

AQUEOUS CARBONATE ISOTOPIC (^{13}C) EXCHANGE WITH CHONDRITIC ORGANIC SOLIDS. G. D. Cody¹, C. M. O'D Alexander¹, D. Foustoukos¹, and C. R. Glein², ¹Earth and Planets Laboratory, 5241 Broad Branch Rd., NW, Washington DC (gcody@ciw.edu), ²Southwest Research Institute, San Antonio, TX.

Introduction: There are three primary reservoirs for carbon in type 1 and 2 carbonaceous chondrites. In order of abundance these are the insoluble organic matter (IOM) at ~ 2 wt % [1], carbonates at 0.6 down to 0.03 wt % [2], and soluble organic matter (SOM) with concentrations on the order of 10's to 1000's of nmoles per gram [3]. ^{13}C isotopic abundances vary considerably across these three reservoirs, e.g. for CM IOM exhibiting on average $\delta^{13}\text{C}$ of ~ -18 ‰ [1], CM carbonates exhibit on average $\delta^{13}\text{C}$ of ~ +42 ‰ [2], and SOM monocarboxylic acids (MCAs) have $\delta^{13}\text{C}$ values ranging from -52 up to +22 ‰ [3], where no systematic relationship is apparent between the three carbon reservoirs. In case of the MCAs $\delta^{13}\text{C}$ it has been suggested that partial equilibration between MCAs and CO_3^{2-} in fluids might explain some of the isotopically heavier values [3]. Exchange between carboxyl groups and CO_3^{2-} in fluids has been observed with simple organic acids [4,5], through a poorly defined reaction. The potential for ^{13}C isotopic exchange between IOM and CO_3^{2-} in fluids either during or after synthesis has not been studied to the best of our knowledge. Here we show that such exchange can occur.

Methods: In the present study the potential for ^{13}C isotopic exchange between IOM and CO_3^{2-} in fluids focuses on exchange during and after syn-IOM synthesis. We build on the proposal that IOM forms through hydrocarbonization rxn's of simple sugars in water during planetesimal interior heating [6-7]. In the first experiment 170 mg of glucose (GLU) was heated with 60 mg of either ^{13}C enriched or natural abundance NaHCO_3 in 1.5 ml of DI H_2O , flame sealed in glass ampules and then heated to 250 °C for 7 hours. The concentration of glucose relative to water was chosen to represent the concentration of formaldehyde (FA) (6 FA = 1 GLU) that has been observed in interstellar ices (e.g. 1-7 FA's per 100 H_2O).

In the second experiment syn-IOM was initially made with just GLU and water at 250 °C for seven hours. The recovered solids were then charged into new ampules with 1.5 ml DI water and 30 mg of either ^{13}C enriched or natural abundance NaHCO_3 . These were then reacted at 250 °C for 7 days.

The solid products were recovered from the tubes after reaction and washed with dilute HCl multiple times before drying. The dry solids were analyzed using ^{13}C solid state NMR.

Results: Reaction of GLU and water in the presence of NaHCO_3 yields 36 mg of black solids, which is ~ 45 % lower yield than that in pure water. The use of ^{13}C enriched NaHCO_3 is not expected to have any effect on the reaction mechanisms.

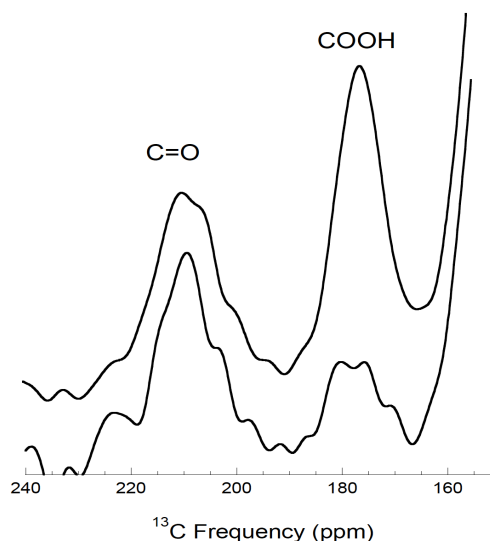


Figure 1: The carbonyl region of the ^{13}C NMR spectrum with C=O (ketone and aldehyde at 210 ppm) and COOH (carboxyl at 175 ppm). Syn-IOM after 7 hrs 250 ° synthesis. TOP, ^{13}C enriched, BOTTOM, normal abundance.

Clear evidence for isotopic exchange is indicated for the syn-IOM in Fig. 1. The area of the COOH peak with enriched NaHCO_3 is 9 X that of the normal indicating that $^{13}\text{CO}_3^{2-}$ exchange with COOH has occurred during syn-IOM synthesis. We estimate that in these experiments there is ~ 23 X more $^{13}\text{CO}_3^{2-}$ than COOH groups in syn-IOM. If all COOH groups were exchanged with $^{13}\text{CO}_3^{2-}$ then the increase in intensity would be ~ 100 X. We estimate ~10 % exchange during syn-IOM synthesis.

Post synthesis exchange of $^{13}\text{CO}_3^{2-}$ exchange with COOH over 7 days at 250 °C exhibits less growth in COOH intensity as compared with exchange during synthesis. As shown in Fig. 2, clearly some $^{13}\text{CO}_3^{2-}$ exchange with COOH has occurred. The area of the COOH peak (enriched) is 1.35 X that of the same peak (not enriched). There is ~ 13 X more $^{13}\text{CO}_3^{2-}$ than COOH groups in the syn-IOM exchange experiments. We estimate ~1.5-2.0 % exchange during syn-IOM after 7 days at 250 °C.

