Using meteorite samples as a test for correlation based analysis of SIMS data from cometary grains

Stenzel O.J.*[1], Varmuza K.[2], Engrand C.[3], Ferrière L.[4], Brandstätter F.[4], Koeberl C.[4,5], Filzmoser P.[2], Paquette J.[1], Hilchenbach M.[1]:

[1] Max Planck Institute for Solar System Research, Justus-von-Liebig-Weg 3, D-37077 Göttingen, Germany (stenzel@mps.mpg.de)

[2] Vienna University of Technology, Institute of Statistics and Mathematical Methods in Economcis, A-1040 Vienna, Austria

[3] Centre de Sciences Nucléaires et de Sciences de la Matière - CSNSM, Bat. 104, F-91405, Orsay, France

[4] Natural History Museum Vienna, Burgring 7, A-1010 Vienna, Austria

[5] University of Vienna, Department of Lithospheric Research, A-1090 Vienna, Austria

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Introduction:

The time-of-flight secondary ion mass spectrometer COSIMA on board the Rosetta spacecraft is analysing cometary grains ejected off the nucleus of comet 67P/Churyumov-Gerasimenko since August 2014 [1]. In our effort to understand the composition and the history of these cometary grains, we studied the characteristics of different meteorite samples with the COSIMA reference instruments at the Max Planck Institute for Solar System Research in Göttingen (Germany), with the goal to separate individual compounds and their fragmentation patterns.

Cosima, the COmetary Secondary Ion Mass Analyzer

is the time of flight secondary ion mass spectrometer on board Rosetta [1]. SIMS data are complex, representing the elements and molecules on the surface area analysed by the primary ion beam. The interpretation of the spectra requires knowledge of the stable molecular ions as well as statistical methods analysing and comparing mass spectra. The spectra are taken from cometary analogue and reference samples analysed with the laboratory reference instrument of COSIMA [2,3].

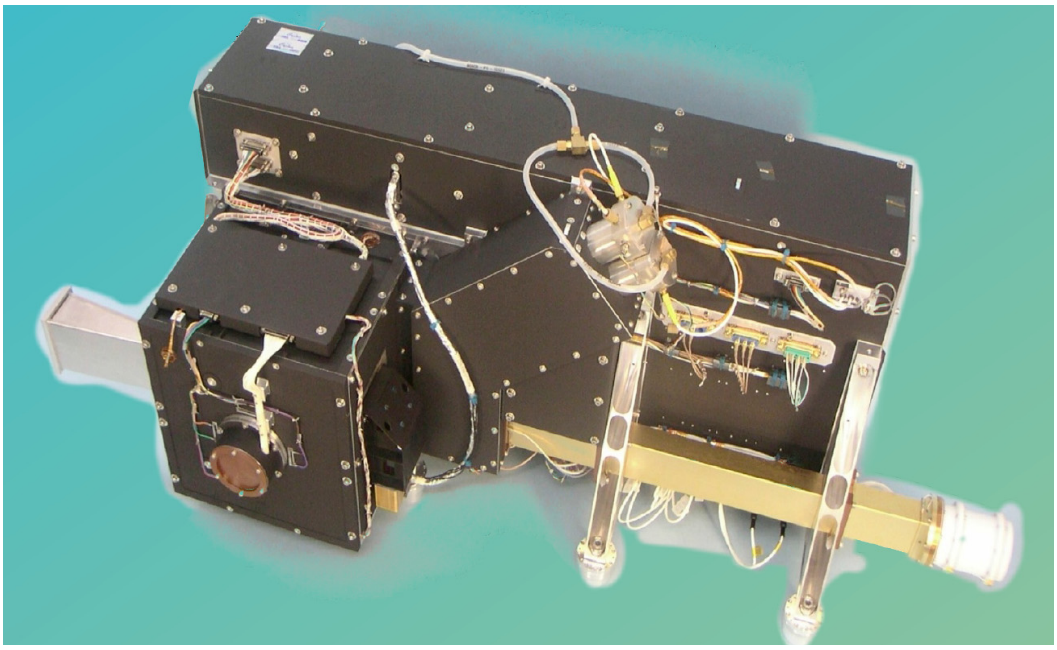

Figure 1: Flight model of Cosima.

