TEM DATA & THERMAL HISTORY MODELS FOR PRESOLAR CORE\RIM CARBON SPHERES.

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Introduction: The subset of presolar grains extracted from meteorites, and made up of s-process isotopes, likely formed around thermally pulsing asymptotic giant branch (AGB) stars "after third dredge-up" of newly made carbon atoms [1]. In particular the core\rim subset of micron-size carbon spheres in presolar collections e.g. from the meteorite Murchison contain unlayered graphene sheets in their core [2,3], whose size and abundance likely provide information on the thermal history during formation. Laboratory evidence for supercooled droplet formation during carbon vapor condensation [4,5], the spherical nature of the cores with their atomically-abrupt transition from core to rim, and TEM evidence for unlayered graphene structures (some in the form of faceted pentacones), have in particular prompted us to construct models for nucleation and growth of these sheets from a supercooled carbon melt for various cooling rates [6].

In particular we show how a Debye scattering analysis of electron powder diffraction profiles from both laboratory grown and presolar onion cores [7] can be used to estimate mass weighted average sheet size and number density, and how a first-order analytical nucleation and growth model can be used therewith to estimate the stellar atmosphere cooling rate *during solidification* from a given microtome-sliced core\rim particle. In particular the literature on containerless solidification of metallic liquids suggests that carbon liquid may supercool further than for common metals, e.g. to 50% of the effective melting temperature.

TEM characterization: The Debye scattering equation [8] allows one to calculate the interference effect of small randomly-oriented crystalline clusters on otherwise diffuse atomic scattering from a specimen. It is ideal for working with oddly-shaped clusters (like unlayered graphene sheets, and faceted carbon pentacones) because molecule shape effects (like the high-frequency tails on powder diffraction peaks from atom-thick sheets [9]) are automatically taken into account in its predictions.

Electron powder diffraction (and HRTEM) observations of presolar onion cores suggest an average graphene sheet size of about 40A coherence width, or $N \approx 612$ atoms per cluster. Diffraction from the labgrown cores instead suggest sheets with only 12A coherence width, or $N \approx 60$ atoms per cluster. This is not surprising since the small size of our oven interior suggests that condensed particles impact an oven wall within about 10 milliseconds, while containerless cooling of carbon condensate in a red giant photosphere might take place over much longer times (limited only e.g. by radiation pressure ejection).

One way to estimate the fraction crystalline at each peak is to measure three heights at the peak frequency on a model "100%-crystalline" Debye system with comparable peak width, namely the *total peak height* s_2, the *estimated background height* s_1 beneath the peak, and the *"diffuse-scattering baseline" height* s_x. Then on an "experimental profile" (see Fig. below) measure the observed *total peak height* h_2 and the corresponding *peak background* h_1 beneath the peak.

core−only Fig. 3 (red) vs. presolar core #3184 (blue)
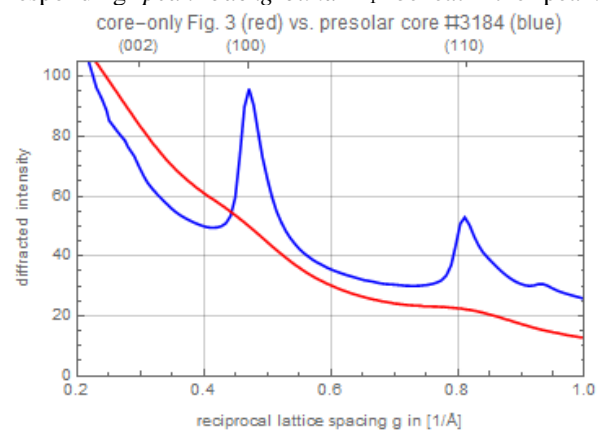
One can infer the *experimental baseline height* h_x by assuming that the incoherent baseline position is where the model predicts i.e. $(h_x-h_1)/(h_2-h_1) = (s_x-s_1)/(s_2-s_1)$, so that $h_x = h_1+(h_2-h_1)(s_x-s_1)/(s_2-s_1)$. The *non-crystalline background component* h_o may then be inferred by assuming that the crystalline-component peak shape follows the prediction i.e. $(h_x-h_o)/(h_2-h_o) = s_x/s_2$ so that $h_o = (h_1s_2-h_2s_1)/(s_2-s_1)$, where any combination of subscripts 1, 2 and x may be used in place of subscripts x and 2 here. Finally, the *fraction crystalline* f_x may be estimated if one divides the inferred crystalline-component baseline by the experimental baseline, i.e. $f_x \approx (h_x-h_o)/h_x = ((h_2-h_1)s_x/((h_2-h_1)s_x+h_1s_2-h_2s_1))$.

This fraction crystalline will be less than one provided that the total peak to (peak-background) height ratio is less in the experimental sample i.e. $h_2/h_1 < s_2/s_1$, and hence that the non-crystalline background height h_o is positive. By measuring this f_x value on a given profile at more than one peak, one might report a mean and a measure of uncertainty as well. For the experimental (e.g. Fig. 1) and model pattern profiles, the fraction of atoms in unlayered graphene sheets about 600 atoms in size (presolar) and 60 atoms in size (lab grown) is estimated to be about 40% and 12%, respectively.

