

SURVIVAL OF CARBON IN MODERATELY TO STRONGLY HEATED IDPS AND MICROMETEORITES

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Introduction: Extraterrestrial dust particles in the 20 to 400 μm size range deliver on the order of 3000 tons of carbon to the Earth each year. When the solar system was young, both the asteroid belt and the Kuiper belt were more fully populated, and the annual accretion of small particles may have been orders of magnitude higher. Dense dust disks are common around young solar-like stars [1], suggesting that extensive accretion of small cometary particles is probably a very common process for planets in their first 400 million years of existence. During its pre-biotic period, Earth could have accreted as much as a centimeter of carbonaceous matter each million years. We are investigating the nature of carbon currently carried to Earth in $< 500\mu\text{m}$ particles in order to better understand the possible roles that small meteoroids may have played in pre-biotic chemical evolution on Earth and in the more general case of habitable zone planets elsewhere. The particles deliver organic material from comets and asteroids but the most abundant form of solid carbon that survives atmospheric entry is probably strongly heated pyrolyzed material, essentially carbonaceous meteor ash. This material has many interesting properties and it may aid the prebiotic synthesis of complex organic compounds on planets or conversely it might actually impede these processes by simply adsorbing complex molecules and isolating them from further processing.

Delivery & heating: Carbon in small meteoroids is delivered to the top of our atmosphere as asteroidal, cometary and interstellar materials. Original organic materials are modified by pulse heating for a few seconds duration at altitudes near 90 km where the ambient pressure is 10^{-6} atmosphere. The carrier meteoroids undergo a range of thermal transformation depending on the degree and duration of atmospheric heating, a process that is strongly dependent on entry speed and particle size. Toppani et al [2], Genge et al [3] and others have described sequential effects of atmospheric pulse heating on micrometeorites of $100\mu\text{m}$ size. Most particles begin as fine grained chondritic composition materials. When heated to high temperatures for just a few seconds they undergo the following series of transformations: A) above 1300°C they develop fine vesicles as trace phases begin to melt and some volatiles are lost, B) at higher temperatures the vesicles grow and the particles become **vesicular**, C) at temperatures near 1500°C they are dominated by large vesicles and become **scoriaceous** and D) at temperatures above 1500°C they totally melt, lose vesicles and form **cosmic spherules**. In addition to the thermal effects on silicates, there is also a thermal alteration sequence on organic components. The general sequence of these steps should include 1) initial partial loss of volatiles such as H_2O , NH_3 , CH_4 and CO as pyrolysis begins, 2) formation of char 3) formation of activated carbon and ultimately 4) complete combustion to CO and CO_2 [4]. We believe that stage 4 is rarely reached even when particles reach the totally melted spherule stage and that solid carbon does survive. We have done heating experiments on pyrolysis char heated under the ram pressure conditions experienced by $100\mu\text{m}$ meteoroids at 90 km altitude. We have found that the carbon "burn rate" is

$< 1\mu\text{m s}^{-1}$. Only micron and thinner carbon flakes on the surfaces of particles should be totally burned. Last year we reported on 10-20 μm IDPs that had been just heated to the point where they form spherules. In these small particles, refractory carbon char (or ash) survived even though the silicates melted and formed spheres. This work suggested that a significant fraction of the total carbon arriving at Earth might survive as nearly pure carbon ash that separated from strongly heated particles that melted and formed cosmic spherules. A unique aspect of the ash is that it is highly porous and contains submicron beads of FeNi metal surrounded by thin (4nm) rims of graphite[5].

Samples: The goal of the present work is to determine the nature of surviving carbon from or in particles that are close to the peak in the meteoroid mass distribution at $200\mu\text{m}$ [6]. The present work includes $< 50\mu\text{m}$ stratospheric IDPs that are minimally heated and Antarctic micrometeorites $> 50\mu\text{m}$ that are usually more strongly heated. Here we will use the modern definitions of IDPs as small extraterrestrial particles ($< 50\mu\text{m}$ diameter) and micrometeorites as particles $\sim 100\mu\text{m}$ in size that can be seen with the naked eye. For the larger particles we studied over a hundred irregular (unmelted) chondritic particles collected from the South Pole water well (SPWW) [7]. These were hand picked from a 75-100 μm size fraction that had been isolated as a weakly magnetic component. We found that over half of the black irregular particles that did not have smooth surfaces were chondritic composition micrometeorites that included all of the types from unmelted to scoriaceous.

