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PIA UPDATE: CORRELATION ANALYSES OF MASS SPECTRA

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The PIA instrument aboard the Giotto spacecraft (a time-of-flight mass spectrometer) has been described elsewhere.[1] The mass spectra used in this analysis were decoded and mass numbers assigned according to the presence of carbon and silver, using the global values for these elements in their spectral absence.[2] The results presented here were obtained using a frequency of occurrence based analysis (similar to ref. 3) which correlates how often mass numbers appear in the mass spectra and which mass numbers tend to occur together in the same spectra; no amplitude information is utilized. The data are presented as plots of mass verses coincident mass for different subsets of the PIA data set, with both axes having units of atomic mass. Frequency contours are plotted at approximately five percent contour intervals, relative to the maximum AMU occurrence in that plot. The plots presented are symmetrical about the matrix diagonal, that is, every mass is coincident with itself in a given spectra. The plus marks indicate local maxima in the correlation profile.

Figure 1 shows the correlation plot for the entire compressed PIA data set consisting of 8030 mode 1, 2, and 3 individual mass spectra which were collected between 50 minutes before and 40 minutes after Giotto's closest approach to comet Halley. Carbon (mass 12) is the most frequently observed element, occurring in 74% of all spectra, as seen in the peak at coordinates 12,12 on the diagonal. The highest correlation which occurs between individual elements (off the diagonal) is seen at 12,16 (C and O). Combinations which occur less frequently are: O and Mg, Si and O, C and Mg, C and Si and so on. Mass 41 and mass 57 show similar patterns in their correlations with H (not shown), C, O, Mg, and Si.

When subsets of the total data set are defined and the resulting correlation matrices plotted, information about the specific relationships between simultaneously occurring mass units can be extracted. Figure 2 shows the profile resulting from all spectra containing Mg but not C. Mass 24 shows coincidence with all other masses by definition. Strong correlations (similar to the patterns seen in Fig. 1) between Mg and O, Si and O, O and 41, and O and 57 are also seen in this plot. Figure 3 shows the reciprocal data subset, that is, all spectra containing C without Mg. Strong correlations are seen between C and N, C and O, and C and Si, but the pattern seen in Fig. 2 at mass numbers 41 and 57 is absent. Two possible explanations for the appearance of these patterns with Mg, and the absence of these patterns without Mg have been postulated and are detailed as follows. The first involves the existance of molecular or cluster ions consisting of H, O and Mg in the mass spectra. The simplest plausible combinations of these elements which sum to the appropriate mass numbers are: $(MgOH)^+$ for mass 41 and $(MgOOH)^+$ for mass 57. The existence of molecular ions in the PIA mass spectra is not proven by this analysis, but the simplicity of the elemental formulas which sum to the appropriate mass numbers is compelling. The second explanation for the observed patterns is that mass 41 is in fact Ca^+, and and mass 57 is Fe^+, with both either assigned to the wrong mass number (off by one), or occurring as the hydrides. The contours in Fig. 2 which range over mass 40 and 41 can be interpreted as support for the second explanation.

Molecular ion detection is indicated in other cases in the PIA data as shown in Figure 4, where all spectra having C but not O are plotted. Note the correlation between mass 26 and C and N (mass 14), allowing speculation that the CN^+ ion is present in a significant fraction of these spectra. PUMA data has shown significant occurrences at 24 major mass lines which were attributed to molecular ions.[3] Of these, only masses 25, 26, and 29 are similar to frequent occurrences in the PIA data. It has been surmised, however, that two of the PIA amplifier stages were non-functional, possibly causing fewer mass lines to appear in these spectra than in the PUMA data.

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REFERENCES

1 Kissel, J. : ESA Spec. Publ. 1077, p.67-8, 1986.
2 Clark, B.C., Mason, L.W., & Kissel, J. : 20th ESLAB Symp., ESA SP-250, Vol III, p. 353-8, 1987.
3 Kissel, J., and Kreuger, F.R. : *Nature* **326**:755-60 (1987).

