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STUDY OF POLYOXYMETHYLENE AND ITS SPUTTERED FRAGMENTS-- IMPLICATIONS FOR COMETS

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ABSTRACT

Laboratory mass spectra of sputtered polyoxymethylene, POM, reveals a fragmentation pattern consistent with observed peaks in the PICCA experiment on board the Giotto spacecraft. Both commercially available POM and radiation synthesized POM have been used in our studies. Synthesized POM was identified using infrared absorption spectra after proton irradiation of H_2CO ice on silicate grains at 20K. Laboratory results suggest that similar type sputtering is a possible mechanism for removing species from comet grains.

INTRODUCTION

A complex line of evidence for a form of formaldehyde (H_2CO) in comet Halley came from the interpretation of data from the PICCA instrument on board Giotto. In the inner coma a repeating mass spectral pattern with peak centers at the approximate locations of 45, 61, 75, 91, 105, and 121 amu was detected. Mitchell et al.[1], Huebner and Boice[2], and Huebner[3] suggested the mass spectrum could be fit with the fragmentation pattern of the polymerized form of H_2CO known generically as polyoxymethylene, POM.

The idea that POM could be present in cometary materials is not new. Wickramasinghe[4,5] proposed that H_2CO condenses on interstellar silicate grains as polyoxymethylene and the possibility of this polymer in cometary dust was discussed by Vanysek and Wickramasinghe[6]. Laboratory experiments by Goldanskii et al.[7] showed that irradiation of condensed H_2CO synthesized polyoxymethylene to temperatures below 20K and Goldanskii[8] discussed the possibility of similar radiation synthesis in ices in molecular clouds. In our laboratory experiment radiation synthesized POM was identified by its infrared absorption features.

EXPERIMENTAL RESULTS

We have sputtered POM in vacuum at 300K using 700KeV protons and recorded the mass spectrum. Fragments are observed at 45, 61, 75, 91, 105 121 and 135 amu and these results are compared with the PICCA data in Figure 1. As shown in Table I, these peaks can be assigned to the fragmentation products of POM with an alternating CH_3 or H end group. The 700KeV proton beam current was near

TABLE I: TENTATIVE ASSIGNMENT OF POM FRAGMENTATION PEAKS

m/e	ION^+	m/e	ION^+
45	$(H_2CO)CH_3$		
61	$(H_2CO)_2H$	60	$(H_2CO)_2$
75	$(H_2CO)_2CH_3$		
91	$(H_2CO)_3H$	89	$(H_2CO)_2HCO$
105	$(H_2CO)_3CH_3$		
121	$(H_2CO)_4H$	119	$(H_2CO)_3HCO$
135	$(H_2CO)_4CH_3$	131&133	unidentified

$1.5x10^{-7}$amps (corresponding to $2x10^{11}$ protons/cm^2-sec). In the region of mass 30 the quadrupole mass spectrometer was saturated and the resulting overlaid data in Figure 1 spanned more than 3 log pressure scales in intensity. All data points had the background subtracted automatically and were recorded using the electron multiplier. A 70 eV electron ionizer voltage was used for these experiments.

Sputtering of thin films of commercially available paraformaldehyde (a polyoxymethylene glycol) gave the same results as sputtered POM synthesized in our laboratory. Other peaks recorded in our sputtered spectrum are listed in Table I and two can be attributed to fragments of POM with an attached HCO group.

In contrast, using direct insertion techniques the mass spectrum of solid polyoxymethylene glycol was analyzed by Moller