C ash from spherule formation: Our initial search was to find $100\mu\text{m}$ pieces of carbonaceous meteor ash, residual carbon left over from the spherule-forming melting of micrometeorites $> 100\mu\text{m}$. We were searching for larger pieces of the same material found as $10\mu\text{m}$ carbon particles in the stratosphere. We examined mounts containing over 100 polished sections of black extraterrestrial SPWW samples. We did find nearly pure carbon particles with tiny FeNi beads but the beads also contained some Cu and Cr and the beads did not have the distinctive graphite rims found in stratospheric ash and laboratory simulations[5]. We believe that most, and likely all, of the pure carbon SPWW particles that we found are terrestrial particles, possibly related to an electrical fire that previously occurred at the top of the well. We estimate that the ratio of chondritic particles to carbon ash particles at $100\mu\text{m}$ size is less than 0.1. This estimate could be misleading if the carbon particles float or if they fragment in the ice, water, or during collection or handling. If the measurement is a correct estimate of the atmospheric ratio then it implies that pure carbonaceous meteor ash only rarely occurs in pieces as large as $100\mu\text{m}$. If most of the carbon from cosmic spherule formation does survive as solids it must be as particles $< 50\mu\text{m}$ in diameter.

C in vesicular & scoriaceous particles: We have also explored the modification and survival of carbon in strongly heated but not totally melted SPWW micrometeorites. Our approach was to examine microtomed sections in the TEM before and after removal of silicates by HF etching [8]. To

understand the nature and heating state of these particles it was essential to section large numbers of particles and examine them in the SEM. The interior can only be understood by sectioning but it was an challenge to do this in a way that does not permanently introduce carbon into the particles and it was also a challenge because particles as large as 100 μm are usually not microtomed due to a variety of difficult ties and risks. We ultimately devised a means where individual micrometeorites were mounted in Crystalbond 509 (a hard transparent wax-like proprietary mounting media) cylinders mounted in Teflon. The particles were sectioned by vibratory polishing techniques and examined in the SEM. Selected samples were dissolved out of the Crystalbond with acetone and then crushed and remounted on special mounts of Crystalbond and epoxy for microtoming. The microtome sections were treated with acetone to remove Crystalbond. After imaging in the TEM the sections were then etched with HF to remove the silicates so that the carbonaceous phases could be seen without interference from other phases.

In the SEM view of strongly heated vesicular to scoriaceous particles we could see no obvious evidence for carbon. In the scoriaceous particles, and in particular the cored particles that have unmelted interiors surrounded by largely recrystallized exteriors, one might expect to see either micron size sections of carbon or lenses of carbon separating strongly heated but immiscible silicates. In etched TEM sections we did see residual amorphous carbon essentially identical to that seen in strongly heated stratospheric particles [8]. Maurette [10] also reports seeing indigenous carbon in TEM sections of scoriaceous particles. It is particularly significant that we saw this material in particles so strongly heated that they were dominated by recrystallized olivine. Particles heated very close to the spherule formation range still retain carbon. The surviving carbon retains the unique signature of <100nm metal beads surrounded by thin layers of graphite.

Conclusions: We have examined particles in the size range that is believed to deliver most of the carbon that has

fallen to Earth since the end of its accretion from the solar nebula. We have not found abundant pure carbon particles as large as 100 μm that may be shed by the process of forming cosmic spheres. If pure carbonaceous meteor ash plays a significant astrobiological role it probably is due to small particles less than tens of microns in size. If its activated carbon plays a role in concentrating pre-biotic molecules it apparently only do it on this size scale. We do see thermally transformed carbon in particles that appear to have been heated to 1500 $^{\circ}\text{C}$. The surviving carbon is amorphous, highly vesicular and contains numerous tiny metal grains coated with thin graphite rims. Other work [10] shows that some IDPs retain C-H and C-O bonds and contain relatively well preserved organic material. The rain of IDP and micrometeorite carbon that falls on the Earth is a rich mix of carbonaceous materials ranging from preserved organic compounds to strongly activated carbon with enormous area/mass ratios and even tiny catalytic metal beads. It is nearly certain that these types of materials are abundant when life first evolves on any planet [9] that forms in a planetary system that has comets, asteroids or other dust producing sources of primitive materials.