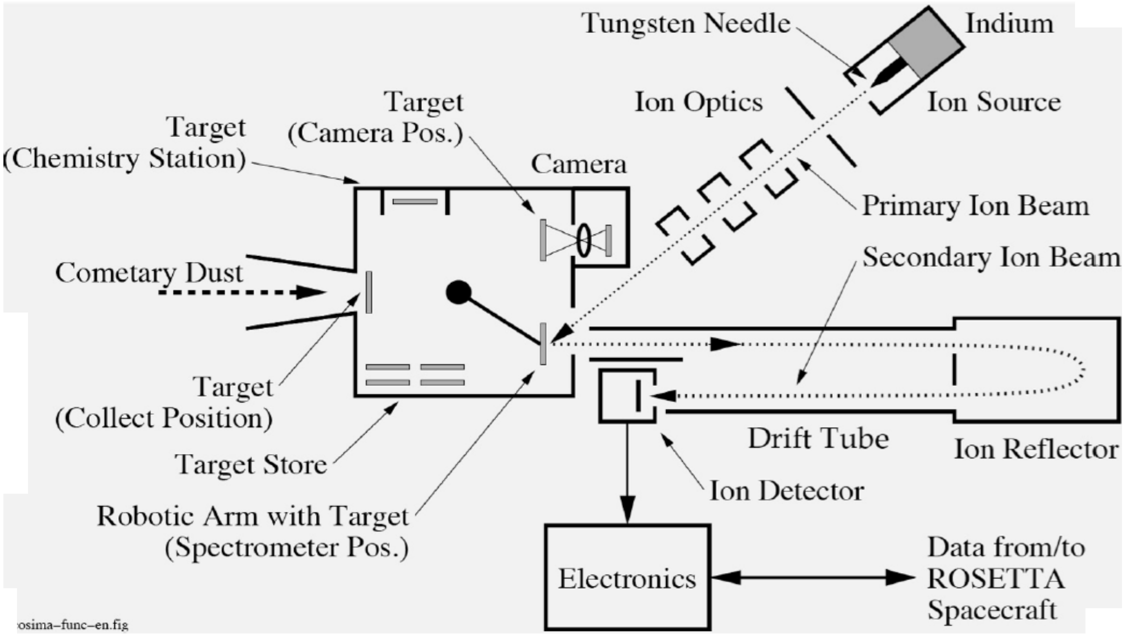

Figure 2: Diagram of the Cosima flight model. Cosima is a time of flight secondary ion mass spectrometer with a resolution mass resolution of about 1:1400 at 100u.

Material and Methods:

Different types of meteorite samples were prepared in the laboratory. Among these were one ordinary chondrite H4 (Ochansk), one unequilibrated ordinary chondrite H3 (Tieschitz), one carbonaceous chondrite CR (Renazzo) [2], and a Martian shergottite (Tissint) [3].

Grains of sizes up to 100 µm were pressed into a blank gold metal target. The grains were identified with the instrument microscope and positive and negative secondary ion mass spectra were accumulated on different positions on selected grains. The mass spectra are accumulating all secondary ions up to mass 300 with reasonable detection efficiency and a mass resolution of 1400@ 100 u/q (unified atomic mass units per elementary charge). This mass resolution is sufficient to separate organic (hydrogen rich) molecule peaks from minerals or elemental mass peaks.

The obtained mass spectra were aligned to a reference mass spectrum taken from the same target but pointing the ion beam at the gold substrate instead of at the meteorite samples. This involves the remapping of the time/mass scale for each single spectrum used. The cross calibration is mandatory to get meaningful correlations between time of flight channels across different spectra. Each spectrum was filtered with a centred running average of width 3 which is the pulse width of the ion beam to reduce noise.

The rebinned spectra were then used to construct a correlation matrix S in which each element r ij is the correlation of the counts in time slot i with the counts in time slot j across a specific sample. Taking an individual column or row of the matrix, yields the correlation of a single time slot with every other time slot. As the time slots translate to specific mass to charge ratios, this method allows to gain information on which elements and molecules are related in the investigated sample.

