

OXYGEN AND CARBON ISOTOPE COMPOSITION OF THE MAGNESIUM CARBONATES IN LEWIS CLIFF 85320: REVISITED. M. I. EL-Shenawy¹, P. B. Niles², R. Socki³, Doug Ming², ¹USRA, NASA Johnson Space Center, Houston, TX 77058 (mohammed.i.elshenawy@nasa.gov), ²NASA Johnson Space Center, Houston, TX 77058, ³Delaware Research and Technology Center.

Introduction: The Antarctic H5 chondrite Lewis Cliff 85320 (LEW 85320), the largest stony meteorite collected in Antarctica, exhibits a wide occurrence of carbonates on its exterior surface and along its fractures. Carbon-14 studies of LEW 85320 carbonates suggested a terrestrial origin for these carbonates with the first generation formed in Antarctica in A.D. 1957 \pm 2 years and the second generation grew in Houston-JSC curation facility in A.D. 1986 [1]. Mineralogical investigation of these two generations confirmed that the majority of carbonate was nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) with traces of hydromagnesite [1,2].

Previous carbon and oxygen stable isotope measurements of the two nesquehonite generations from LEW 85320 have shown that the Antarctica generation has higher $\delta^{13}\text{C}$ (+7.9 ‰) and $\delta^{18}\text{O}$ (+17.95 ‰) values than those measured in the Houston generation (i.e., $\delta^{13}\text{C}$ = +4.2 ‰ and $\delta^{18}\text{O}$ = +12.15 ‰) [3]. In contrast, earlier study of subsamples of the two generations measured a higher $\delta^{18}\text{O}$ value (+11.35 ‰) in the Houston generation than that reported in the Antarctica generation ($\delta^{18}\text{O}$ = +9.39 ‰) [2]. However, the $\delta^{13}\text{C}$ value of the Antarctica generation was 1.1 ‰ higher than that measured in Houston generation (+4.28 ‰) [2]. This discrepancy between the two studies [2,3] suggested that both nesquehonite generations formed under kinetic isotope effects resulting in heterogeneous isotopic compositions.

The goal of this study is to quantify the magnitude and direction of these kinetic isotope effects in order to reconstruct the environmental conditions under which the nesquehonite formed. To achieve this goal: (1) We sampled carbonates from five different locations on the exterior surface of LEW 85320, (2) We analyzed these new samples and previously collected samples for their mineralogy and isotopic compositions, (3) We determined the temperature - oxygen isotope fractionation between synthetic nesquehonite and water relation, and (4) We measured oxygen isotope composition of melted ice from the Lewis Cliff Ice Tongue (e.g., parent water of LEW carbonates).

Samples and Methods: Five new samples were scraped off the surface, sides and bottom of the LEW 85320; namely, LEW 85320, 119; 120; 121; 122; 123). In addition, three other samples (i.e., LEW 85320, 93; 98; 104) were obtained from JSC-curation archive. The samples LEW 85320, 93 and 104 were aliquots prepared from Houston nesquehonite generation (i.e., LEW 85320, 15 and 22 in [3] and [2], respectively), whereas LEW 85320, 98 was prepared from the Antarctica generation (i.e., LEW 85320, 39 and 40 in [3]

and [2], respectively. All samples (except samples of very small size; LEW 85320, 121 and 123) were investigated for their mineralogy by X-ray diffractometry (XRD). Based upon the XRD results, samples showing amorphous features were ran under scanning electron microscope (SEM) coupled with an energy-dispersive x-ray spectrometer (EDS). Nesquehonite was synthesized in a closed vessel over 20 years at room temperature (20.8 ± 2.5 °C) following the procedures in [4]. The long duration of synthesizing this nesquehonite allowed continuous oxygen isotope exchange between the DIC species and water, assuring the precipitation of nesquehonite at equilibrium oxygen isotope.

Stable isotope compositions of carbonates and water were measured using the Gas Bench II system coupled with a Finnigan MAT 253 continuous flow isotope ratio mass spectrometer (CF-IRMS) at JSC. Long-term internal precision of the reference materials used to normalize the samples is better than 0.1 ‰ for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ which were reported on the VPDB and VSMOW scale, respectively.

