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ANALYSIS OF LASER EXTRACTED VOLATILES IN CARBONACEOUS CHONDRITES

Final Report

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ABSTRACT

It is scientifically important to understand the composition of volatile compounds from interplanetary dust particles (IDP's) because they may be related to the primordial inventory of planetary materials which were necessary to provide environments conducive to the formation of life. The principal task for this project was to evaluate the use of a laser microprobe to measure volatiles in IDP's. Because primitive meteorites are thought to be closely related to IDP's, carbonaceous chondrites were used for the evaluation. Three sets of experiments were performed to determine the volatiles released from potential substrate materials, to analyze the volatiles released from matrices of bulk samples of carbonaceous chondrites, and to analyze volatiles released from ~100-200 μm meteorite particles to simulate IDP's. Aluminum appeared to be the best choice of substrate material. Mass ratios between carbonaceous chondrite matrices of Allende and Murchison show fair reproducibility with somewhat high uncertainties. Particles (~100 - 200 μm) from the Orgueil, Murchison, and Allende meteorites produced measurable quantities of volatiles that appear to have mass spectra comparable to the bulk matrices.

INTRODUCTION

We used a laser microprobe to study volatile compounds released from meteorites. Our ultimate view is to apply the laser microprobe to the study of interplanetary dust particles (IDP's) (Gibson and Sommer, 1986). These particles are so small ($\sim 10^{-6}$-10^{12}g) that the laser microprobe may be one of the few practical ways to study volatile compounds in them. These compounds probably played an important role in establishing life in the solar system when similar materials were accreted to form the Earth or were captured after the Earth cooled. IDP's may be similar to primitive classes of meteorites and, therefore, meteorite studies provide useful preliminary work for establishing quantitative methods and for determining limits of reproducibility.

Laser Microprobe

The laser microprobe (Sommer and Gibson, 1985, 1986; Carr and Gibson, 1987) consists of a sample chamber mounted on a microscope stage which has a mass spectrometer in its evacuation line. The sample can be viewed and aligned using microscope optics. A mirror permits focusing a laser beam on the same spot. The laser is a Jarrell-Ash Q-switched Nd-glass laser with energy input to the sample of 0.1-1.0 J. When the laser is fired heat generated by the beam volatilizes part of the sample. The energy mode that was used for most of the analyses reported here (~0.56 J) created a heat-damaged crater of ~200-300 μm diameter in most samples. The gases released passed through a Hewlett-Packard model 5970 Mass Selective Detector (MSD). In this instrument the the gases are ionized, selected by a quadrupole mass spectrometer, and detected by an electron multiplier. The MSD is controlled automatically by a Hewlett-Packard model 9000 series 300 microcomputer using Hewlett-Packard ChemStation software. This instrument and software are more conventionally used with a gas chromatograph replacing the laser excited sample chamber.

Interplanetary Dust Particles

Dust particles in the solar system are a valuable resource for planetary materials. These particles can be collected on spacecraft and high altitude aircraft, found in sea sediments, cryoconite deposits in Greenland, and in the ice sheet of Antarctica. Currently the curated particles (Zolensky et al., 1986) collected in the stratosphere provide the best source of documented particles many of which are IDP's.

Interplanetary dust particles must be selected from the many particles collected in the stratosphere. We attempt to do this by finding similarities in the composition and structure of the particles with known extraterrestrial materials. Many IDP's seem to have compositions closely related to meteorites, especially the more primitive classes of meteorites (Brownlee et al., 1987; Blanford et al., 1987). Recently direct measurements of cometary dust have been made and some IDP's seem to have compositions related to cometary dust as well (Kissel et al., 1986a, b; Balsiger et al., 1986). The most interesting fact is that, although compositions are closely related to other solar system materials, IDP compositions show their own uniqueness. Some of the IDP's are rich in carbon which may be present in organic species (Fraundorf, 1981; Blanford et al., 1987). These organic species are particularly important because of their possible relation to the formation of life in the solar system. Increased knowledge of the primordial organic inventory of the solar system will probably provide strong constraints on life forming events.