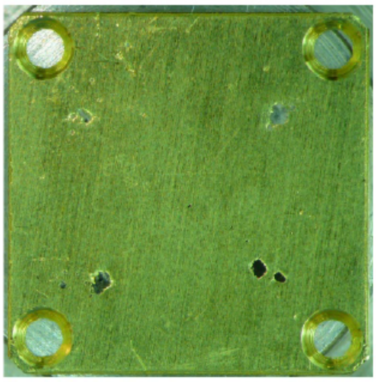

Figure 3: Gold target plate with four meteorite samples.

Results:

Here, we show the correlation analysis of samples from Tissint and Renazzo. Figures 5-9 show the Pearson correlations of counts at the time slots, which translate to the masses of $^{24}Mg^+$, and $^{56}Fe^+$, with the counts across different time/mass ranges for the Tissint sample on the left side and the Renazzo sample on the right side. To keep the text concise from now on, we just write of “correlation of ion abundance at mass x with masses from range y to z”.

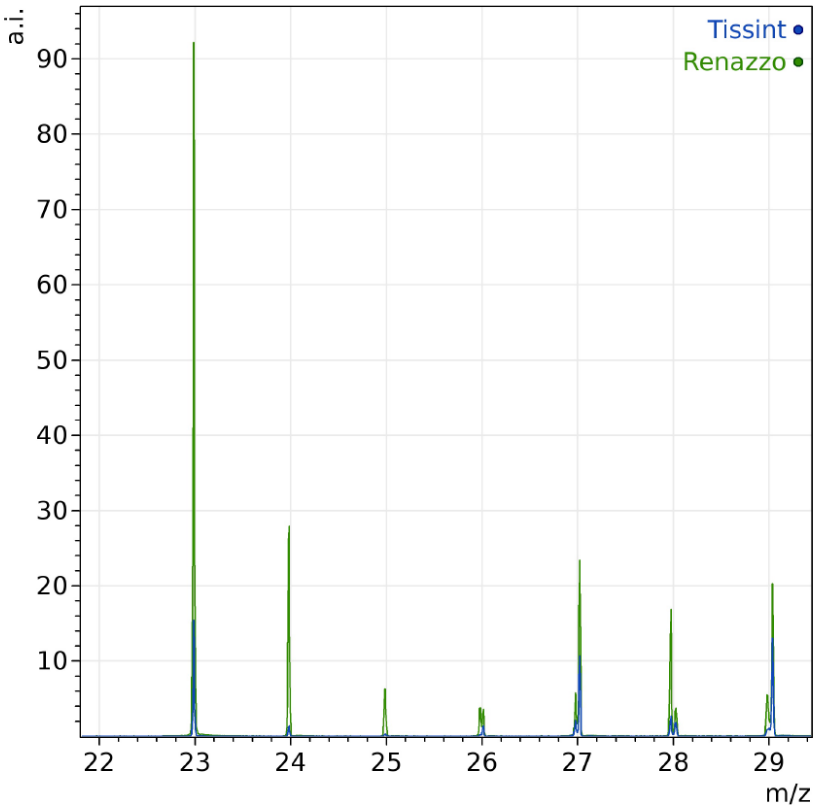

Figure 4: TOF spectra of meteorite samples from Renazzo and Tissint in green and blue, respectively. Both spectra are normalized to the counts of the gold peak at 197 u.

