Making Unique Samples for the Cosmochemistry Community

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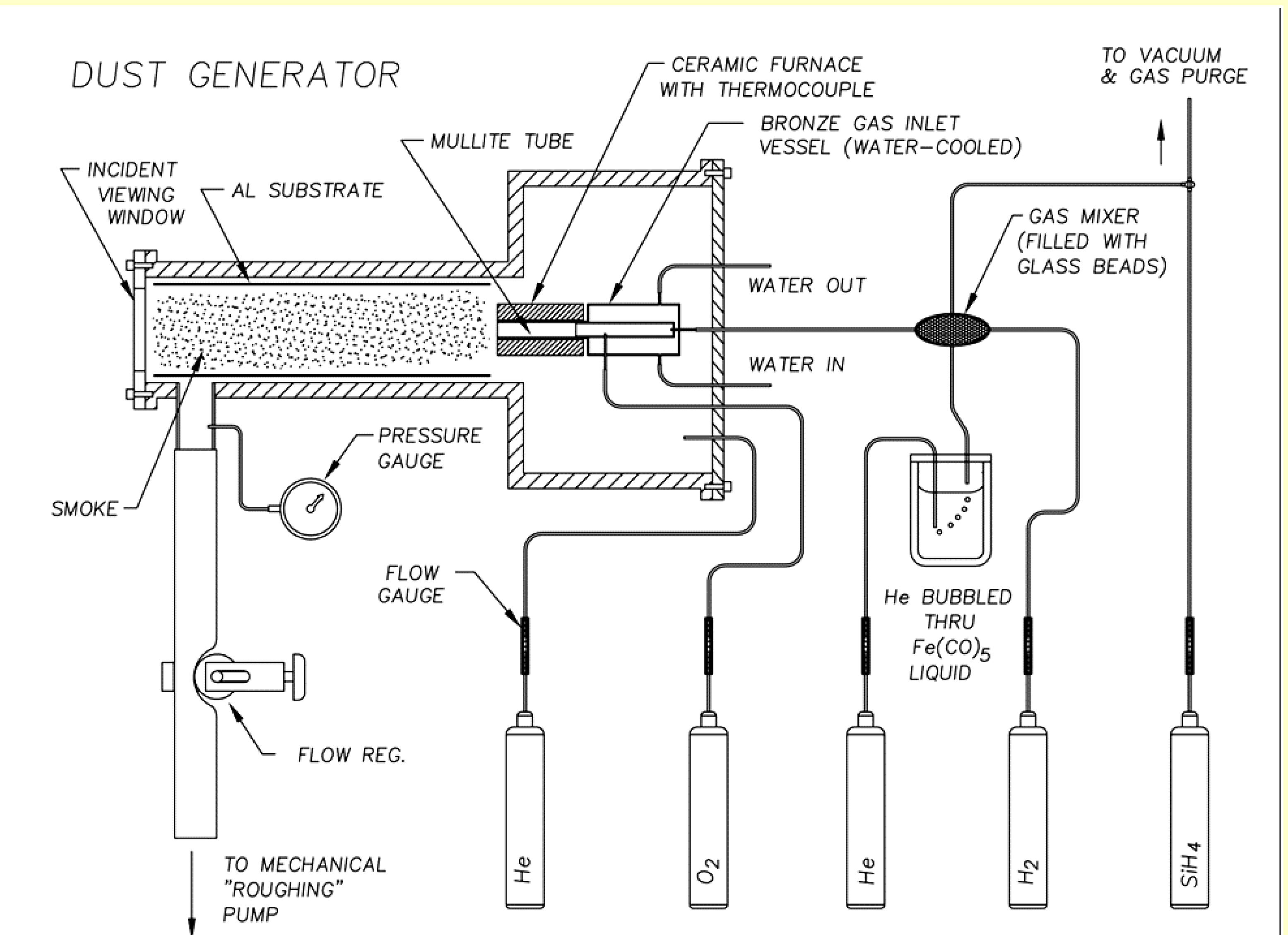
Summary

