotic CO_2 degassing. These same mechanisms may also be responsible for the formation of the ALH 84001 carbonates under lower atmospheric pressure.

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