Results and Discussion : The XRD analyses confirmed that the synthesized carbonate was nesquehonite (Fig. 1).

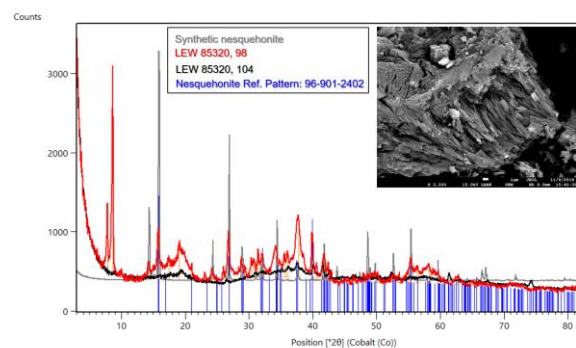


Fig. 1: XRD patterns of synthetic nesquehonite and LEW carbonates against the nesquehonite reference pattern. SEM Image of LEW 85320, 104.

However, all the LEW 85320 carbonates appear to be amorphous in the XRD scan with exception to the LEW 85320, 98 (i.e., Antarctica generation) which shows a good match to the nesquehonite Ref. peaks (Fig. 1). Under the SEM, the sample LEW 85320, 104 (Houston generation) demonstrates the characteristic elongated habit of nesquehonite (Nanocrystalline) which is confirmed by the EDS analysis (Fig. 1). This difference in the degree of crystallinity between the two generations was reported in pervious study [i.e., 3], suggesting that nesquehonite precipitation was slower in Antarctica than in Houston.

The oxygen isotope fractionation factor between synthetic nesquehonite and water at 20.8 ± 2.5 °C was measured (i.e., $1000\ln^{18}\alpha_{\text{nesq-H}_2\text{O}} = 33.16$ ‰). This measured nesquehonite value is 4.24 ‰ higher than its corresponding value for calcite (Fig. 2), arguing against the use of calcite- CO_2 - H_2O fractionation factors as an approximation to those in the nesquehonite- CO_2 - H_2O system [e.g., 2].

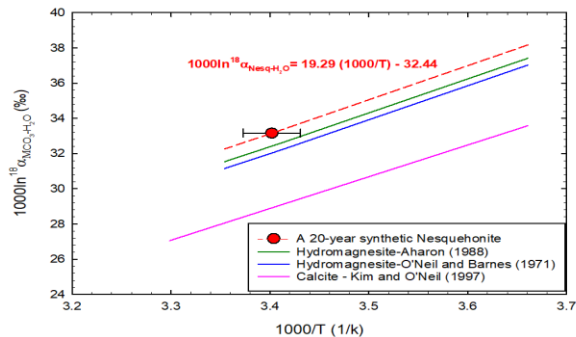


Fig. 2: The temperature - $1000\ln^{18}\alpha_{\text{MCO}_3\text{-H}_2\text{O}}$ relation for different carbonate minerals.

Our measured $1000\ln^{18}\alpha_{\text{nesq-H}_2\text{O}}$ value is close to, but 0.7 ‰ higher than, those values reported in hydromagnesite [5,6]. The temperature dependency ($1000\ln^{18}\alpha_{\text{MCO}_3\text{-H}_2\text{O}} / T$) among carbonate minerals is quite similar (e.g., -0.22 for calcite and -0.24 for hydromagnesite; Fig. 2) [7, 6]. A dashed line with a typical temperature dependency to that of hydromagnesite has been drawn through our single point of nesquehonite to provide a satisfactory estimation of $1000\ln^{18}\alpha_{\text{nesq-H}_2\text{O}}$ between 0 and 25 °C (equation shown in Fig. 2). The temperature uncertainty associated with our nesquehonite thermometer is ± 3.5 °C, considering the temperature uncertainty in our experiment and the typical analytical error.