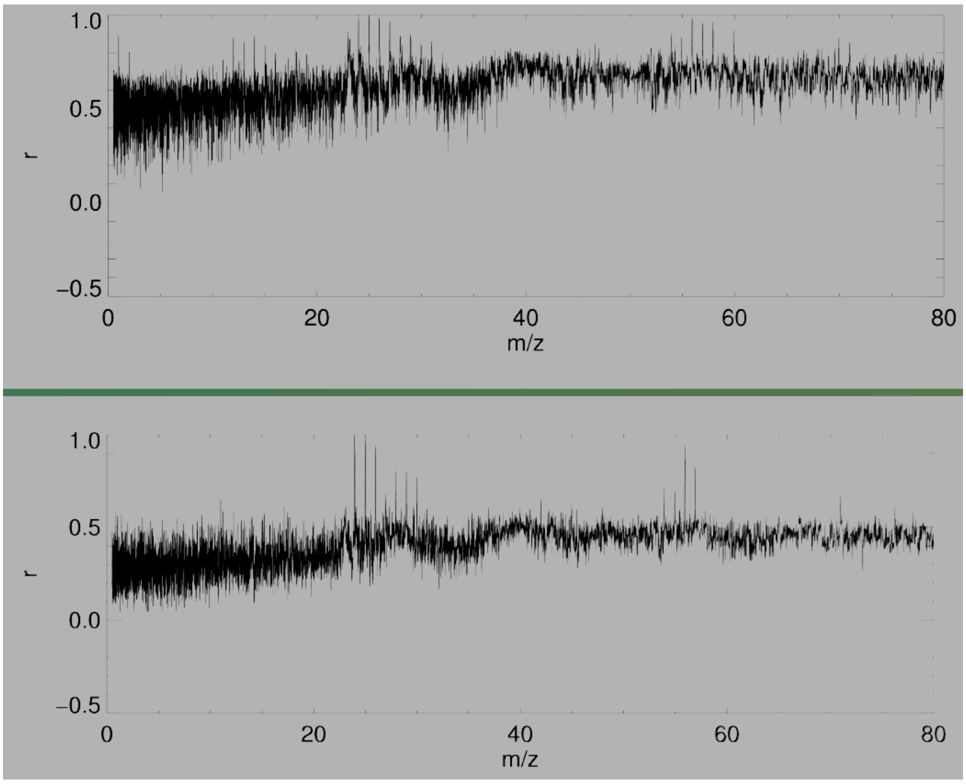

Figure 5: Correlations of mass 23.98 u (24Mg+) with masses 0 u - 80 u.
The top panel shows the Renazzo sample, the bottom one the Tissint sample.
Magnesium shows different correlations between the two samples.

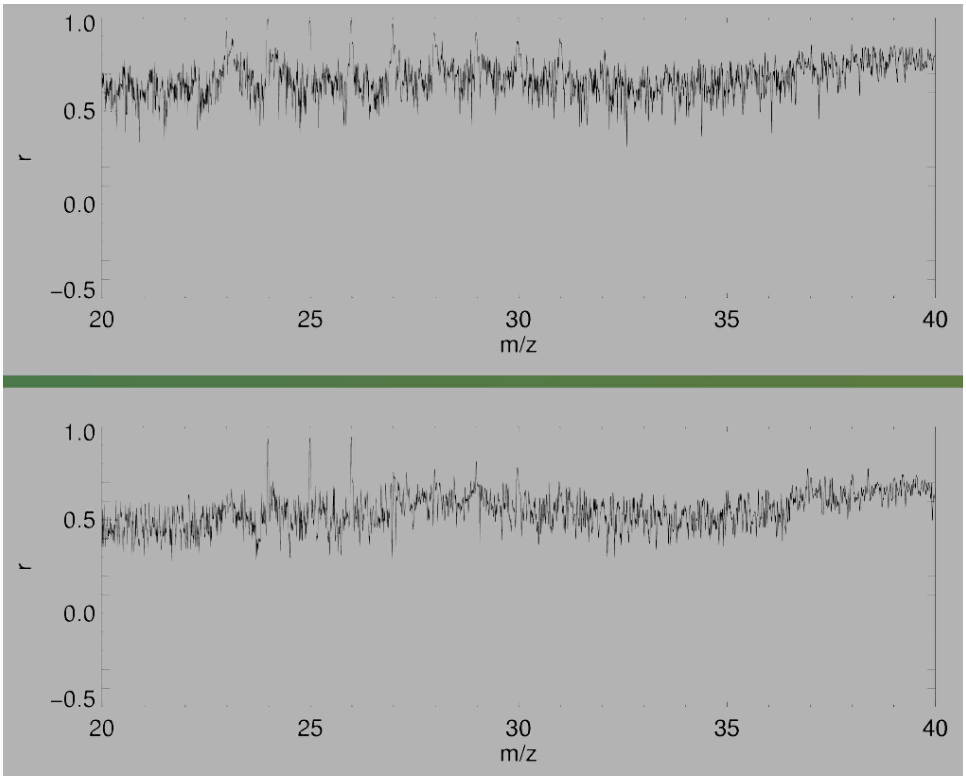

Figure 6: Correlations of mass 23.98 u (24Mg+) with masses 20 u - 40 u. The top panel shows the Renazzo sample, the bottom one the Tissint sample. The Renazzo sample shows correlations above the background with mass 23.98 u at several more masses then the Tissint sample. Especially the masses 23 (Na), 27 (Al), and 28 (Si) show higher correlations.