EXPERIMENTAL WORK

To obtain useful information from IDP's it will be necessary to analyze small particles quantitatively and reproducibly. Three sets of experiments were performed to determine the volatiles released from potential substrate materials, to analyze the volatiles released from matrices of bulk samples of carbonaceous chondrites, and to analyze volatiles released from ~100-200 μm meteorite particles to simulate IDP's.

Substrate Selection

The laser beam will necessarily be larger than particles analyzed. Consequently the particles must be placed on substrates which, when cleaned, contribute either an insignificant amount of released volatiles when compared to the intended samples or a measurable background of volatiles that can be subtracted from unknowns. The following materials were examined: aluminum, beryllium, indium, tungsten, tantalum, alumina, fused silica, silica air gel, borosilicate glass, metallized Kapton®, and Torr Seal®. The metals showed the lowest backgrounds consisting essentially of adsorbed air, but the metals themselves vaporized and condensed on the chamber window. Cleaning materials, namely detergents, isopropanol, and Freon®, did not give significant mass peaks. Aluminum appeared to be the best choice for present because the vaporized metal could be easily removed at the end of a sample run by chemical dissolution. A sample of polished aluminum did not give any improvement over conventional sheet aluminum. Total background signals from aluminum are as high as 25% of the signal from the small Allende grains to be discussed below, but become less significant to insignificant for samples with high volatile contents. Figure 1 is a mass spectrum from a single laser shot on cleaned aluminum which can be compared to other mass spectra of meteorites to be presented.

Stratospherically collected IDP's are entrapped on a plate covered with silicone oil which is subsequently dissolved with hexane (Zolensky et al., 1986). We measured laser

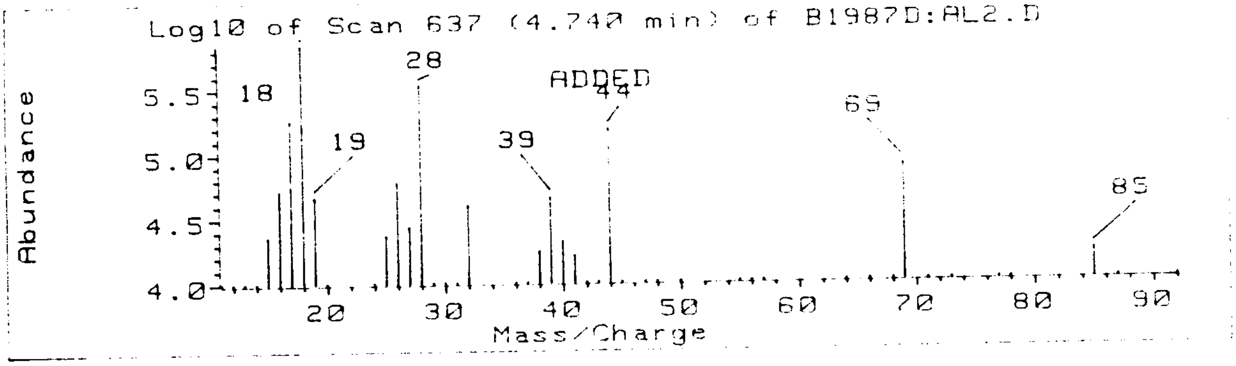

Figure 1. Mass spectrum of released volatiles from a single laser shot on cleaned aluminum.

extracted volatiles from silicone oil (on aluminum) and from a similar sample disk cleaned with hexane. Silicone oil produces a substantial amount of vaporized gas (Fig. 2) although a sample disk cleaned with hexane (Fig. 3) appears little different from aluminum cleaned normally (Fig. 1). We intend to continue to monitor for the presence of silicone oil and hexane to determine whether the collection and curation procedures disturb the laser extracted volatiles that will be measured from IDP's.