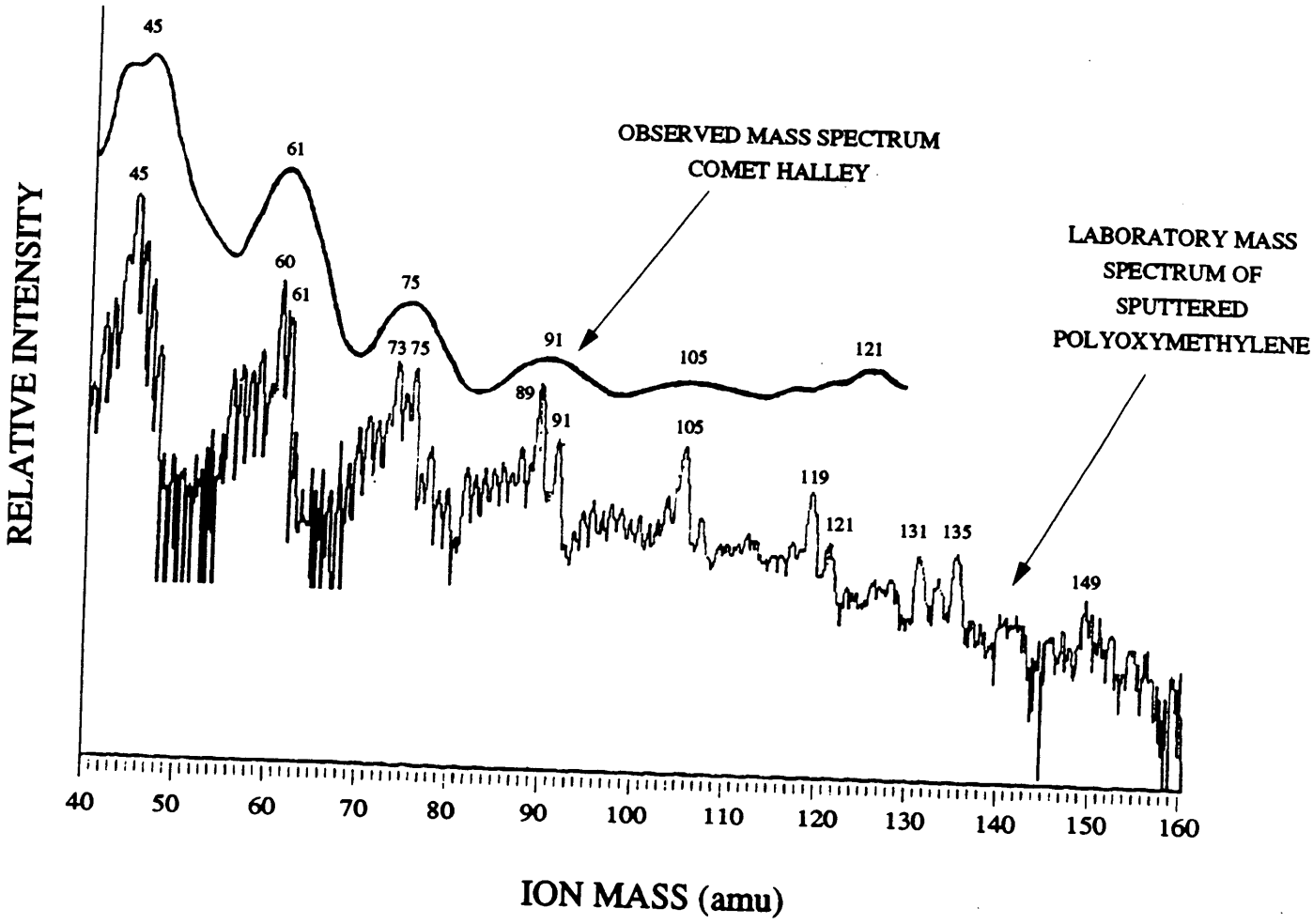

FIGURE 1. The upper curve reproduces the mass spectrum measured by the PICCA instrument on board the GIOTTO spacecraft in the inner coma of comet Halley. This is compared with our laboratory mass spectrum of fragments produced during sputtering polyoxymethylene at 300 K with 700 KeV protons.

and Jackson[9]. At 300K peaks were observed at 47, 61, 77, 91, 107, 121 amu, consistent with a fragmenting polymer with alternating H and OH groups attached. The peaks do not fit the central peak assignments of the PICCA spectrum but could contribute to its width.

Figure 2A shows the infrared spectrum from 2.5um to 25um of an amorphous silicate smoke. It's dominate SiO stretch feature is near 10um, the SiO bend is near 21um. H_2CO gas was condensed onto this smoke at 20K and the resulting ice-silicate was irradiated with 700KeV protons to a total incident dose of 1.5×10^{15} protons/cm^2. Polymerization of formaldehyde occurred at 20K and the POM remained on the silicate when warmed to 300K. The infrared spectrum of the POM-silicate is shown in Figure 2B. The ratio spectrum (POM-silicate/silicate) in Figure 2C reveals the major absorptions of POM on silicate at 8.99um and 10.7um. This sample was subsequently sputtered.

CONCLUSION

Our laboratory results suggest that sputtering of POM is a possible origin of the peaks measured in the PICCA data. Sputtering experiments in which solar wind type ions are used need to be studied since 700KeV protons are not dominate in the inner coma. Each PICCA peak appears to be composed of 3 or more closely spaced masses[1]. Sputtering of POM may contribute to the peak, but other processes such as sublimation may contribute to the width. Also we suggest that other complex non-volatile organic residues may exist on comets and fragments from these may be sputtered from grains in the coma contributing to the observed data. The study of sputtered fragments from other organic residues is currently under investigation.