Condensates formed in astrophysical environments are difficult to access as starting materials for laboratory studies of processes that might occur in protostellar nebulae. The original materials are more than 4 billion years old and have been modified to some unknown degree with time. While micrograms of such materials might be found in the heart of rare, unprocessed, primitive meteorites such as Acfer 094, much larger quantities of material are required in order to conduct multiple experiments at a variety of temperatures and pressures. To solve that problem we manufacture several different varieties of "natural" simulants from flowing hydrogen gas seeded with appropriate metals and exposed to a hydrogen-oxygen flame. These samples range from simple SiO_x smoke, to more complex Fe_aSiO_x, Mg_bSiO_x and $Fe_aMg_bSiO_x$ smokes that mimic the reactivity and spectral properties of fresh, vapor-phase condensates such as those that might form in circumstellar outflows or from materials vaporized by energetic processes in protostellar nebulae. In addition, we also make carbonaceous samples formed from a flowing stream of CO on the surfaces of various catalysts during surface mediated reactions in an excess of hydrogen and in the presence of N_2. Carbon deposits do not form continuous coatings on the catalytic surfaces, but instead form extremely high surface area per unit volume "filamentous" structures. While these structures will form slowly but over longer times in protostellar nebulae than in our experiments due to the lower CO pressure, such fluffy coatings on the surfaces of chondrules or CAIs could promote grain-grain sticking during low velocity collisions and might provide carbonaceous feedstock for the synthesis of interesting biochemical precursors to life during metamorphism on or in meteorite parent bodies. Both silicate smokes as well as carbonaceous solids have been made available to the scientific community for use in their own cosmochemical experiments. Thanks to support from NASA Headquarters, similar analog samples are available free of charge to the wider planetary science community.

