Icarus 247 (2015) 71–76

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus

Aerogel dust collection for in situ mass spectrometry analysis

S.M. Jones [a,*], M.S. Anderson [a], A.G. Davies [a], J.P. Kirby [b,c], M.J. Burchell [d], M.J. Cole [d]

[a] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099, United States
[b] Planetary Science Institute, Tucson, AZ 85719, United States
[c] University of Washington, Seattle, WA, United States
[d] Centre for Astrophysics and Planetary Sciences, University of Kent, Canterbury, Kent CT2 7NH, UK

ARTICLE INFO

Article history:
Received 18 December 2013
Revised 22 September 2014
Accepted 24 September 2014
Available online 13 October 2014

Keywords:
Interplanetary dust
Experimental techniques
Impact processes

ABSTRACT

The current technique for conducting in situ mass spectroscopic analysis of dust around extraterrestrial bodies is to have the dust impact a solid plate and analyze the atoms and molecular fragments resulting from the high speed impact. Due to the fact that the kinetic energy from the impact is converted primarily to thermal energy, much of the organic compounds present in the dust may be significantly altered or destroyed. To avoid this problem, aerogel could be used to capture the dust grains, largely intact, maintaining the integrity of the organic compounds in the interior of the dust grains. To demonstrate that organic molecules, present as minor components of silica particles, would survive hypervelocity capture in aerogel and can then be analyzed with mass spectrometry, several light gas gun impact tests and analyses were conducted. Fine particles containing polycyclic aromatic hydrocarbons (PAHs) were captured in aerogel at 5.5 km s^{-1}. The flow of metastable helium from a Direct Analysis Real Time (DART) source was used to desorb and ionize the organics, which were then analyzed with a mass spectrometer. The PAHs were detected and identified by the DART-MS, demonstrating that this method could be used on future flight instruments.

1. Introduction

The analysis of the dust grains associated with interplanetary space is a significant source of information about the planets, their moons, asteroids and comets. The particles present in the exospheres of the Galilean and saturnian moons are of particular interest, due to the fact that these particles provide information about their parent bodies, i.e., Enceladus, Io, Ganymede, Europa, Callisto. Dust analyzers have been flown on many missions, including Ulysses (Grün et al., 1992a), Galileo (Grün et al., 1992b), Cassini–Huygens (Srama et al., 2006; Postberg et al., 2008) and Stardust (Kissel et al., 2004). These instruments were designed to provide information about the flight direction, electric charge, speed, mass and composition of these particles. The composition of the dust grains is determined by a time-of-flight mass spectrometer. The dust grains enter the instrument and impact a target plate. The kinetic energy of the dust grains is more than sufficient to break up the constituent components to form molecular and atomic ions. The ions are directed into the mass spectrometer by electromagnetic fields, where they are differentiated by their masses based on their time of flight and assuming $m/z = 1$.

A different approach is to use capture cells to collect material in space and then conduct analysis using a DART-MS in-situ. This method of using aerogel for sample capture could be used during a mission to complement the existing method of using an impactor plate. Cells of gradient density silica aerogels were the particle capture material in the cometary and interstellar particle collector grids for the Stardust Mission (Brownlee et al., 2003) which flew past Comet 81P/Wild-2 at 6.1 km s^{-1} and returned captured cometary dust samples to Earth in 2006. Aerogels are extremely porous materials composed of submicron sized filaments that form a solid network. Since the filaments are so much smaller than the high velocity particles being captured, they are crushed and melted during the capture process, allowing for the capture of the particles with intact core domains (Tsou, 1995; Burchell et al., 2006). The cometary particles captured by the Stardust aerogel cells have provided information about the origin of our Solar System (Brownlee et al., 2006). In addition to minerals, the cometary particles captured by the Stardust aerogels were also found to contain polycyclic aromatic hydrocarbons (PAHs) as well as aliphatic hydrocarbons (Sandford et al., 2006). It was found that the aliphatic hydrocarbons present in some of the particles survived the highly energetic capture process, yet were sufficiently labile to have migrated from the captured particle into the surrounding aerogel where it was retained and eventually observed. The amino acid

* Corresponding author.

http://dx.doi.org/10.1016/j.icarus.2014.09.047
0019-1035/

glycine has also been reported in laboratory analysis of returned Stardust aerogels (Glavin et al., 2008). However, it was difficult to clearly establish an extra-terrestrial origin for the glycine based on analysis of the aerogel alone – instead analysis of the surfaces of nearby aluminum foils was required (Elsila et al., 2009). Laboratory impact experiments firing glycine grains into aerogel (Nixon et al., 2012) showed that in impacts at 6 km s^{-1} the captured grains had lost the majority of their pre-impact mass in the capture process, but no tests were carried out on the aerogel to determine where the missing material had gone or how it may have been processed in the impact event. Similarly, impacts on aerogel by polystyrene microparticles show that 84% of the mass is lost during capture at speeds of 6 km s^{-1} (Burchell et al., 2009a).

