

LABORATORY SYNTHESIS OF CHONDRITIC ORGANIC SOLIDS (syn-IOM): INSIGHTS AND CONSEQUENCES. G. D. Cody¹, D. I. Foustoukos¹, and E. Bullock¹, ¹Geophysical Laboratory Carnegie Institution for Science (gcody@ciw.edu).

Introduction: Carbonaceous chondrites contain large quantities of solid organic matter that is chemically complex (with regards to molecular structure and the distribution of organic functional groups [1]); these solids are termed Insoluble Organic Matter (IOM). There are a number of different IOM synthesis scenarios. The scenario we focus on is where IOM synthesis occurs post-planetesimal accretion and within planetesimal interiors [2-4], i.e., interstellar formaldehyde polymerizes with itself to make various sugar molecules ($C_nH_{2n}O_n$); under aquathermolytic conditions driven by radiogenic parent body heating, these sugar molecules then undergo subsequent reaction to form IOM.

We find that polymers made with formaldehyde are compositionally and morphologically very similar to IOM [2,3]. Thus, this synthesis is a potential source of syn-IOM for various experimental studies, without consuming actual IOM (rare and expensive). The problem is that in addition to formaldehyde, the formose dimer glycolaldehyde is also required (and is very expensive) if large amounts of syn-IOM is required. Here we show that starting with a C6 sugar ($C_6H_{12}O_6$) we achieve similarly satisfactory syn-IOM, but at a low cost that allows gram quantities if desired. Using a simple C6 sugar also allows us to gain insight into the syn-IOM reaction mechanism and identify potentially interesting consequences to planetesimal evolution.

Experimental: Aqueous solutions of C6 sugar (glucose) with a composition of 1 formaldehyde (equiv) : 100 H₂O (in the range of interstellar ices [5]) are flame sealed into glass ampules and heated isothermally at 150, 200, and 250 °C (36, 5, and 3 hrs duration). ***Warning: this reaction at the higher temperatures can generate potentially dangerous gas pressure! Be careful!*** After reaction the ampules are immersed in Liquid N₂ before opening. In the case of the 200 and 250 °C one observes nearly colorless liquid and a brown-black solid and considerable gas pressure in the ampule head space- see warning above. In the case of the 150 °C reaction, even after 36 hours, the aqueous solution remains strongly colored and noticeably viscous indicating the syn-IOM reaction has not yet gone to completion; gas pressure is also lower. The mass recovery of solids was ca. 48 %, 60 % and 40 %, for reactions at 150, 200, and 250 °C.

These solids were analyzed chemically using ¹H-¹³C cross polarization solid state NMR (e.g. [1]). The presence of different organic functional groups are determined by their characteristic resonance frequencies, with concentration by peak integration .

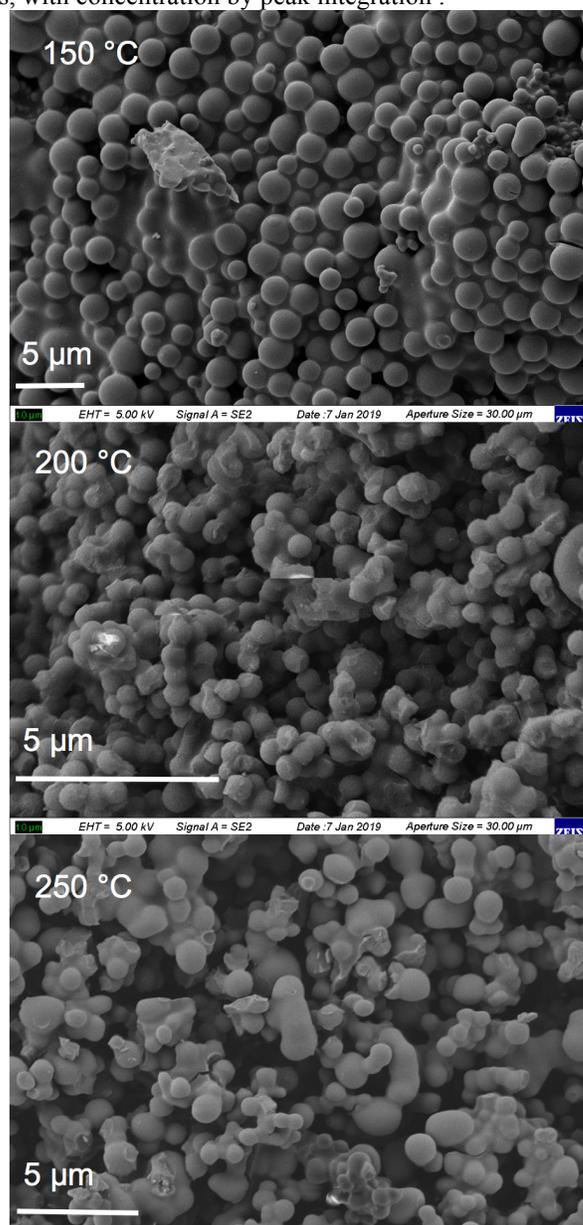


Figure 1: SEM images of syn-IOM recovered from aqueous reactions at 150, 200, and 250 °C. The spheroidal particles are a characteristic phase morphology derived from polymerization induced liquid immiscibility.

