LAB SIMULATION OF CARBON DROPLET COOLING IN AGB STAR ATMOSPHERES.

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Introduction: A significant fraction of micron-sized presolar “high-density” graphite onions (e.g. from Murchison KFC1) likely formed in AGB star atmospheres[1], and have concentric graphite shells surrounding a core of unlayered graphene [3,4]. HR-TEM images suggest flat 4[nm] wide graphene sheets connected by pentagonal defects [5-7]. The absence of “carbide seeds” sometimes found in presolar onions without these cores, plus their “almost graphitic” densities [8] and spherical shapes with a sharp transition to a graphitic rim, all suggest homogeneous nucleation and atom-by-atom growth *from the vapor phase onto a super-cooled liquid droplet*, followed by graphite rim growth after droplet solidification [9,10]. The absence of otherwise ubiquitous (002) layering, seen even in highly disordered carbons on earth, may be explained by the proximity of unsolidified carbon atoms during melt solidification.

On warming, carbon at pressures below 10.8[MPa], sublimates to a vapor at around 3915K. On cooling, however, containerless metals in general supercool as liquids until as much as 30% below the boiling point [11], depending on the amount of rearrangement needed between liquid and solid state configurations. This led us to conjecture [9] that carbon, with a liquid to vapor point nearer to 4600K, and the need for rearrangement of atoms from 12 nearest-neighbor coordination in the liquid to a graphene sheet structure, might predictably supercool to temperatures as low as 3200K in the absence of condensation seeds.

In fact, the formation of liquid carbon droplets at low pressure in laser ablation experiments has been experimentally documented [12,13]. However, the rapid radiative cooling (e.g. on microsecond timescales) of micron-sized carbon droplets in “earth-ambient” environments may limit the growth of large (e.g. 4-nm coherence width) graphene sheets during the solidification process.

In this context, computer simulation of carbon droplet solidification might help explore both: (i) graphene sheet nucleation on pentagonal versus hexagonal loops, and (ii) growth of flat sheets and e.g. faceted pentacones in the solidifying melt [10]. For the latter application, however, these simulations generally take place over much shorter (i.e. picosecond) time scales [14]. Although graphitization can sometimes be achieved [15], this might a result of annealing done at temperatures just below melting. So far these simulations have not generated the unlayered graphene structures seen in the presolar onion cores. Can simulations with real carbon atoms do better?

Laboratory cooling rates for carbon particles condensing from the vapor phase near 3900K will be dominated by radiative heat transfer, and be quite rapid unless the radiative environment surrounding the condensing gas is comparably hot. Control of the cooling rate, however, might be possible with a closed millimeter-scale resistively heated carbon oven whose evaporation is the source of the carbon vapor [10]. This will have particle settling times on earth in the millisecond instead of microsecond time scales, and allow introduction of ambient gases as well. A larger oven, or one in microgravity, might allow one to explore even slower cooling rates, if needed.

Experimental Methods: Following earlier work by Melanie Lipp [10], we’ve run anneals so far with three 6.2 mm diameter hollow graphite ovens, resistively heated in a Balzer’s turbopumped vacuum evaporator. Exterior color temperatures maps (Fig. 1) were estimated with Nikon 1 camera images of the oven seen through neutral density filters, and well as cellphone camera “movies”. Particles were collected using a Pt loop from deposited material on a “flat” inside the oven cavity, and examined on holey or lacey carbon supports at 250 keV in an EM430ST TEM.

Results: Graphite onion structures appeared in each of specimens examined, along with irregular graphite flakes and likely carbon nanotubes (Fig. 2). The onions had diameters in the 0.1 to 0.4 micron range, making them possible to characterize by diffraction contrast (unlike many of the micron-sized presolar onions) without slicing via microtome. Many of these had a core-rim configuration, like that shown at top in Fig. 2, and in Fig. 3a.

Preliminary analysis of the “whole onion” diffraction pattern (Figs. 3b and 3c) shows the expected (002) spacing from the rim, as well as unexpectedly strong (hk0) spacings with high frequency tails. The tails are expected from rim “random-layer-lattice” graphite, but are also consistent with diffraction from an unlayered graphene core, which in this case constitutes about 60% of the particle by volume.

Discussion: Observations confirm that condensing carbon vapor can create core-rim graphite onions with prospects for cooling rate control, and that future lab simulations may help us interpret the conditions behind unlayered-graphene crystallization in presolar onion cores, following precipitation in cool star atmospheres.