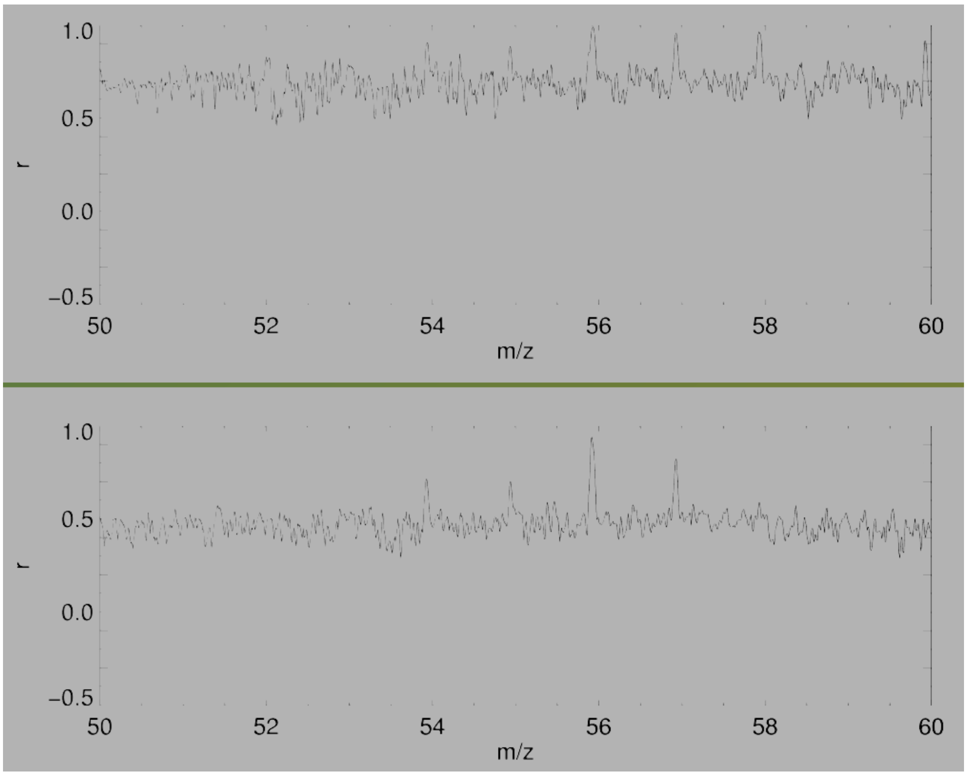

Figure 7: Correlations of mass 23.98 u (24Mg+) with masses 50 u - 60 u. The top panel shows the Renazzo sample, the bottom one the Tissint sample. Renazzo shows correlations of mass 23.98 u with masses of all Fe isotopes, Tissint does not.