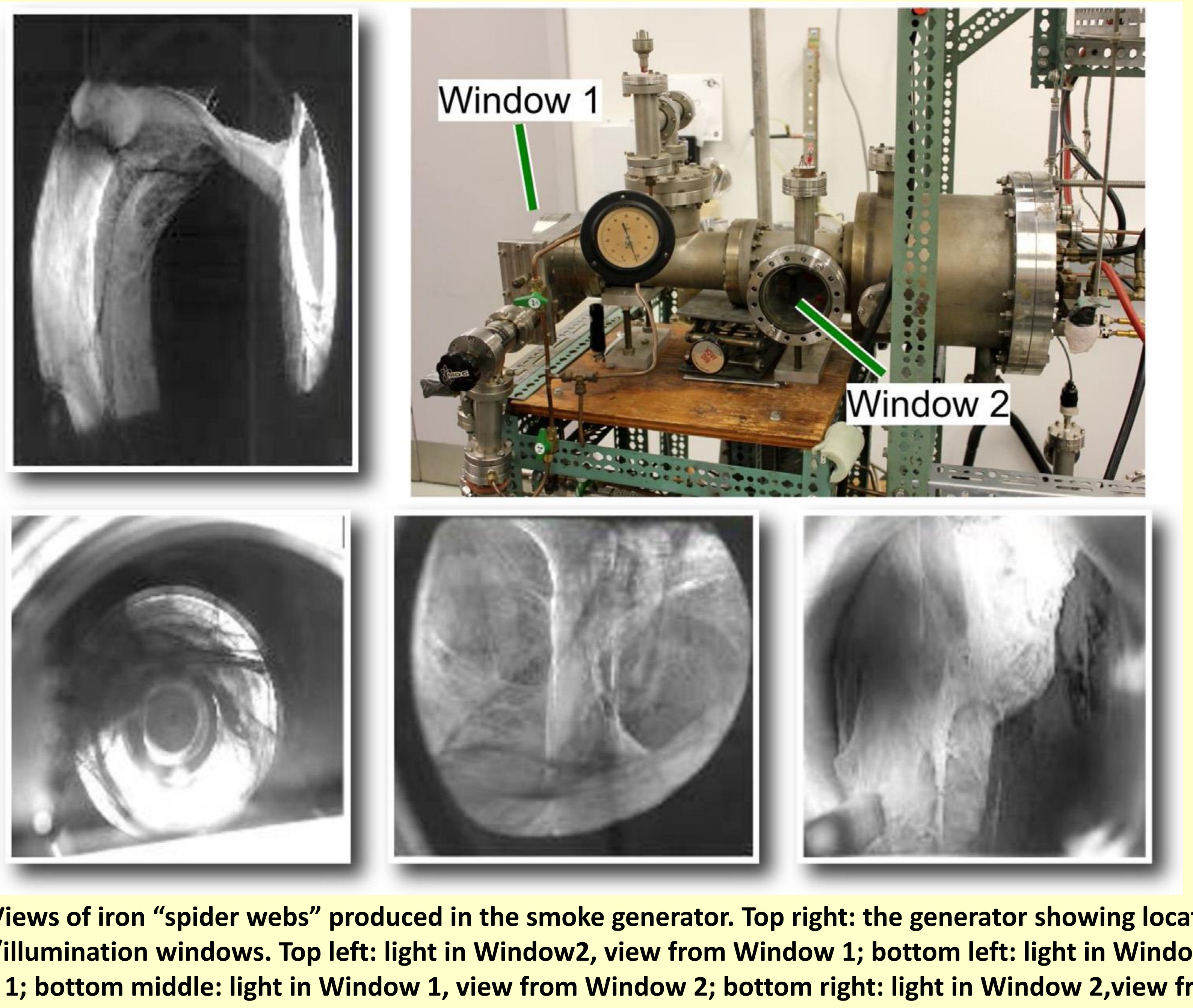
Making Silicate Smokes



Schematic diagram of the dust generator used to manufacture 10 nm scale smoke particles *via* the combustion of hydrogen gas containing small amounts of silane, iron pentacarbonyl, trimethyl aluminum, titanium tetrachloride and metal vapors such as magnesium, calcium, sodium and potassium. Molecular oxygen is typically used as the oxidant. The reaction occurs across a flame front within a resistively heated furnace at temperatures between 500 and 1500 K. Condensates are rapidly quenched and are collected on an aluminum substrate downstream of the furnace at temperatures below 350 K.