[1] Habing, H. J., et al. (1999) *Nature* 401, 456-458. [2] Toppani, Libourel, A., G. Engrand, C. & Maurette, M. (2001). *MAPS* 36, 1377-1396. [3] Genge, M. J., Grady, M. M. & Hutchison, R. (1997) *GCA* 61, 5149. [4] Smith, K.L. et al, *The structure and reaction processed of coal*, Plenum Chem. Engineering Series, Ed Dan Loss Plenum Press 1994. [5] Brownlee, D. E., Joswiak, D. J., Bradley, J. Kress, M. Pepin, R. Schlutter, D. & Palma, R. (2001) *LPSC* 32, 2170. [6] Kyte, F. T. & Wasson, J. T. (1986) *Science* 232, 1225-1229 [7] Taylor, S. et al, (1998) *Nature* 98, 392, 899-903. [8] Brownlee, D. E., Joswiak, D. J., Bradley, J. P, Gezo, J. C. and Hill H. G. M. (2000) *LPSC* 31, 192. [9] Maurette, M. (1998) in *Origins of Life and Evolution of the biosphere*, 28; 385-412, Kluwer [10] Flynn, G. et al. *LPSC* 2002.

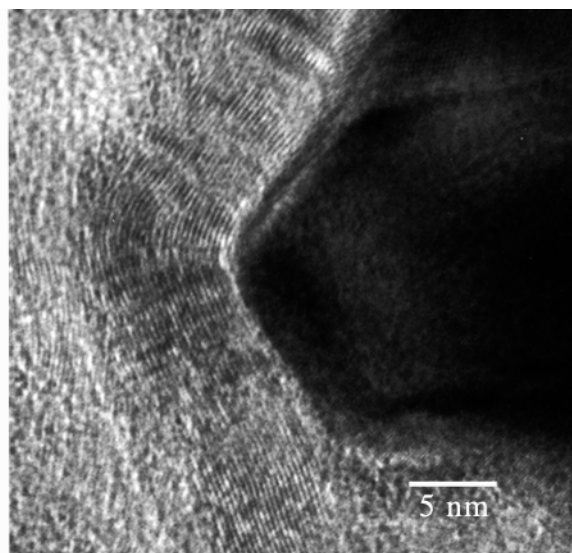
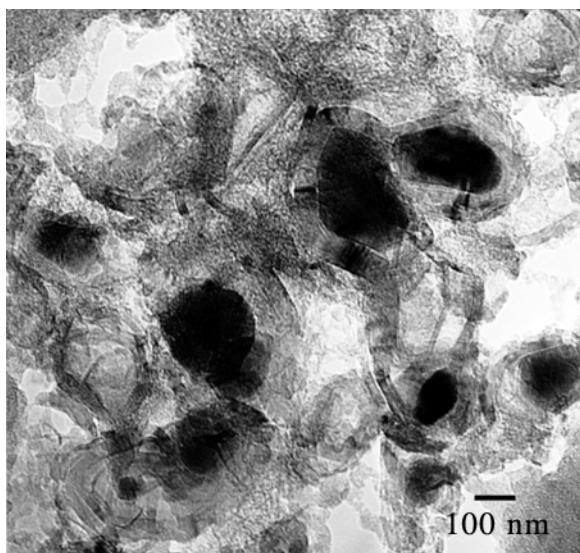


Figure 1 Low magnification image of carbonaceous meteor ash showing amorphous carbon and small FeNi metal beads coated rimmed with thin graphite layers. Image on right is a higher magnification view of a graphite rim on a metal bead (dark grain).