Meteorite Matrices

Laser extracted volatiles were measured from the matrices of bulk samples of the Murchison C2 and the Allende C3 carbonaceous chondrites to determine the amount and

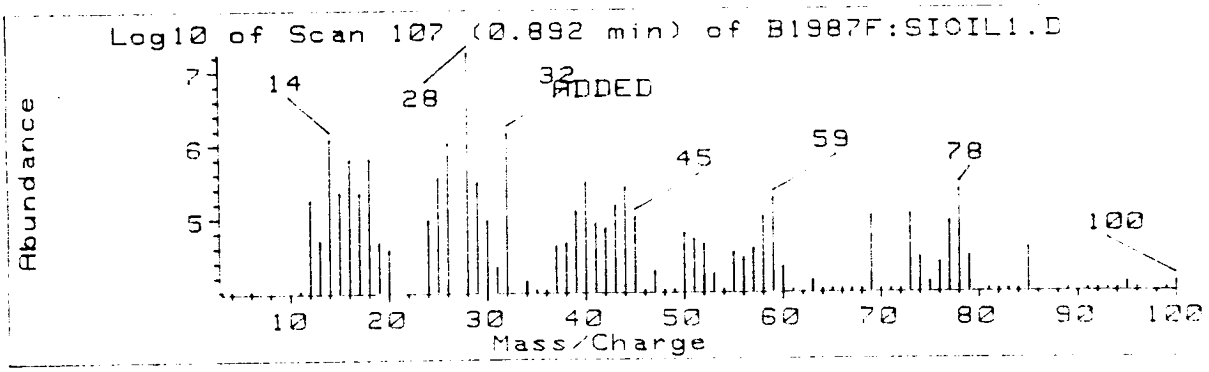

Figure 2. Mass spectrum of released volatiles from a single laser shot on aluminum covered with silicone oil.

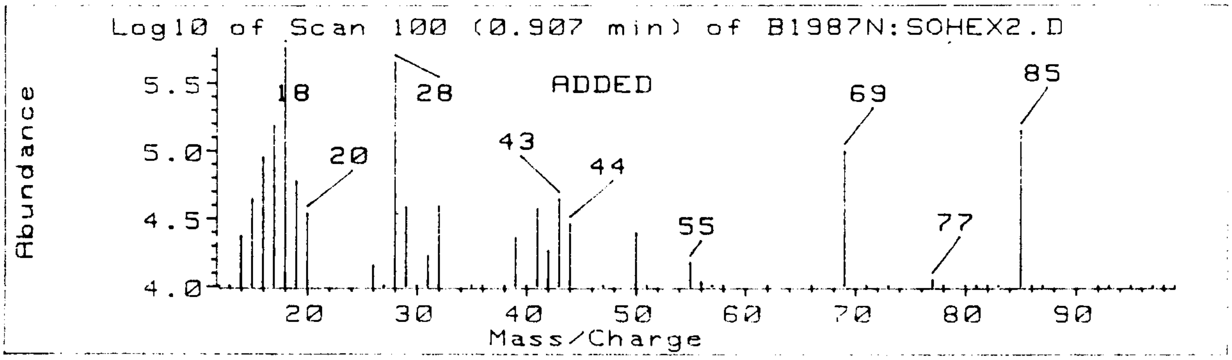

Figure 3. Mass spectrum of released volatiles from a single laser shot on aluminum, previously covered with silicone oil and then cleaned with hexane.

spectrum of gases that could be obtained from a fixed laser energy (~0.56 J). Data have been gathered for 20 spots in each meteorite from bulk samples each having ~1 cm^2 cross-section. Figures 4 and 5 show mass spectra from a single laser shot for Murchison and Allende respectively. It is difficult to compare the spectra from these graphs, however, because the volatile yield (counts) from Allende is lower than that for Murchison. Complete analysis of the data awaits the connection of the Hewlett-Packard computer to a Digital Equipment Corporation VAX® computer to statistically analyze the output. Because this connection has not been made, we must report incomplete analyses. Figure 6 shows averaged mass spectra for five laser shots on Murchison that

