

Impact ionisation mass spectra of polypyrrole-coated pyrrhotite microparticles

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Abstract

Impact ionisation mass spectra of polypyrrole-coated (PPY) pyrrhotite particles are presented and discussed. The mass spectra were generated by the Boulder Large Area Mass Analyzer (LAMA [1]) instrument, at the Max Planck für Kernphysik's accelerator facilities in Heidelberg [2]. The mass spectra demonstrate the high sensitivity of impact ionisation mass spectrometry to even minor particle components. Cation species clearly identifiable as fragments of the PPY overlayer are found. A thin layer of oxidation on the pyrrhotite surface is indicated by weak spectral features due to iron oxides and oxy-hydroxides. The affinity of the target material, Ag, to the CN^- anion from the PPY, and subsequent cluster formation, increased the sensitivity of the mass spectrometer to a particle component of great astrobiological interest.

1. Introduction

Core-mantle particles have been postulated as an explanation for features seen in absorption spectra of the interstellar medium and cometary particles [3,4] as well as mass spectra of particles from Enceladus [5]. Space-based dust detectors (e.g. Cassini's Cosmic Dust Analyser [6]) that measure the composition of such particles require calibration, to enable the original dust parameters (composition, structure) to be linked to instrument measurements.

1.1 Large Area Mass Analyzer (LAMA)

LAMA is an impact ionization time of flight mass spectrometer that uses a complex field arrangement (reflectron) to obtain a mass resolution of 150-300. Particles striking the instrument target at hypervelocities (speeds greater than that of the speed of sound in the particle and target material) form a plasma. The plasma is separated by a strong electric

field and ions are directed towards a detector, with the effects of the initial ion energy distribution on their times of flight removed. Mass spectra composed of positively or negatively charged species may be recorded.

1.2 Particles

The particles were PPY-coated (6.8 wt%, ~20nm thick layer) pyrrhotite. PPY is an inert, conductive polymer of pyrrole ($\text{C}_4\text{H}_5\text{N}$). Three bonded pyrrole molecules possess one unit positive charge, balanced in the polymer backbone by the intercalation of an HSO_4^- anion. PPY, previously used to coat particles for use in hypervelocity impact experiments (e.g. [7]), is used as an analogue for the kerogen-type, carbonaceous and polyaromatic hydrocarbons found in space (e.g. [8]). Pyrrhotite ($\text{Fe}_{(1-0.83)}\text{S}$) is an iron sulphide mineral similar in composition, and elementally identical, to troilite. FeS is cosmochemically relevant, believed to be the source of the 23.5 micron spectral feature seen in cometary dust and around stars (e.g. [9]) as well as being found in meteorites (e.g. [10]).

1.3 Van de Graaff accelerator

To reach impact velocities higher than ~7 km/s, a Van de Graaff electrostatic accelerator is used [2] to charge dust grains and accelerate them through a large potential ($V \sim 2$ MV), producing dust (m) with impact speeds (v) of up to >100 km/s, with kinetic energies proportional to their charges (q): $\frac{1}{2} mv^2 = qV$.

2. Data

150 cation mass spectra, from particles impacting at 2.5-37.1 km/s ($2.4 \times 10^{-14} - 1.7 \times 10^{-18}$ kg), and 216 anion mass spectra from particles impacting at 2.3-33.3 km/s ($2.5 \times 10^{-14} - 5.3 \times 10^{-19}$ kg) were obtained.

The mass spectra were calibrated onto a mass scale using bespoke software and, for peak identification, aligned and coadded in 5 km/s bins.

3. Summary and Conclusions

Iron, from the pyrrhotite, was reliably detected in cation spectra at velocities above 6 km/s, but not seen in anion spectra at even the highest impact velocity. Sulfur was observed in both cation and anion spectra, reliably appearing at lower velocities in cation spectra (9 km/s) than anion spectra (16 km/s). Low abundance iron oxide and hydroxide species (e.g. FeOH^+ , FeO_2H^+ , FeO_2^- and FeO_2H^-) were observed in both anion and cation spectra. An analysis of the hydrogen sulfate anion peak (Fig. 1), shown to decrease with particle mass, indicates dominant HSO_4^- contributions to the spectra from the PPY layer.

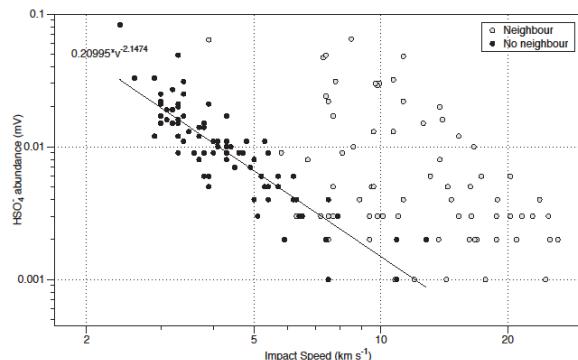


Figure 1: The trend of HSO_4^- amplitude with velocity.

In the anion spectra, molecular series from the PPY overlayer can clearly be seen, dominating the sulfur anion peaks, despite the fact that the organic layer was <10% by mass of the grains. In the cation spectra, we identify a series of high mass peaks (Fig. 2), created by the breakup of the PPY, that provide an excellent diagnostic for this particular polymer. Easily identifiable double, triple and quadrupole-peaked features, due to clusters of the 107 and 109 u Ag isotopes, with each other and with projectile species, are visible in both polarity spectra (Fig. 4). These features often contain CN^- (forming molecular ions such as $\text{Ag}_3(\text{CN})_2^+$), whose affinity for metals increases the sensitivity of the LAMA instrument to cyanide ions, which may be formed during the breakup of amino acids during hypervelocity impacts.

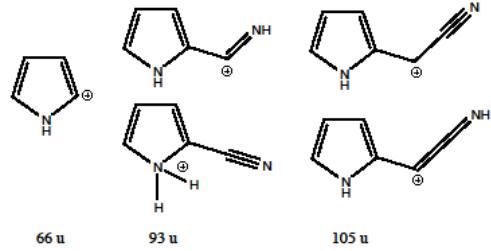


Figure 2: Cation molecular fragments from the PPY overlayer.

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