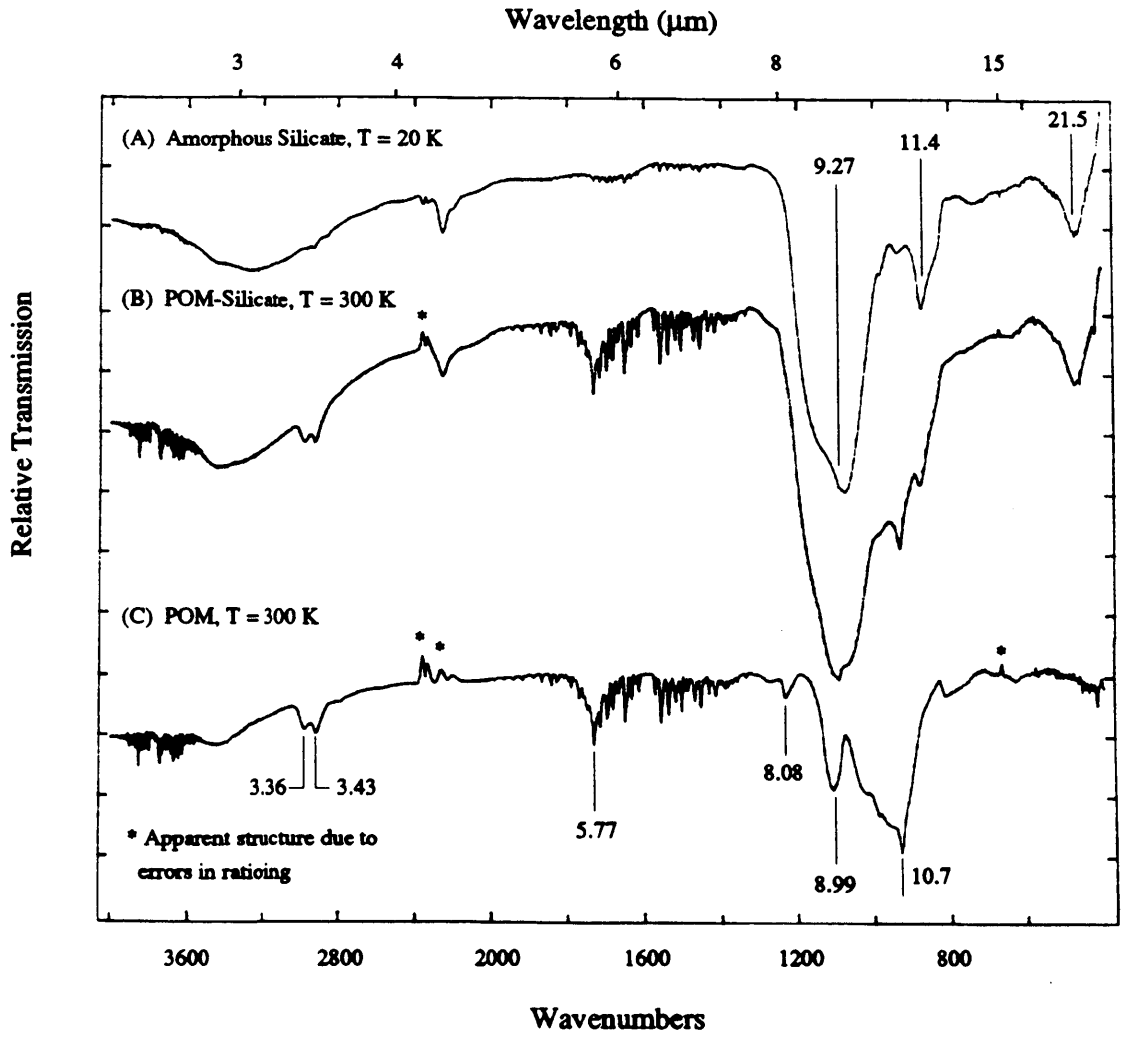

FIGURE 2. (A) Infrared spectrum of amorphous silicate smoke at 20 K. The SiO stretch band is near 10 μm. (B) Formaldehyde ice formed on the silicate smoke was irradiated causing polymerization at 20 K. The resulting POM-silicate spectrum at 300 K is shown. (C) Ratio spectrum, POM-silicate/silicate. Spectral features of POM are revealed allowing identification.

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