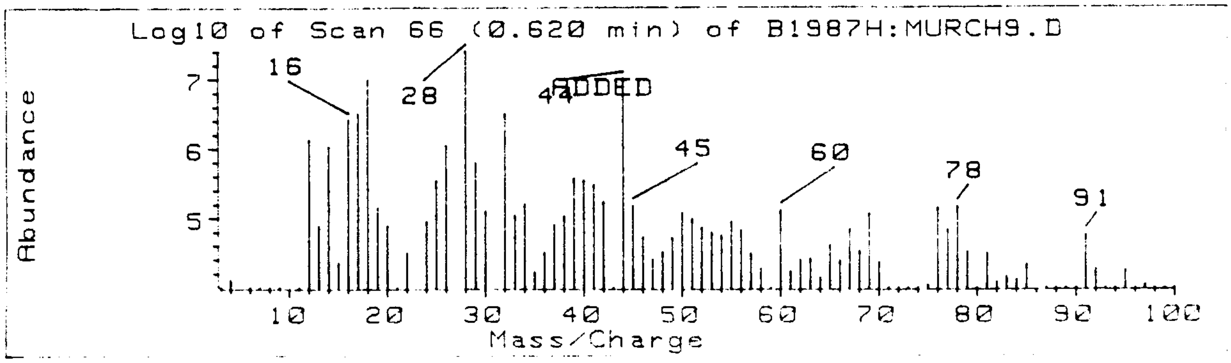

Figure 4. Mass spectrum of released volatiles from a single laser shot on the matrix of the Murchison meteorite.

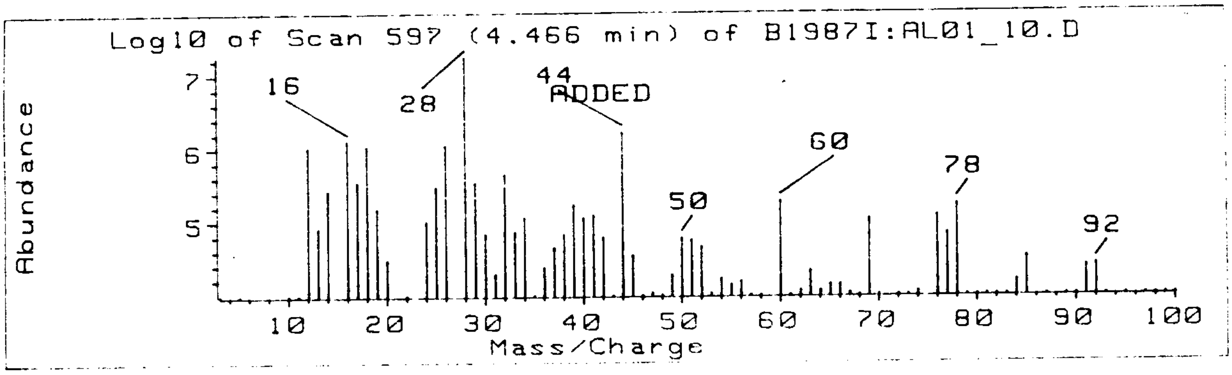

Figure 5. Mass spectrum of released volatiles from a single laser shot on the matrix of the Allende meteorite.