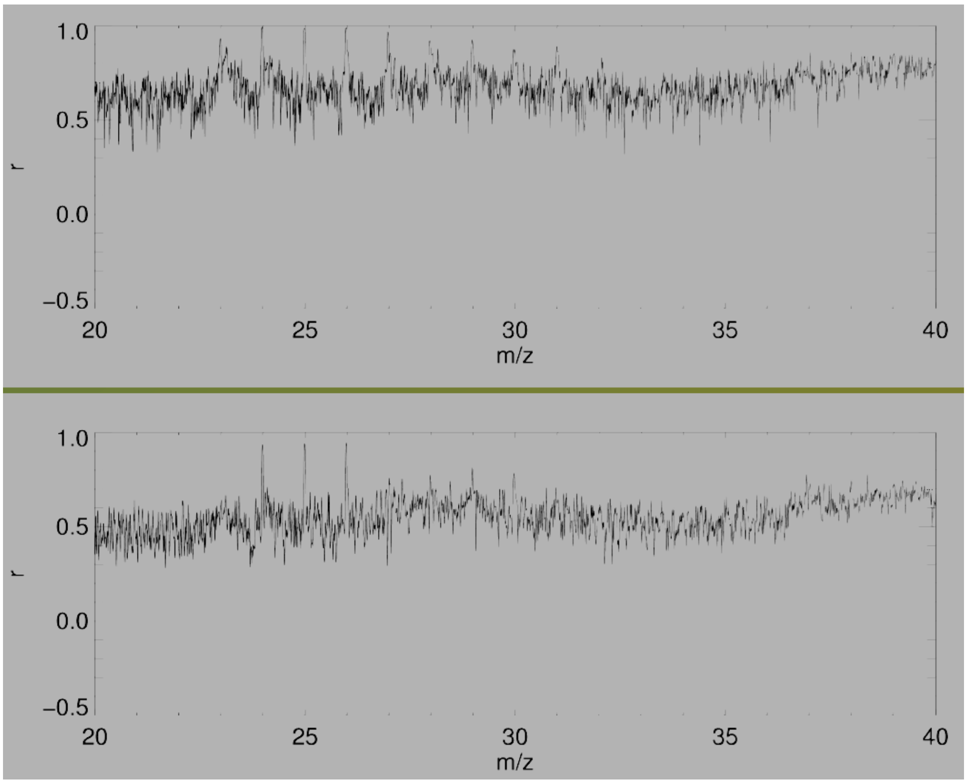

Figure 8: Correlations of mass 55.93 u (56Fe+) with masses 50 u - 60 u. The top panel shows the Renazzo sample, the bottom one the Tissint sample. Renazzo shows higher correlation of mass 55.93 u with masses 27 (Al), and 28 (Si), among others.

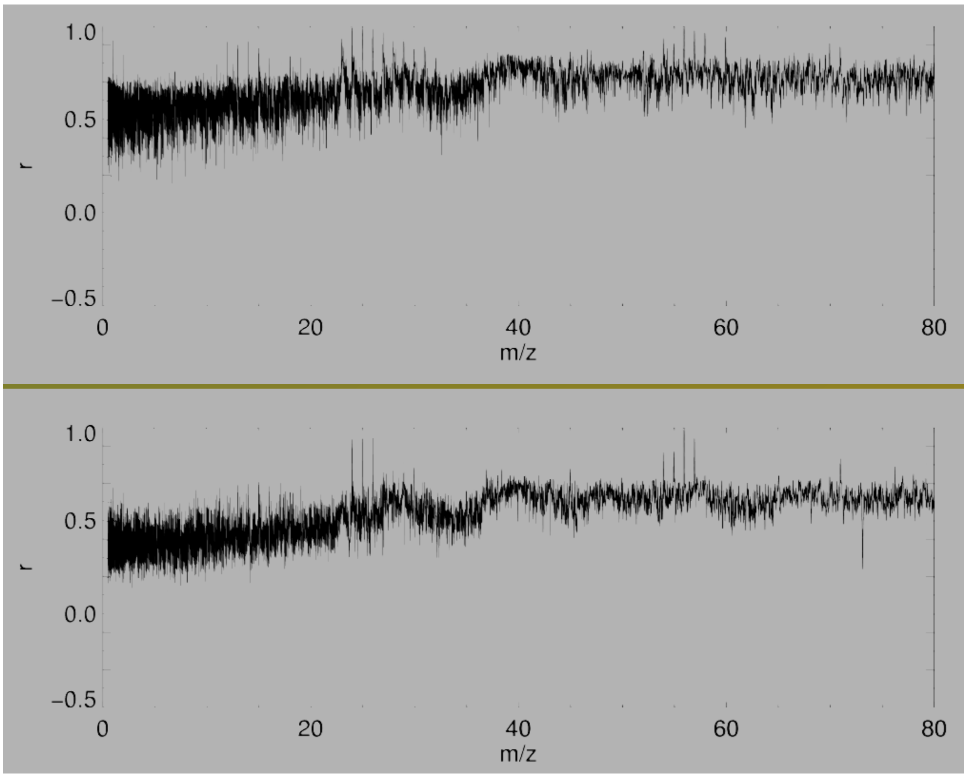

Figure 9: Correlations of mass 55.93 u (56Fe+) with masses 0 u - 80 u. The top panel shows the Renazzo sample, the bottom one the Tissint sample. The mass 55.93 u shows a different pattern for Renazzo and Tissint, showing high correlations for many more masses in Renazzo than for Tissint.