Models: The nucleation and growth of carbon is different than most elemental systems as the amorphous liquid is 3D and the corresponding nucleation seed and graphene sheet growth is 2D. Our nucleation model builds on the classic and modern approaches of classical nucleation theory [10,11,12,13]. The growth model follows a single fixed Arrhenius activation energy model [14,15], starting with our independent DFT and experimental work predictions of 5- and 6-atom critical nucleus rings. Our models use data from electron microscope study of presolar and lab grown "cores", DFT predictions from other works, and data obtained from our own molecular dynamics studies.

n_c versus s_{avg} red for cooling rates > 31000K/s
from 3250 to 1750K; saturation: green dashed
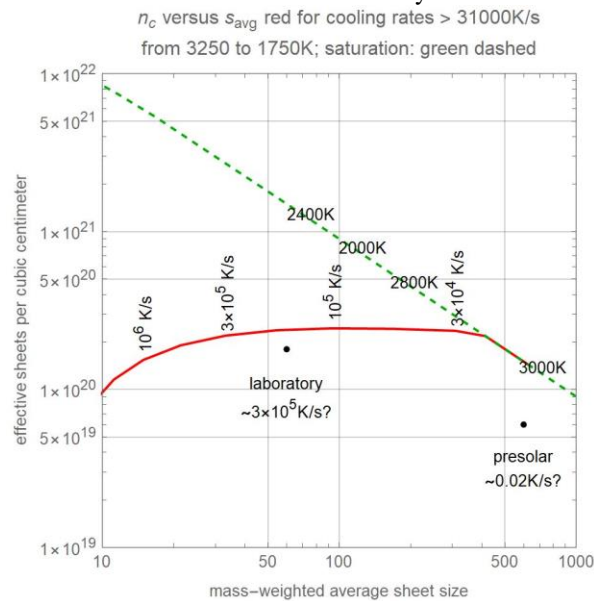
Results: The current model (outlined in terms of measureable quantities in the 2nd figure) is consistent with 50% supercooling to 2350 K, deeper than the 30% "containerless" for most elemental metallic liquids. The nucleation model is sensitive to the ratio between the latent heat of fusion and the edge energy (analogous to the surface tension). The ratio between these two parameters is key to having a model of nucleation of liquid carbon make physical predictions and have different critical nucleation temperature dependence when considering 3D or 2D classical nucleation.

A physical mechanism to explain the greater abundance of smaller sheets in rapidly-cooled lab-grown cores, than in the presolar cores, also emerged. The presolar cores have much more time to grow sheets until "saturation", when they run out of conveniently placed atoms for growth, while mobility is high and well before the nucleation rate peak e.g. at 2350K. Using a numerical approach for the slow cooling saturation caused an asymptotic low cooling rate and when comparing to our analytical model, we saw the numerical model lineup exactly where this switch occurred.

Discussion: Run in reverse, from TEM observations of the number density of graphene sheets and fraction crystalline in a given core, we can put constraints on the thermal history of that particle e.g. during formation in a stellar atmosphere. As discussed in a separate abstract to this meeting, in fact, this model already help put the formation location for core\rim particles deeper into the stellar atmosphere, and likely in regions with a lower O/C ratio.

Further work on these individual particle cooling rate models is clearly needed, as is further work on slow-cooled carbon vapor in the laboratory. In particular, a more sophisticated (but still crude) model for saturation assuming a kind of Ostwald ripening might allow for better resolution at inferring stellar atmosphere cooling rates for a given particle. Of course, the astrophysical applications of this work are predicated on the future availability of presolar core\rim carbon particles, in the kind of collections made available e.g. by researchers at U. Chicago.

The results are also relevant to the materials science community, in understanding metastable liquid carbon at low pressures as well as in exploring the possible diffusion-barrier properties of unlayered-graphene composite materials. We should add that the likely phenomenal diffusion barrier properties of this material are very likely locking observable heavy atoms in place from those stellar atmospheres, for inventory in modern TEM's here on earth.

References: [1] cf. Croat T. K. et al (2005) *ApJ*, **631**, 976-987. [2] Fraundorf P and Wackenhut M. (2002) *ApJLett* **578**(2):L153-156. [3] Croat T. K. et al, (2014) *Elements* **10**, 441-446. [4] De Heer W. A. et al. (2005) *Science* **307**:5711, 907–910. [5] Hundley T. J. and Fraundorf P. (2018) *49th LPSC (#2083), 2154-2155.* [6] Chrostoski P. C., (2021) PhD dissertation, UM St. Louis. [7] Fraundorf P. et al (2020) *Microscopy and Microanalysis*, **26**:S2, 2838-2840. [8] Warren B. E. (1969) X-ray diffraction (Reading MA). [9] Warren B. E. (1941) *PhysRev* **59**(9), 693. [10] Los J. H. et. al. (2015) *Phys. Rev. B*, **91**, 045415. [11] Turnbull D. and Fisher J. C. (1949) *J. Chem. Phys.*, **17**, 71. [12] Kelton K. and Greer A. L. (2010) *Elsevier.* [13] Callister W. D. and Rethwisch D. G. (2007) *Wiley New York.* [14] Chrostoski P. et. al. (2021) *MRS Advances*, **6**, 713–717. [15] Laidler K. J. (1987) *Harper & Row.*