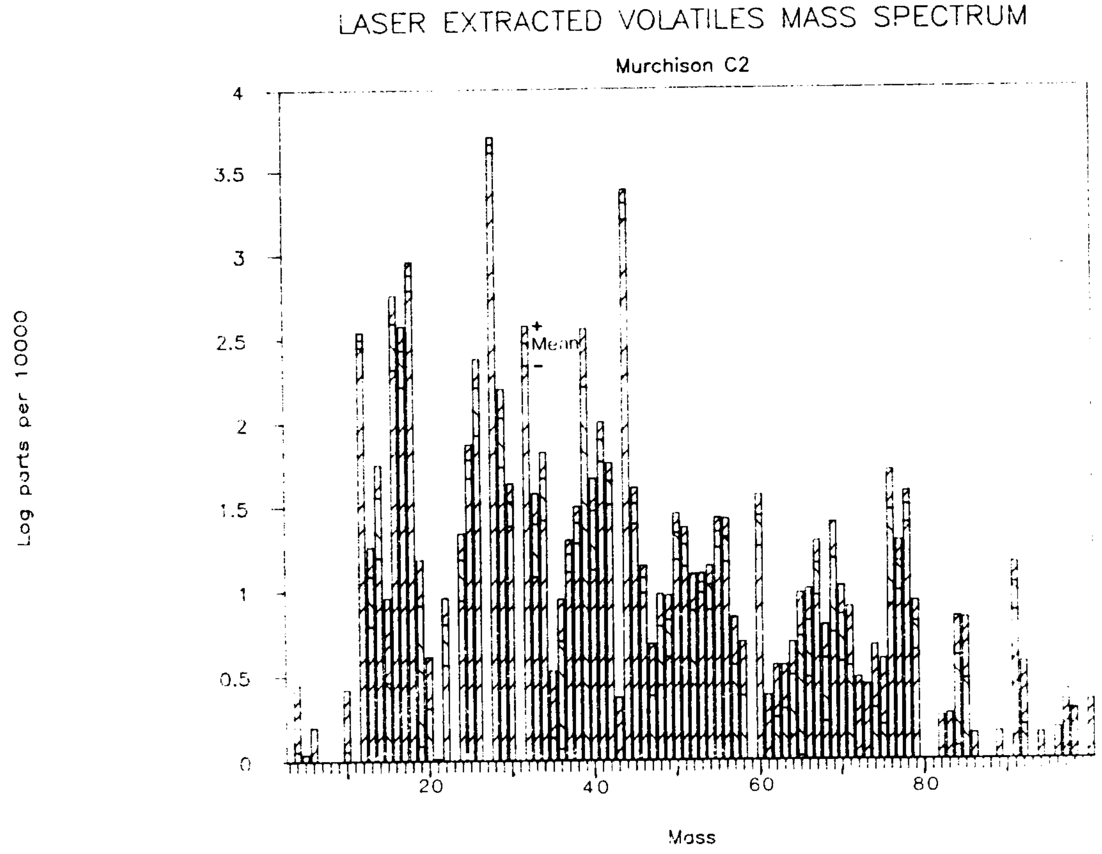

Figure 6. Average mass spectrum of released volatiles from five laser shots on the matrix of the Murchison meteorite showing the standard deviation for each mass.

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was obtained by transferring data by hand. The data are expressed as parts per ten thousand of the total volatile signal and the mean and standard deviations are shown for each mass peak. Determining the standard deviation for each mass will enable us to find the reproducibility of successive analyses and the noise level for each mass. Table 1 shows a comparison of several selected masses and the total signal from a small subset of the Murchison and Allende bulk data. As expected the Allende meteorite yields a smaller volatile component than the more primitive Murchison meteorite. However, this initial look at the reproducibility of the data show uncertainties which seem large.

Meteorite Grains

Our final experimental data has been taken from 100-200 μm particles of the Orgueil C1, Murchison C2, and Allende C3 carbonaceous chondrites. The particles are larger than we expect for IDP's, but we will work with a set of smaller particles after evaluating the current experimental data. Again we need the computer link to complete the analyses of these data. Figures 7, 8, and 9 show mass spectra of a single particle from Orgueil, Murchison, and Allende respectively. Orgueil and Murchison seem to have similar yields which are higher than that of the less primitive Allende meteorite.

Table 1

Allende/Murchison

Mass	Signal	Fraction
18	0.032 ± 0.024	0.075 ± 0.068
28	0.632 ± 0.272	1.388 ± 0.263
44	0.272 ± 0.137	0.642 ± 0.200
Total	0.444 ± 0.202	