Discussion and Conclusion:

As can be seen from the figures above, there are some subtle and some larger differences between the samples from the Martian Shergottite and the CR chondrite. Especially the correlations with different masses in the 20 u to 30 u range that $^{56}Fe^+$ (mass 55.93 u) show that iron may be associated with different elements in Tissint and in Renazzo. In turn $^{24}Mg^+$ shows a strong correlation with all Fe isotopes for Renazzo but not for Tissint. Mg shows no correlation with Al in the Tissint sample but in the Renazzo one. These few elements already show that the two distinct samples can clearly been distinguished from each other by correlation analysis. This makes us confident in our use of this technique to further characterize the spectra of the cometary dust particles.

The correlation analysis is just one step to really identify compounds from the samples. Other methods are also needed, e.g., to look at absolute and relative abundance of specific elements, etc. We continue to apply and improve these tools for the use with cometary data.

Acknowledgements:

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References:

[1] Kissel J. et al. (2007), Space Sci Rev, 128, 823-867. [2] Mason BH and Wiik HB (1962), American Museum Novitates 2106. [3] Ibhi A. et al. (2012), J. Mater. Environ. Sci. 4 (2) 293-298.

USING METEORITE SAMPLES AS A TEST FOR CORRELATION BASED ANALYSIS OF SIMS DATA FROM COMETARY GRAINS. O.J. Stenzel[1], K. Varmuza[2], C. Engrand[3], L. Ferrière[4], F. Brandstätter[4], C. Koeberl[4,5], P. Filzmoser[2], J. Paquette[1], and M. Hilchenbach[1]. [1]Max Planck Institute for Solar System Research, Justus-von-Liebig-Weg 3, 37077 Göttingen, Germany (stenzel@mps.mpg.de), [2] Vienna University of Technology, Department of Statistics and Probability Theory, A-1040 Vienna, Austria, [3]Centre de Sciences Nucléaires et de Sciences de la Matière - CSNSM, Bat. 104, 91 405 Orsay, France, [4]Natural History Museum, Burgring 7, A-1010 Vienna, Austria, [5]Department of Lithospheric Research, University of Vienna, A-1090 Vienna, Austria.

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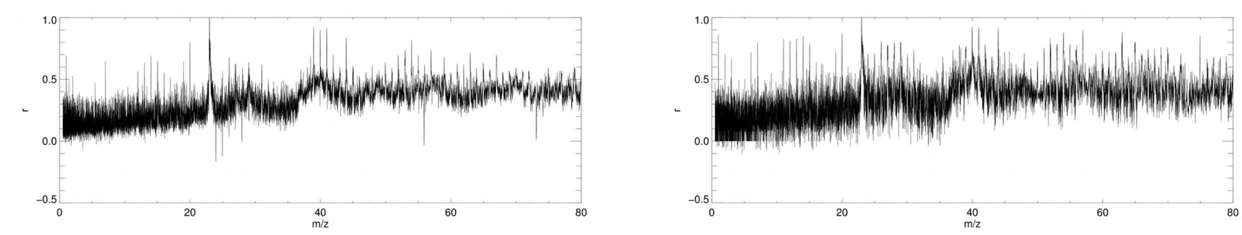

Figure 1: Correlation of ion abundance at mass 22.99 u (sodium) with masses between 0 u and 80 u from the Tissint (left) and Renazzo samples (right).

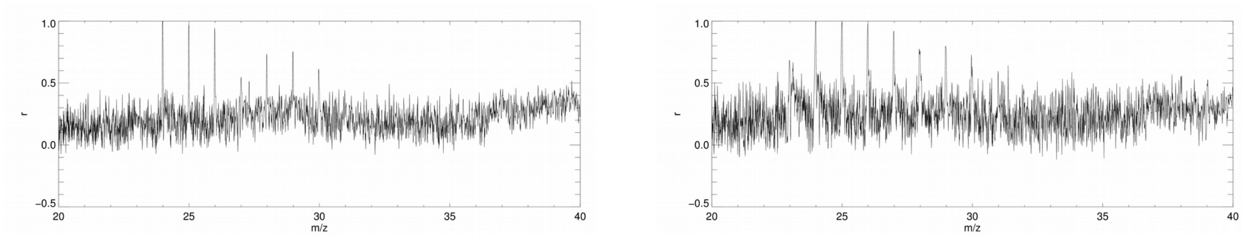

Figure 2: Correlation of ion abundance at mass 23.98 u (magnesium) with masses between 20 u and 40 u from the Tissint (left) and Renazzo samples (right).