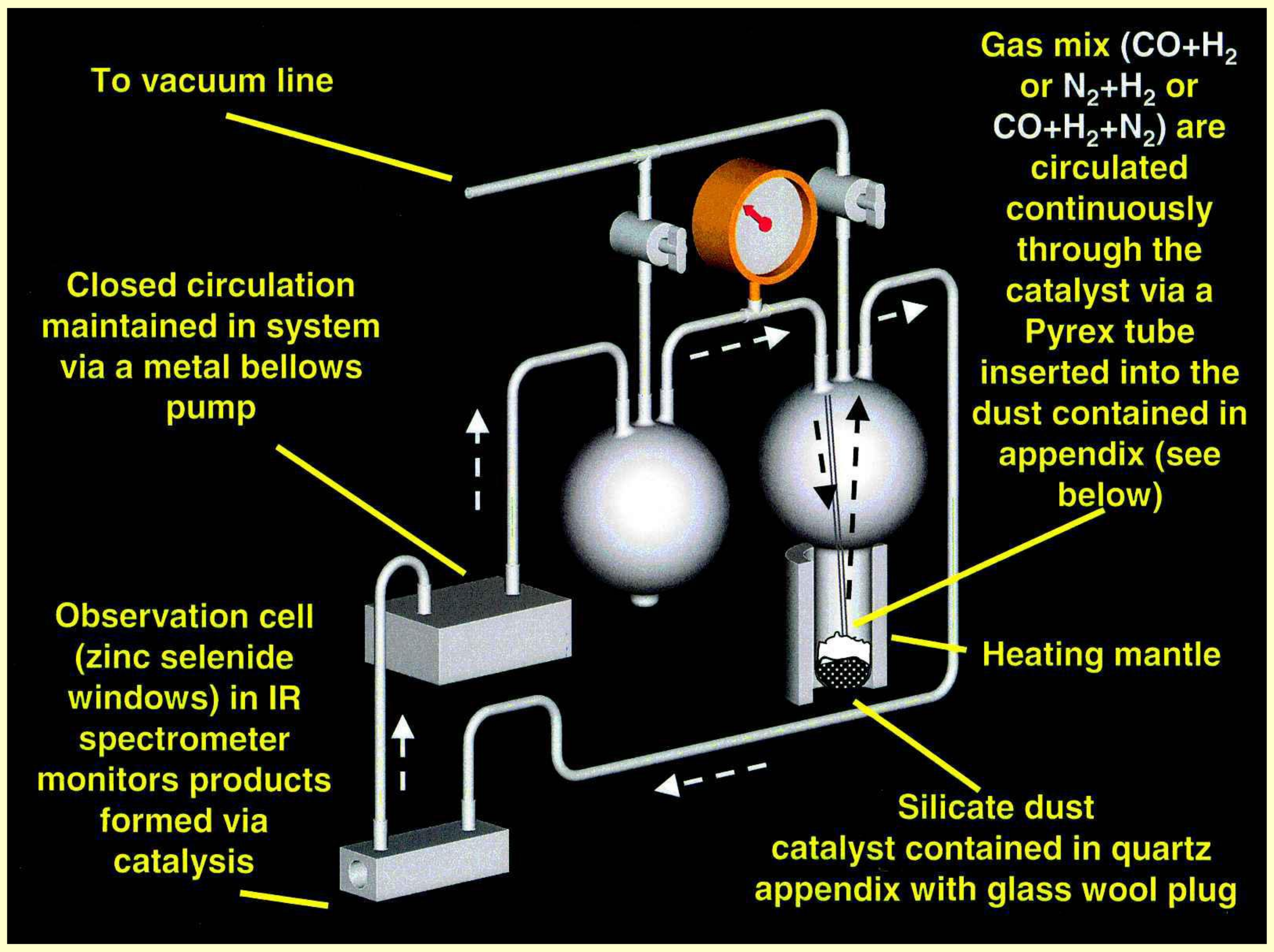
Many Oxide Grain Analogs Can Be Produced in This System

In addition to silicate smokes we have produced a variety of metal and metal oxide smokes including Ca_cSiO_x, Mg, MgO, TiO_x, AlO_x, Fe, FeO_x and CaO_x. We are currently producing amorphous spinel smokes: Mg_dAlO_x, Fe_eAlO_x and $Mg_dFe_eAlO_x$. These experiments occasionally produce unexpected results such as the single magnetic domain iron particles pictured below.



Above: Views of iron "spider webs" produced in the smoke generator. Top right: the generator showing locations of the viewing/illumination windows. Top left: light in Window2, view from Window 1; bottom left: light in Window 1, view from Window 1; bottom middle: light in Window 1, view from Window 2; bottom right: light in Window 2,view from Window 2.

Making Carbonaceous Solids



The catalyst is in the bottom of a quartz finger (attached to a 2–L Pyrex bulb) that can be heated to a controlled temperature. A Pyrex tube brings reactive gas to the bottom of the finger. The gas passes through the catalyst into the upper reservoir of the bulb and flows through a stainless steel tube at room temperature to a glass-walled cell (ZnSe windows) in an FTIR spectrometer. A metal bellows pump returns the gas via to the bottom of the catalyst finger to start the cycle over again. We have ten identical experimental systems: the total volume of each system is 4.7 +/- 0.1 liters.