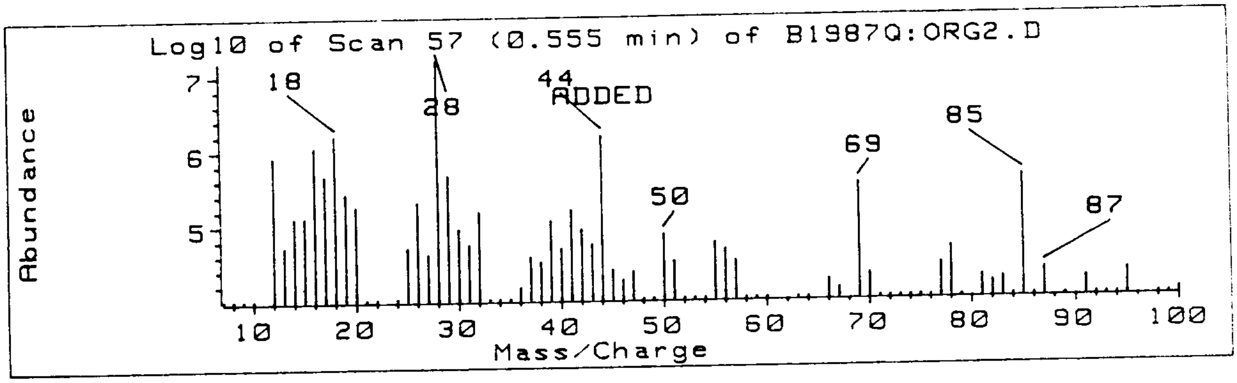

Figure 7. Mass spectrum of released volatiles from a 200 μm particle of the Orgueil meteorite.

The mass spectra of several grains of the Murchison meteorite have been averaged together in Fig. 10 which can be compared to Fig. 6 for the bulk meteorite. Table 2 compares some of the mass peaks obtained from the bulk and from the grains.

CONCLUSION

Considerable experimental data has been collected from carbonaceous chondrites to quantify and to test reproducibility of a laser microprobe. Until the data analyses are complete it is premature to examine the details of the mass spectra. It is clear, however, from the meteoritic mass spectra shown in this report that the laser microprobe releases fairly reproducible amounts of high mass volatiles from these meteorites both in bulk and as particles. However, the laser vaporized gases may react with themselves in

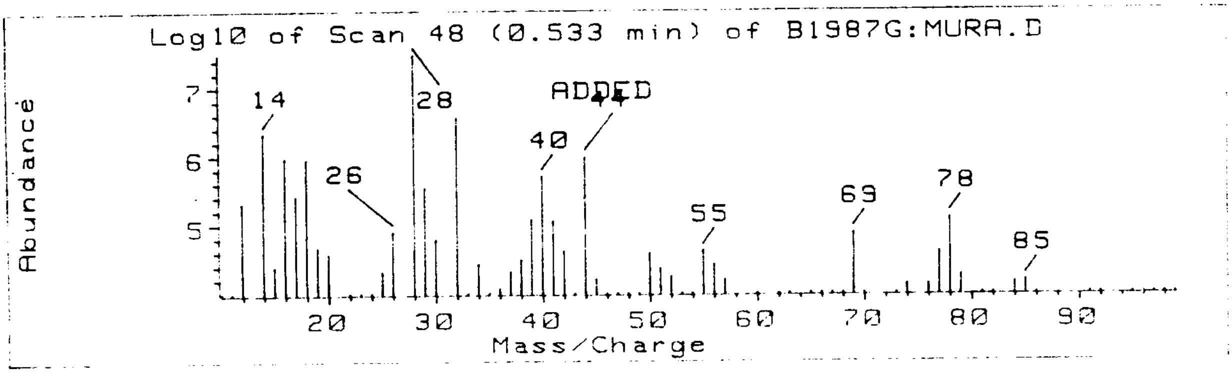

Figure 8. Mass spectrum of released volatiles from a 150 μm particle from the Murchison meteorite