References::

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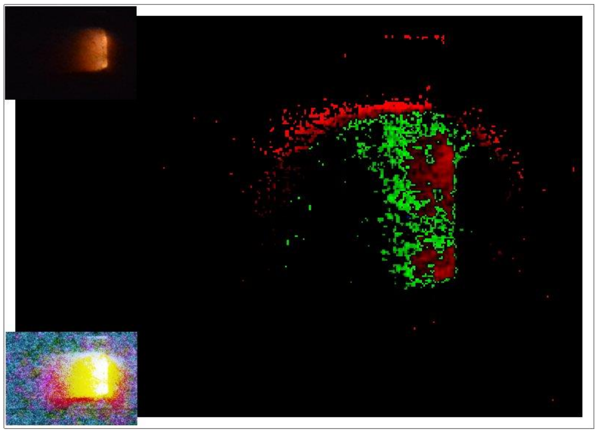

Figure 1. Color-temperature map of a 1/16000 second oven image from our first 6 minute "oven burn" in the upper left inset, with temperatures between 3000K and 4000K in red, between 2000K and 3000K in green, between 1000K and 2000K in blue, and black where the brightness is "down in the weeds". At lower left is a histogram-linearized version of the top left image, to highlight faint structures.

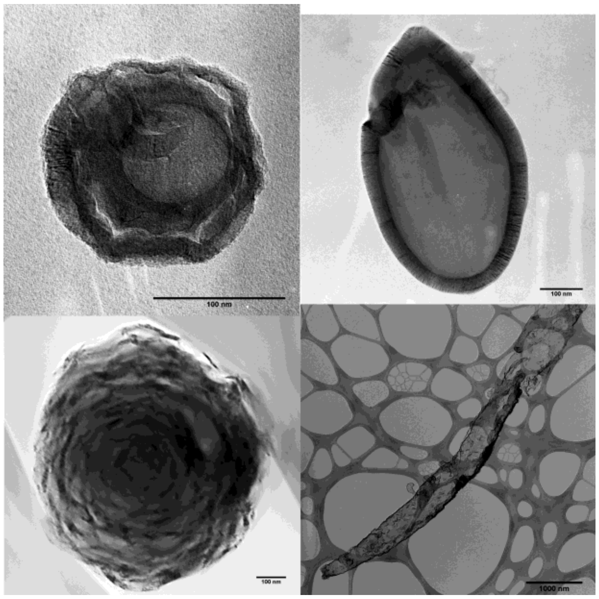

Figure 2. At top are core-rim onions, one small and another oval in shape, at bottom are a rim-only onion (left) and a likely wall-grown nanotube (right).

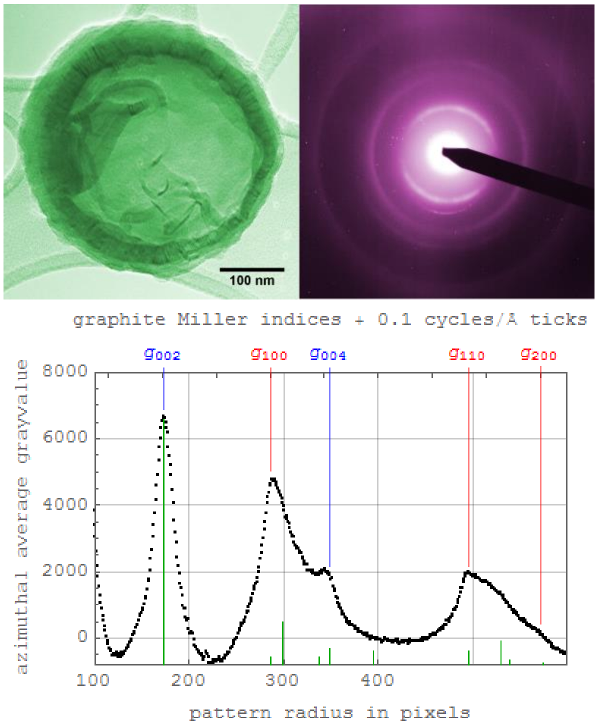

Figure 3. Brightfield TEM image (a) at top left of a graphite particle from our third annealing run, (b) a selected area diffraction pattern of the whole particle at top right, and (c) a background subtracted azimuthally-averaged profile analysis at bottom.