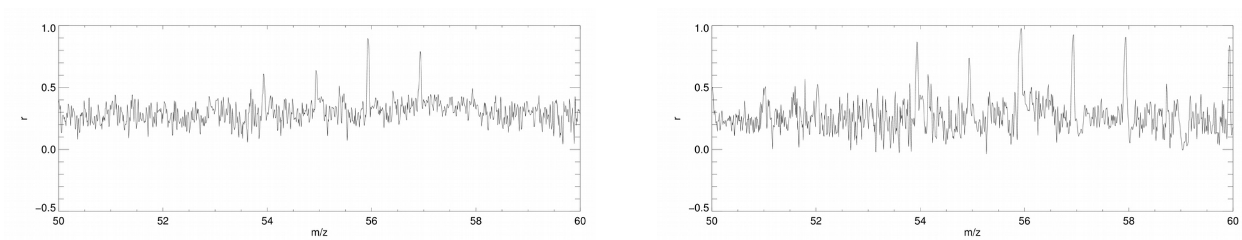

Figure 3: Correlation of ion abundance at mass 23.98 u (magnesium) with masses between 50 u and 60 u from the Tissint (left) and Renazzo samples (right).

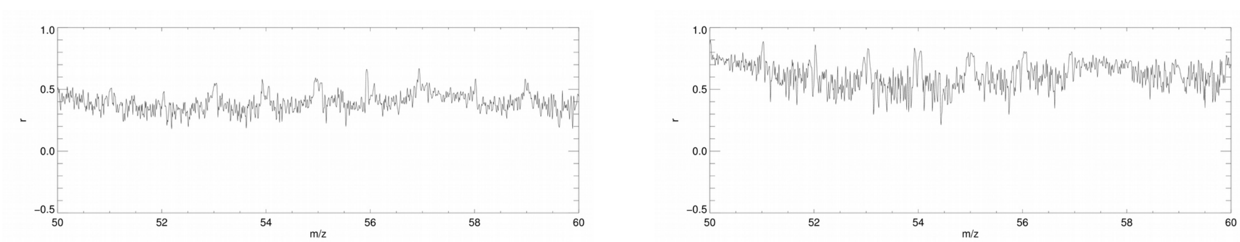

Figure 4: Correlation of ion abundance at mass 27.98 u (silicon) with masses between 50 u and 60 u from the Tissint (left) and Renazzo samples (right).

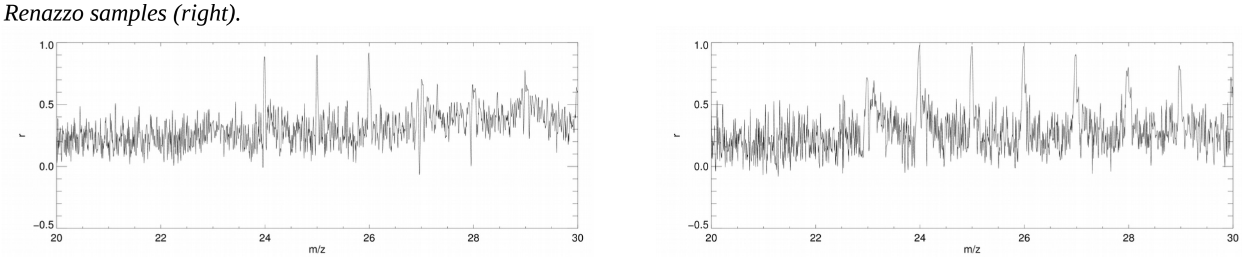

Figure 5: Correlation of ion abundance at mass 55.93 u (iron) with masses between 20 u and 30 u from the from the Tissint (left) and Renazzo sample (right), in which iron seems to be correlated with all three Mg isotopes, but different from the Tissint sample, there are positive correlations with Al and Si, too.