Results: SEM: In fig 1 SEM images of the syn-IOM highlight the signature texture of the reaction: micron scale spheroidal particles (with a moderate size range dispersity- ~ order of 10 to 0.1 μm in diameter around 1 μm) and many particles are also likely to be hollow [2,3]. Chondritic IOM is morphologically similar to syn-IOM formed from either formaldehyde [2,3], C4 [6] or C6 sugars (e.g. nanoglobules [2,7]). The spheroidal shapes of syn-IOM particles records the physics of liquid-liquid phase separation driven by the emergence of a polymerization induced immiscibility gap. Whether similarity in morphology is evidence of similarity in physico-chemical process remains to be determined. It is reasonable to assume that process-morphology relationships should occur and any chemical scenario proposed for IOM synthesis should also explain IOM morphology.

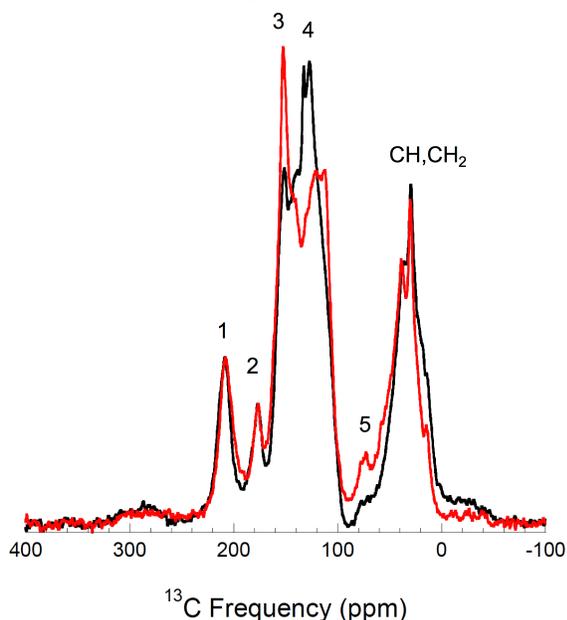
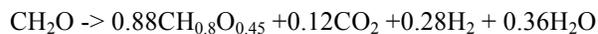


Figure 2: ^{13}C SSNMR of syn-IOM, 200 $^{\circ}\text{C}$ (red) and 250 $^{\circ}\text{C}$ (black). Peaks: 1-carbonyl, 2-carboxyl, 3-furan, 4-aromatic, 5-alcohol, CH,CH₂-aliphatic carbon.

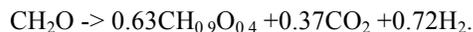
^{13}C NMR: In fig 2 ^{13}C SSNMR spectra are shown for 200 and 250 $^{\circ}$ C syn-IOM (note for 150 $^{\circ}\text{C}$ it is more difficult to separate solids from partially polymerized material in the aqueous phase and these data are not included here). The molecular transformation from C6 sugar to syn-IOM is profound- dehydration and hydrogenation reactions yield predominantly sp^2 hybridized carbon (olefinic, furanic and aromatic) and $\text{CH}_{1,2}$ (sp^3) carbon. The fraction of aromatic carbon (F_A) is 0.56 in both cases.

The ^{13}C SSNMR spectra enable an estimate of atomic composition of syn-IOM via determining the quantity of a given functional group, e.g. COOH.

Combined with mass yield enables an estimate of the reaction stoichiometry which (on a formaldehyde equivalent basis) going from C6 to product at 200 $^{\circ}\text{C}$ is:



And for C6 to product at 250 $^{\circ}\text{C}$ we find:



One can immediately see why the syn-IOM generating reaction demands respect. For example, with heating to 250 $^{\circ}\text{C}$ one mole (formaldehyde equivalent) yields 1.1 mole of gas. We can estimate the volume necessary for the gas pressure to equal the vapor pressure of water at 250 $^{\circ}\text{C}$ (39 bar), which leads to potential ΔV for the reaction equal to 33x the initial volume.

Implications for Planetesimal Evolution: There are two potentially interesting implications for planetesimal evolution. First, as noted previously [8], if the fluid pressure (P_F) exceeds the sum of the confining pressure (P_{IS}) and the tensile strength of the planetesimal (τ), then fracturing will occur. If we assume a planetesimal composed of 50 % silicate and 50 % ice ($\rho \sim 2 \text{ g/cm}^3$), we recognize that for small bodies the P_{IS} is not large ($\sim 140 \text{ bar}$ - $R=50 \text{ km}$, $\sim 500 \text{ bar}$, $R=100 \text{ km}$ in the center). This suggests that the IOM forming reaction will greatly enhance the probability of “hydro” fracturing of the planetesimal.

The second interesting implication is that as the planetesimal interior heats above 473-523 K, excess gas pressure will force reduced gasses and water outwards through towards cooler regions. Whereas H_2O and CO_2 may condense close to the surface of the planetesimal, it appears unlikely that H_2 will and will be vented into space. Thus, in the range of 273 to 523 K the fluids will be CO_2 rich and reduced.

Acknowledgments: We are grateful for financial support though NASA EW (NNX16A30G)-GDC. Syn-IOM has also been made to support NASA EW grant NNX15AH77G (DF) and to obtain optical constants in support of NASA ERP NNX17AB91G (AW).

References: [1] Cody G. D. and Alexander C. M. O'D. (2005) *GCA*, 69, 1085. [2] Cody G. D. et al. (2011) *PNAS* 108, 19171. [3] Kebukawa Y. et al. (2013) *ApJ* 771, 1-12. [4] Kebukawa Y. and Cody G. D. (2015) *Icarus* 248, 412. [5] Greenberg J.M. (1998) *Astro.Astrophys* 330, 375. [6] Weber A. L. (2005) *OLEB* 35, 523. [7] De Gregorio B. T. et al.. (2013) *Meteoritics & Planet. Sci.*, 48, 904. [8] Grimm R. E. and McSween H. Y. (1989) *Icarus* 82, 244.