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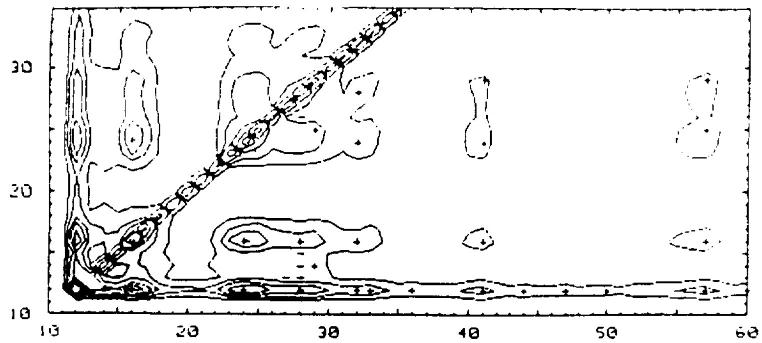

Figure #1 *Frequency of occurrence contours for entire compressed PIA data set consisting of 8030 individual mass spectra. Axes are in units of atomic mass.*

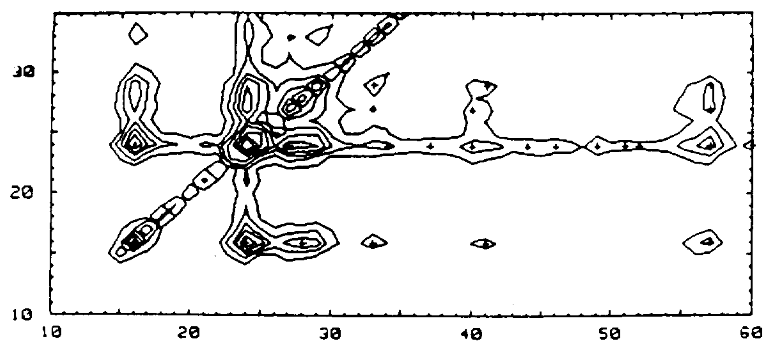

Figure #2 *Subset of 321 spectra containing magnesium (mass 24) but not carbon (mass 12).*

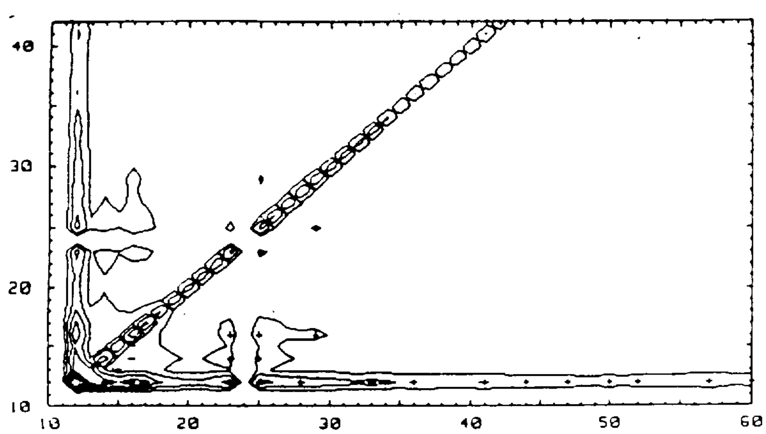

Figure #3 *Subset of 4198 spectra containing carbon but not magnesium.*

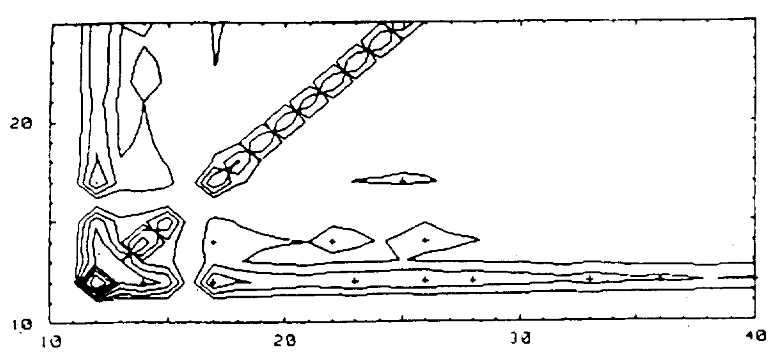

Figure #4 *Subset of 3561 spectra containing carbon but not oxygen (mass 16). Presence of CN^+ ion may be indicated by correlations between mass 26 and carbon and nitrogen (mass 14).*