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Impact ionisation mass spectrometry of polypyrrole-coated pyrrhotite microparticles

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ABSTRACT

Cation and anion impact ionization mass spectra of polypyrrole-coated pyrrhotite cosmic dust analogue particles are analysed over a range of cosmically relevant impact speeds. Spectra with mass resolutions of 150–300 were generated by hypervelocity impacts of charged particles, accelerated to up to 37 km s⁻¹ in a Van de Graaff electrostatic accelerator, onto a silver target plate in the Large Area Mass Analyzer (LAMA) spectrometer. Ions clearly indicative of the polypyrrole overlayer are identified at masses of 93, 105, 117, 128 and 141 u. Organic species, predominantly derived from the thin (20 nm) polypyrrole layer on the surface of the particles, dominate the anion spectra even at high (> 20 km s⁻¹) impact velocities and contribute significantly to the cation spectra at velocities lower than this. Atomic species from the pyrrhotite core (Fe and S) are visible in all spectra at impact velocities above 6 km s⁻¹ for ⁵⁶Fe⁺, 9 km s⁻¹ for ³²S⁺ and 16 km s⁻¹ for ³²S⁻ ions. Species from the pyrrhotite core are also frequently visible in cation spectra at impact speeds at which surface ionisation is believed to dominate (< 10 km s⁻¹), although the large number of organic peaks complicates the identification of characteristic molecular species. A thin oxidised surface layer on the pyrrhotite particles is indicated by weak spectral features assigned to iron oxides and iron oxy-hydroxides, although the definitive identification of sulfates and hydrated sulfates from the oxidation process was not possible. Silver was confirmed as an excellent choice for the target plate of an impact ionization mass spectrometer, as it provided a unique isotope signature for many target-projectile cluster peaks at masses above 107–109 u. The affinity of Ag towards a dominant organic fragment ion (CN⁻) derived from fragmentation of the polypyrrole component led to molecular cluster formation. This resulted in an enhanced sensitivity to a particular particle component, which may be of great use when investigating astrobiologically relevant chemicals, such as amino acids.

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1. Introduction

Space-based dust detectors that actively measure the composition of impinging dust particles in situ provide unique insights into the sources of cosmic dust, its formation mechanisms, evolution and modification. In recent years dust detectors have measured the composition of interplanetary dust (Dietzel et al., 1973;

Hillier et al., 2007a), cometary dust (Kissel et al., 1986a,b, 2004; Langevin et al., 1987; Kissel and Krueger, 1987; Schulze et al., 1997), jovian stream dust from Io's volcanoes (Postberg et al., 2006), saturnian stream dust (Kempf et al., 2005), saturnian ring dust (Hillier et al., 2007b; McBride et al., 2007; Postberg et al., 2008), dust from within Saturn's moon, Enceladus (Postberg et al., 2009b) and interstellar dust (Kissel et al., 2004; Krueger et al., 2004). The sampling method (Section 2) used by the spacecraft which made these discoveries is inherently destructive, relying on the creation (and subsequent mass spectrometric analysis) of a plasma when a particular dust particle strikes the instrument

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target. It is unclear whether the ions created from the particle impact are always representative of its bulk chemical composition, or instead derive more from the surface region during low velocity impacts, with ions originating from the core of the particle becoming increasingly prevalent at higher velocities. For monomineralic, or extremely homogeneous ultrafine-grained polyminerallitic particles, this is not an issue. However, particles possessing a more complex structure, such as a core and mantle composed of different compounds, may generate spectra that are not necessarily representative of the true particle composition. This problem may be particularly pronounced if the particles were sampled over a limited velocity regime, as changes in spectral behaviour with impact velocity would be difficult to quantify.

Particles with a core–mantle structure have been postulated to explain certain features in the spectra of the interstellar medium (e.g. Pollack et al., 1994; Li and Greenberg, 2002), cometary particles (e.g. Kolokolova et al., 2001) and particles from within Enceladus (Postberg et al., 2009b, 2011). It is also highly likely that any particles exposed to the radiation and cosmic ray flux in space for a suitable amount of time will form a mantle with a different (devolatilised etc.) structure and/or composition to that of the original grain.

In this work, particles with an organic mantle and a simple well-defined mineral core were used. The organic coating used was polypyrrole (Section 5), which was selected for both pragmatic and scientific reasons. The electrical conductivity of polypyrrole is high enough to facilitate successful electrostatic acceleration (Section 3). Polypyrrole is also a reasonably good synthetic analogue for the kerogen-type and carbonaceous compounds found in meteorites (Sandford et al., 2008), some outer-solar system objects (e.g. Brown, 2000; Clark et al., 2005) and interplanetary dust (Clemett et al., 1993; Keller et al., 2004), the polyaromatic hydrocarbons (PAHs) found in the interstellar medium (Keller et al., 2004; Wooden et al., 2007), comets (Fomenkova et al., 1994; Fomenkova, 1999; Sandford et al., 2006; Keller et al., 2006; Lisse et al., 2007; Leitner et al., 2008) and around some stars (Matsuura et al., 2004; Sandford et al., 2008).