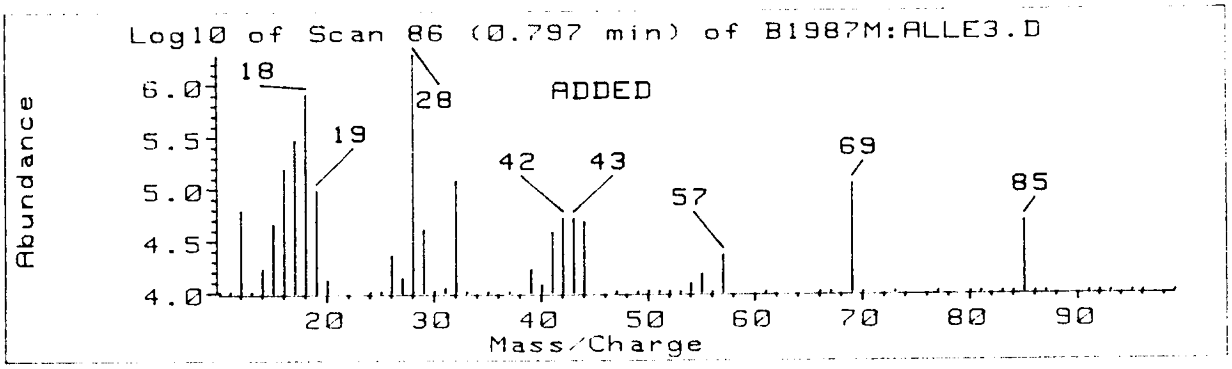

Figure 9. Mass spectrum of released volatiles from a 100 μm particle from the Allende meteorite.

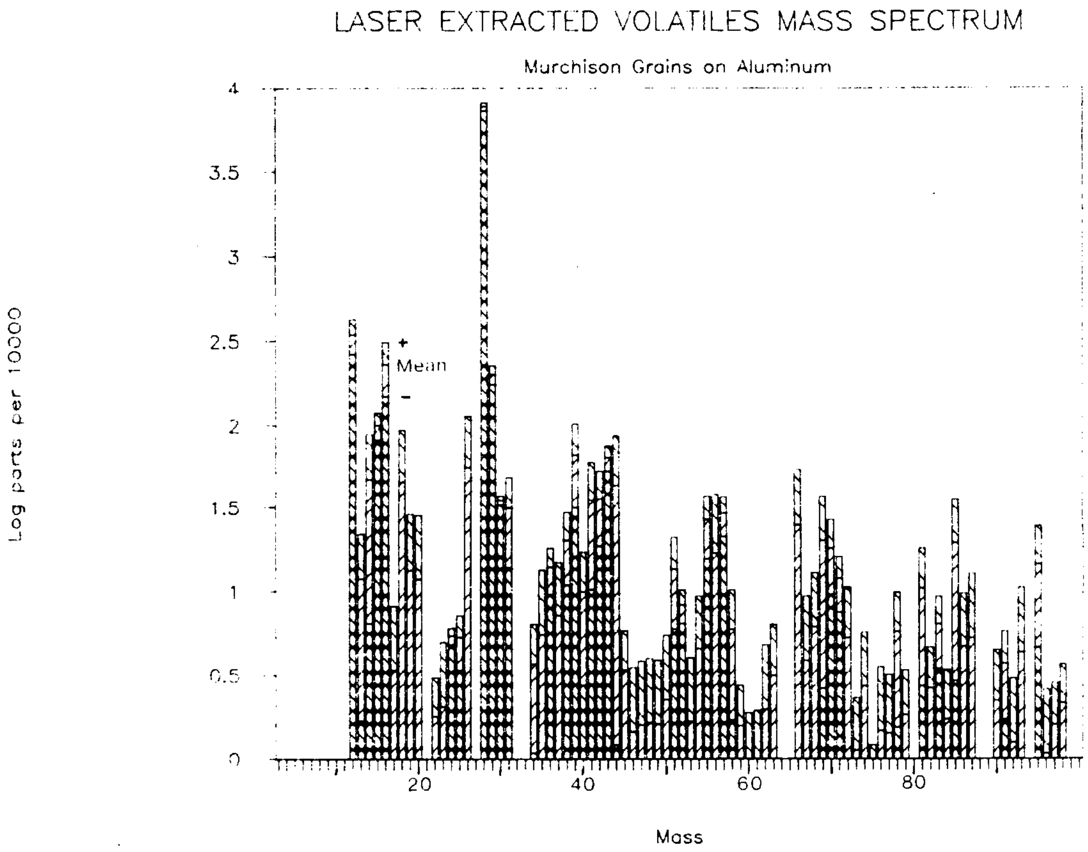

Figure 10. Average mass spectrum of released volatiles from three 100-200 μm particles from the Murchison meteorite showing the standard deviation for each mass.