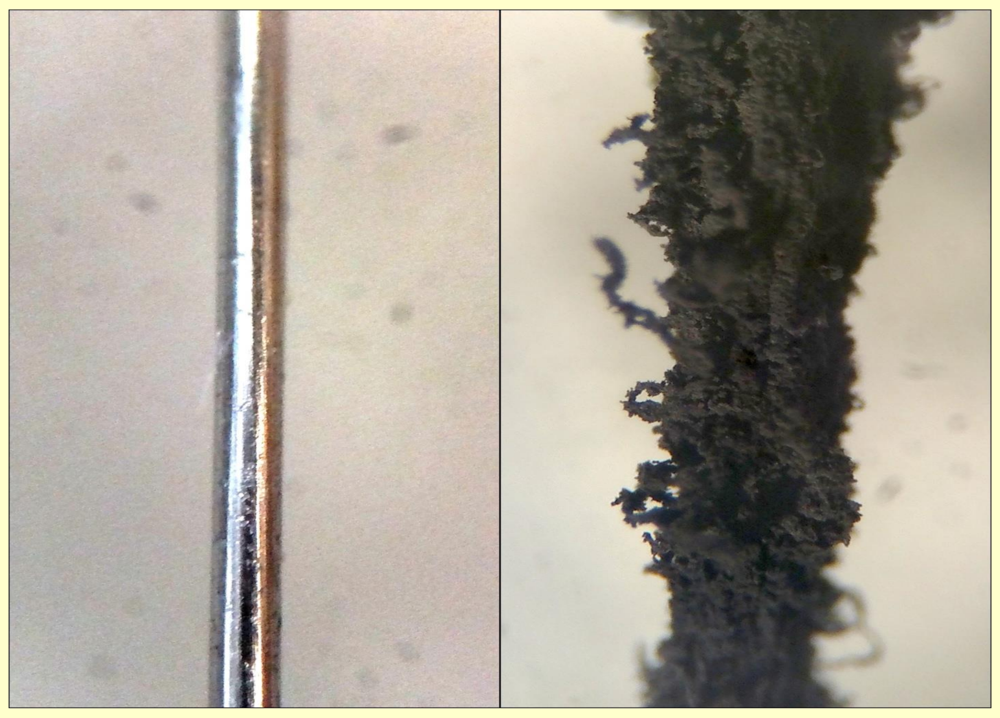
Surface Mediated Reactions and Carbonaceous Dust

We are not claiming here that surface mediated reactions constitute the single – or even the most important - mechanism that forms the full distribution of organic molecules in asteroids or comets or that are found in meteorites or IDPs. There are many different processes that can be important sources for particular compounds in many different meteorite types. However, we do believe that surface mediated reactions are a very efficient mechanism for converting nebular CO or CO_2 into solid carbonaceous materials. Such solids should be easy to incorporate into planetesimals and these carbonaceous grains could then serve as the feed stock that is transformed by various thermal or hydrothermal processes on parent bodies into the myriad organic molecules found in natural sources.

In addition, while we use various industrial reactions as models of nebular processes; e.g., the Fischer-Tropsch reaction: $CO + 3H_2 \Rightarrow CH_4 + H_2O$; the Haber-Bosch reaction: $N_2 + 3H_2 \Rightarrow 2NH_3$; the water-gas shift reaction: $CO + H_2O \Rightarrow CO_2 + H_2$; or the Boudouard Reaction: $2CO \Rightarrow CO_2 + C_{solid}$; natural reactions on grain surfaces in protostellar nebulae are much more complex. For this reason it can be extremely misleading to discuss a specific model reaction in isolation when describing natural reactions that might occur on the surfaces of grains in the Solar Nebula. Hereafter we will simply discuss measurements of *surface mediated reactions*.