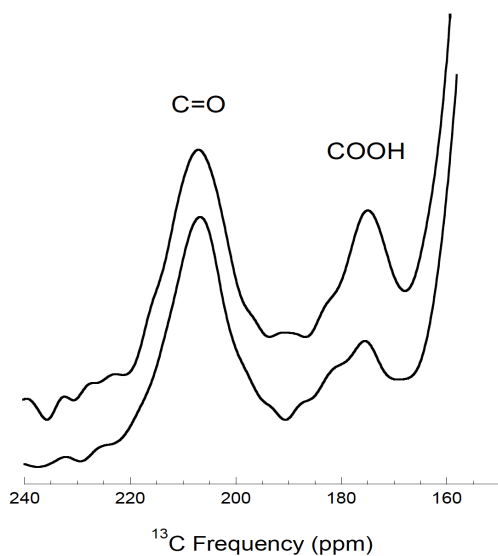


Figure 2: The carbonyl region of the ^{13}C NMR spectrum with C=O (ketone and aldehyde at 210 ppm) and COOH (carboxyl at 175 ppm). Syn-IOM after 7 days exchange at 250 °C. TOP, ^{13}C enriched, BOTTOM, normal abundance.

These results indicate that $^{13}\text{CO}_3^{2-}$ exchange with COOH is much more facile during synthesis. Considerable exchange likely occurs in the soluble molecular states that exist before syn-IOM precipitates as an insoluble black solid [8]. This is very similar to D-H exchange between water and sugars during syn-IOM synthesis which is fast, but where D-H exchange between syn-IOM solids and water after synthesis is sluggish [9]. It has been previously shown that syn-IOM synthesis kinetics are complex and evolve through two distinct soluble molecular states before syn-IOM precipitates [8]. It is anticipated that isotope exchange (either ^{13}C - ^{12}C or D-H) will precede further at lower temperatures before syn-IOM precipitates, which occurs at a much later time than at 250 °C (many hours vs. minutes) [8]. The extent to which the kinetics of isotope exchange slow as temperature is lowered has yet to be determined for $^{13}\text{CO}_3^{2-}$ exchange with COOH, it has been established for D-H exchange [9]. Experiments at 160 and 180 °C spanning 40 and 10 hours, respectively, are ongoing and will resolve this.

There is one very interesting consequence of syn-IOM rxns in the presence of NaHCO_3 . As shown in Fig. 3, the syn-IOM ^{13}C NMR spectrum (with NaHCO_3) is different than that of syn-IOM (water only) in three significant ways. First for syn-IOM (with NaHCO_3) the carbonyl and COOH (1&2, Fig.3) are considerably weaker, furanic carbon (3, Fig. 3) is reduced, and methyl groups (4, Fig.3) are greatly enhanced. The syn-IOM ^{13}C NMR spectrum (with NaHCO_3) is more similar to that of actual IOM [10]. These differences are

undoubtedly due to the higher pH NaHCO_3 bearing fluids (pH ~ 10). It is likely that actual IOM, if synthesized during parent body alteration, was likely exposed to high pH fluids due to serpentinization-like reactions.

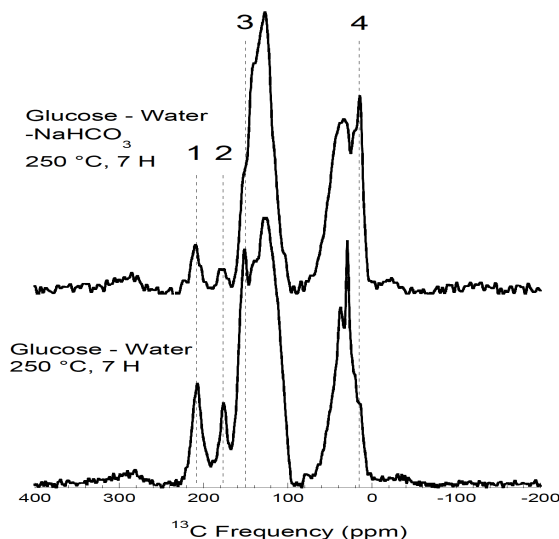


Figure 3: ^{13}C NMR spectra of syn-IOM. TOP, syn-IOM made in water with NaHCO_3 and, BOTTOM, syn-IOM made in water (only) at 250 °C 7 hours. 1) C=O, 2) COOH, 3) Furan, and 4) methyl.

These data indicate that it is likely that the ^{13}C abundances of chondritic IOM are affected by CO_3^{2-} exchange with COOH where the evidence suggests that that the CO_3^{2-} is isotopically heavy relative to the precursor material from which IOM is derived [2]. The extent to which this has occurred maybe constrained through experimental determination of exchange kinetics and determination of fractionation factors. The amount of fluid interacting with IOM during parent body processing is not well understood. Understanding the nature and relationships of isotopic abundances in IOM and carbonates may reveal more about the nature of these fluids.

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References: [1] Alexander C. M. O'D. et al. (2007), *GCA*, 71, 4380. [2] Alexander C. M. O'D. et al. (2015) *MAPS*, 50, 810. [3] Aponte J. C. et al. (2019) *MAPS*, 54, 415. [4] Seewald J. S & Boekelheide N. (2005) *GCA*, 69, supp. A558. [5] Glein C. & Cody G.D. 2013, *AGU Fall Abs* ID B13B-0459, [6] Cody G. D. et al. 2011 *PNAS*, 108, 19171, [7] Kebukawa Y. et al. 2013 *ApJ* 771, 1 [8] Cody G. D. et al. 2020 *LPSC* # 2291. [9] Kebukawa Y. et al. 2021, *MAPS*, 56, 440. [10] Cody G.D & Alexander C. M. O'D., 2005 *GCA*, 69, 1085.