The $\delta^{18}\text{O}$ value of the melted ice from Lewis Cliff was -28.78 ‰. The $\delta^{13}\text{C}$ values of the eight LEW 85320 carbonates measured in this study range from +3‰ to +7.03 ‰, and the $\delta^{18}\text{O}$ values vary between +10.72 and +16.50 ‰ (Fig. 3). However, previous published data [2,3] extends the range of the LEW 85320 carbonates isotopic values from +3 ‰ to +7.9 ‰ for $\delta^{13}\text{C}$, and from +9.39 ‰ to +17.95 ‰ for $\delta^{18}\text{O}$ (Fig. 3). Figure 3 shows two clusters of data (i.e., Antarctica and Houston generations) with a similar trend which starts with a linear $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ covariation followed by continuous increase in $\delta^{18}\text{O}$ with little to no change in $\delta^{13}\text{C}$. This trend suggests that both carbonate generations formed due to CO_2 outgassing from a thin water film under evaporative conditions.

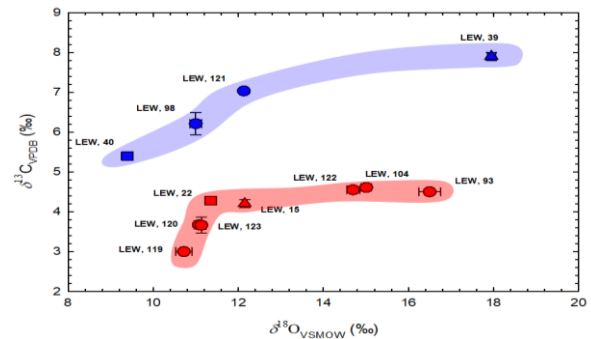


Fig. 3: Variation in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in LEW 85320 carbonates. The blue and red shaded areas delineates the Antarctica and Houston carbonate generations, respectively. Data points in circles, squares and triangles are from this study, [1] and [2], respectively.

Under such conditions, carbonate precipitation starts at isotopic equilibrium with the parent water; however progressive CO_2 outgassing enriches the later stages of carbonate precipitate in both ^{13}C and ^{18}O until the DIC reservoir in the thin film approaches chemical equilibrium with atmospheric CO_2 (i.e., carbonate precipitation becomes very slow and the increase in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ becomes minimal) [8]. Then evaporation enriches water in ^{18}O , but not in ^{13}C , and thus in carbonates. We estimated a formation temperature of -1.4 ± 3.5 °C for the Antarctica carbonate generation by plugging the measured fractionation $1000\ln^{18}\alpha_{\text{LEW,40-melted ice}}$ (38.55 ‰) into the equation from Fig. 2. As evaporation proceeded in Antarctica, the $\delta^{18}\text{O}$ value of the thin film of water increased by about 8.56 ‰ (i.e., $\delta^{18}\text{O}_{\text{LEW, 39}} - \delta^{18}\text{O}_{\text{LEW, 40}}$). If the Houston carbonate generation formed from this enriched water, the estimated formation temperature of LEW, 119 carbonate would be 29.4 ± 5 °C which is fairly close to the room temperature in the curation facility. In addition the drift in the $\delta^{13}\text{C}$ between the two carbonate generations is most likely due to the difference in ambient temperature and the $\delta^{13}\text{C}$ of atmospheric CO_2 in both locations (Antarctica and Houston).

Conclusions: For the first time, this study uses carbonate minerals to differentiate the environmental conditions of carbonates forming in Antarctica and in the JSC curation facility under extremely low water/rock conditions. This is important for understanding terrestrial weathering of meteorites in Antarctica as well as extraterrestrial carbonates formed in cold, arid environments.

References: [1] Jull A. J. T. et al. (1988) *Science*, 242, 417–419. [2] Gooding J. L. et al. (1988) *LPS XIX*, 397–398. [3] Grady M. M. et al. (1988) *Geochim. Cosmochim. Acta*, 52, 2855–2866. [4] Ming D. W. and Franklin W. T. (1985) *Soil Sci. Soc. Am. J.*, 49, 1303–1309. [5] O'Neil J. R. and Barnes I. (1971) *Geochim. Cosmochim. Acta*, 35, 687–697. [6] Aharon P. (1988) *Chem. Geol.*, 69, 127–145. [7] Kim S.-T. and O'Neil J. R. (1997) *Geochim. Cosmochim. Acta*, 61, 3461–3475. [8] Deiningner M. et al. (2012) *Geochim. Cosmochim. Acta*, 96, 57–79.