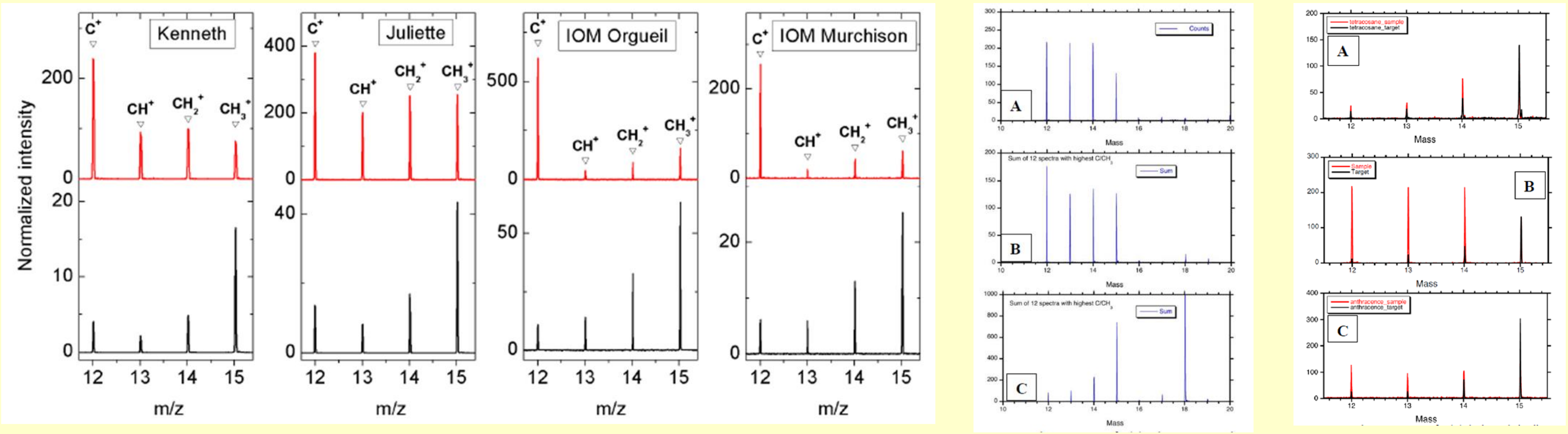
The Morphology of Carbonaceous Grains

Our experiments demonstrate that carbon deposited on grain surfaces via Surface Mediated Reactions do NOT form a grain coating. Instead, solid carbon grains appear to form as isolated islands on the catalytic surface and these island deposits also serve as catalysts that are at least equal in efficiency to the original surface (and in many cases are much more efficient). This leads to the formation of long fibrous growths and to a continuous increase in the active catalytic surface.



Right: An optical microscope image of iron wire (0.009" diameter) before (left) and after (right) use as the catalyst for a single 873K run of $CO + N_2 + H_2 \Rightarrow$ solid products

Comparison with COSIMA Measurements of Grains from 67P



Left: COSIMA spectra of two grains from 67P compared to lab spectra of IOM from Orgueil and Murchison (data in red, background in black) from Fray, N., Bardyn A., Cotton, H., et al., Nature 538,72–74 (2016). Middle: Carbon mass spectra for (A) carbon-coated grains on amorphous iron silicate smokes produced via surface mediated reactions (SMR) of $CO+N_2+H_2$ at 723K compared with similar spectra of (B) graphite grains and (C) diamond grains obtained using the COSIMA ETU. Right: Carbon mass spectra for (A) the long-chain aliphatic molecule tetracosane (6) (B) carbon-coated grains on amorphous iron silicate smokes produced via surface mediated reactions (SMR) of $CO+N_2+H_2$ at 723K and (C) the aromatic molecule anthracene (6). Each spectrum is normalized to mass 15. Red denotes sample spectra; black is background.

Implications of COSIMA Measurements: The best match for the dust collected by Rosetta and analyzed by COSIMA may be a mixture of graphite and SMR-produced carbon.