It is clearly important to understand how these various forms of organic materials may be captured in the aerogel surrounding an impact track and subsequently analyzed. Therefore, to demonstrate that organic compounds from fine particles captured in aerogel can be detected and identified by mass spectroscopy several laboratory impact tests were conducted. The organics used were polycyclic aromatic hydrocarbons and niacin. This study is intended to establish and validate the methodology, while later studies will examine a larger variety of organic compounds and the concentration limits at which they can be detected.

The COSIMA instrument on the Rosetta spacecraft is designed to capture cometary dust grains and conduct mass spectrometric analysis (Kissel and Krueger, 2007). Targets with porous metal black layers are being used to collect the particles, so that they can be moved to a chemical station and then the mass spectrometry station, where they are hit by ions to desorb and ionize them for analysis. Aerogel collectors could be used to complement current collection methods, since there advantages and disadvantages to each. Current impact ionization targets have the advantage of producing data in real time and from specific particles. Their disadvantage is that the particles are subjected to extreme thermal and mechanical shocks, when impacting the target plate. Aerogel presents the advantages of reducing the impact shock, thus reducing thermal and mechanical alterations, and adds the capability of compiling impacted particles and storing them for later analysis. The disadvantage of aerogel collection is that the resultant spectra are of many particles.

2. Experimental

2.1. Aerogel

Gradient density silica aerogel cells were produced according to the method developed for the Stardust Mission aerogel (Jones, 2007). The aerogels produced were nominally 15–50 mg/cc and 20–60 mg/cc density gradients. The individual cells were 3 cm deep with front faces of 4 cm by 2 cm.

2.2. Projectiles

Table 1 lists the impact test number, the projectiles use and the impact speed. PS PAHs were produced by the sol–gel method using a variation of the Stober method for producing porous silica aggregates (Stober et al., 1968). Naphthalene, phenanthrene and pyrene were added to the solvent so that they would be incorporated into the projectiles as they condensed. Fig. 1 shows porous silica particles (PS PAHS) containing PAHs used in impact test 130017. For impact test G030713#3 the niacin crystals were mixed with 35 μm glass microspheres.

2.3. Ames advanced vertical gun range (AVGR) impact tests

For each of the AVGR test shots done, four aerogel cells were arranged around a central hole in the mounting board (see Fig. 2). A central hole is required because the particles are launched in a metal carrier, which must pass through the target. The barrel of the gun is rifled, causing the carrier to spin and spread the projectiles into a cloud of discrete particles that then impact the aerogel cells. After each test the aerogel cells were removed from the AVGR target chamber and placed in individual plastic boxes.

2.4. Kent Light Gas Gun Facility impact test

One impact test was conducted at the Light Gas Gun Facility at the University of Kent (Burchell et al., 1999). This shot used 35 μm glass microspheres and niacin crystals as the projectiles. Niacin ($C_6H_5NO_2$) is a water soluble organic compound with a density of 1.47 g cm^{-3} and a melting point of 510 K.

2.5. Direct Analysis Real Time (DART)-mass spectrometry

The DART ionization source produces metastable helium (He^*) that is used to provide soft ionization and enhanced desorption of molecules from a sample. Even relatively non-volatile molecules such as amino acid zwitterions may be detected (Cody et al., 2005). The flow from the DART unit is a mixture of helium and neutral, long lived He^*, which can be heated to enhance analyte desorption from a sample. Analyte ionization occurs when the He^* impacts on sample surfaces placed in the gap between the DART outlet and the mass spectrometer sampling inlet orifice. Additional ionization processes also occur when surrounding gasses are ionized. The presence of water vapor or ammonia surrounding the sample may be used to form hydrogen or ammonium adducts. The DART/MS system consists of a DART ion source (IonSense, Danvers, Massachusetts, USA) and a JEOL AccuTOF high-resolution TOF mass spectrometer (JEOL USA). The DART experimental parameters were: Positive Ion Mode, He flow-rate: 0.55 L min^{-1}; needle voltage: 3000 V; discharge electrode: 150 V; grid electrode: 250 V; beam temperature 250 °C. The DART meta stable helium source has a 7 mm diameter nozzle. The mass resolving power of the JEOL mass spectrometer is 6000, which is the observed mass divided by the difference in the masses that can be separated.

The control spectrum of the projectiles that were not impact tested was done by pressing them into Teflon and placing them in the metastable helium flow. The sample preparation for the impact samples was for the aerogel section (~1 cc) containing tracks and terminal particles to be pressed flat on a glass slide. Since low-density aerogels are more than 99% pore volume, they can be flattened to a very small fraction of their original volume. This is done so that the full lengths of the tracks formed by the captured particles and the terminal particles are brought to the surface of the aerogel. This means that the analytes present in the captured particles are now at the surface of the aerogel network. A flow of

Table 1
Hypervelocity impact tests.

Impact test	Projectile label	Projectile description	Speed (km s^{-1})
130117	P S PAHs	Porous silica grains with PAHs	5.65
G030713#3	Niacin	35 μm glass beads with niacin	6.31