The grain core material, pyrrhotite (Fe_{1-x}S), was similarly chosen for both pragmatic and scientific reasons. Pyrrhotite is a “simple” mineral which consists of just two elements, Fe and S, both of which have numerous stable isotopes (Table 1), making the definitive identification of the species in spectra easier in the case where isobaric (within the limits of the instrument mass resolution) species are present. In practice the ^{58}Fe , ^{33}S and ^{36}S isotopes are unlikely to be detectable given the sensitivity of the instrument (Section 2) used here. Pyrrhotite (together with the elementally identical and compositionally similar troilite) is also cosmologically relevant. Troilite is predicted to form by equilibrium condensation of nebular gas (Lauretta et al., 1996) and Fe–Ni sulphides may be the source of the 23.5 μm feature detected by ISO around young and old stars and in the dust of Comet Hale-Bopp (Keller et al., 2002). Fe-rich sulphides are known to be present in cometary dust (e.g. Jessberger et al., 1988; Lawler et al.,

1989; Leitner et al., 2008; Leroux et al., 2008; Zolensky et al., 2006, 2008; Kissel et al., 2004; Wozniakiewicz et al., 2011), interplanetary dust (e.g. Zolensky et al., 1995; Zolensky and Thomas, 1995; Dai and Bradley, 2001; Christoffersen and Buseck, 1986), meteorites (e.g. Kerridge et al., 1979; Dai and Bradley, 2001) and in carbon-rich planetary nebulae (Hony et al., 2002).

The relevance of both polypyrrole and pyrrhotite is emphasised by previous examples of their separate use in simulating the hypervelocity impacts of cosmic dust (e.g. Srama et al., 2004b; Burchell et al., 2008) into aerogel and for the generation and analyses of impact ionisation time of flight mass spectra.

2. The large area mass analyser – LAMA

Time of flight mass spectroscopy (TOF-MS) using ions created by hypervelocity impacts is the primary method for the in situ compositional analysis of dust particles in space. With the notable exception of the Cosima (Kissel et al., 2007) instrument onboard the Rosetta spacecraft, all previous instruments for in situ compositional analyses (e.g. Dietzel et al., 1973; Kissel et al., 1986a,b, 2003; Kissel and Krueger, 1987; Srama et al., 2004a) have used this method.

Hypervelocity impact ionisation mass spectrometers utilise the plasmas created during the rapid deceleration and dissociation of dust grains as they strike a solid target plate. In its most basic form, an impact ionisation time of flight spectrometer consists of a target plate and a series of grids held at different potentials, which separate the impact plasma and accelerate it towards a detector, such as a micro-channel plate (MCP). For a spectrometer with a single, small acceleration region, followed by a drift region and a detector, the masses (m_i) of the ions detected are related to their arrival times (t_i) by $t_i = a\sqrt{m_i} + b$, where a and b are referred to as the stretch parameter (related to the acceleration voltage and drift distance) and the shift parameter (related to instrument trigger timing) respectively. Spectra produced by such simple arrangements are affected by the initial velocity (energy) distribution of the ions within the impact plasma (e.g. Hillier et al., 2006), as well as shielding effects, which tend to broaden peaks within spectra and thus reduce the mass resolution.

A more complex arrangement of electric fields within an instrument, known as a reflectron (Alikhanov, 1957), reduces the effect of the initial plasma energy distribution, as well as increasing the distance travelled by the ions before detection, thus improving the mass resolution of the generated spectra. The Large Area Mass Analyser (LAMA) instruments, developed by groups at the Max Planck Institut für Kernphysik, Germany (Srama et al., 2007) and the Laboratory for Atmospheric and Space Physics, University of Colorado at Boulder (Sternovsky et al., 2007a,b, 2011), use just such a reflectron system, combined with large instrument apertures, large target areas and highly sensitive dust charge trajectory sensors, to enable the detection and characterisation of dust at extremely low fluxes. In this work the Boulder LAMA is used, with an Ag foil (Goodfellow) target which was cleaned prior to the experimental work using organic solvents, to remove any high-mass anthropogenic hydrocarbons (e.g. triglycerides). This instrument has a mass resolution of $m/\Delta m \approx 150\text{--}300$ and is capable of running in both positive and negative modes, creating cation and anion mass spectra respectively. The laboratory-based calibration of such an instrument necessitates the production and acceleration of model particles of known chemical composition to hypervelocity speeds.

3. Electrostatic acceleration

The controlled acceleration of single nano- or microparticles to hypervelocities (where hypervelocity is, in this instance, defined as

Table 1
Isotope masses and abundances for the stable (or extremely long-lived) isotopes of Fe and S.

Isotope	Mass (u)	Abundance (%)
^{54}Fe	54	5.8
^{56}Fe	56	91.72
^{57}Fe	57	2.2
^{58}Fe	58	0.28
^{32}S	32	95.02
^{33}S	33	0.75
^{34}S	34	4.21
^{36}S	36	0.02

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