Table 2

Selected Masses from Murchison C2

(parts per 10 000)

Mass	Particles	Bulk
12	344 ± 80	315 ± 32
13	12 ± 10	12 ± 6
14	48 ± 41	36 ± 20
15	100 ± 18	3 ± 6
16	229 ± 81	392 ± 183
17	3 ± 5	271 ± 106
18	46 ± 48	765 ± 148
24	5 ± 1	15 ± 7
25	5 ± 2	61 ± 14
26	56 ± 57	162 ± 78
28	7757 ± 433	4522 ± 475
29	200 ± 26	107 ± 52
30	35 ± 2	34 ± 10
32	0 ± 0	296 ± 78
44	44 ± 43	2005 ± 406
69	20 ± 17	15 ± 10
91	4 ± 2	11 ± 3
95	15 ± 10	2 ± 2

unknown ways and the ionizer may break them up further so that the indigenous volatiles in the meteorites are not immediately evident from the mass spectra. Interpretation of the mass spectra will require additional study. Almost certainly, however, a database of mass spectra from 38 000 compounds that is part of the ChemStation software will be useful in this interpretation.

REFERENCES

Balsiger H., Altwegg K., Bühler F., Geiss J., Ghielmetti A.G., Goldstein B.E., Goldstein R., Huntress W.T., Ip W.-H., Lazarus A.J., Meier A., Neugebauer M., Rettenmund U., Rosenbauer H., Schwenn R., Sharp R.D., Shelley E.G., Ungstrup E., and Young D.T. (1986) Ion composition and dynamics at comet Halley, Nature, 321, 330-334.

Blanford G.E., Thomas VerPloeg K., McKay D.S. (1987) Microbeam analysis of interplanetary dust particles for major elements, carbon and oxygen. Submitted to Proc. Lunar Planet. Sci. Conf. 18.

Brownlee D.E., Wheelock M.M., Temple S., Bradley J.P., and Kissel J. (1987) A quantitative comparison of comet Halley and carbonaceous chondrites at the submicron level. In Lunar and Planetary Science XVIII, pp. 133-134. Lunar and Planetary Institute, Houston.

Carr R.H., and Gibson E.K. (1987) A quadrupole mass spectrometer - laser microprobe system for the analysis of gases released from geologic samples. In preparation.

Fraundorf P. (1981) Interplanetary dust in the transmission electron microscope: diverse materials from the early solar system, Geochim. Cosmochim. Acta, 45, 915-943.

Gibson E.K., and Sommer M.S. (1986) Laser microprobe study of cosmic dust (IDPs) and potential source materials. In Lunar and Planetary Science XVII, pp. 260-261. Lunar and Planetary Institute, Houston.

Kissel J., Sagdeev R.Z., Bertaux J.L., Angarov V.N., Audouze J., Blamont J.E., Büchler K., Evlanov E.N., Fechtig H., Fomenkova M.N., von Hoerner H., Inogamov N.A., Khromov V.N., Knabe W., Krueger F.R., Langevin Y., Leonas V.B., Levasseur-Regourd A.C., Managadze G.G., Podkolzin S.N., Shapiro V.D., Tabaldeyev S.R., and Zubkov B.V. (1986a) Composition of comet Halley dust particles from Vega observations, Nature, 321, 280-282.

Kissel J., Brownlee D.E., Büchler K., Clark B.C., Fechtig H., Grün E., Hornung K., Igenbergs E.B., Jessberger E.K., Krueger F.R., Kuczera H., McDonnell J.A.M., Morfill G.M., Rahe J., Schwehm G.H., Sekanina Z., Utterback N.G., Völk H.J., and Zook H.A. (1986b) Composition of comet Halley dust particles from Giotto observations, Nature, 321, 336-337.

Sommer M.A., and Gibson E.K. (1985) Determination of volatile components of fluid inclusions in Archean rocks using micro-crushing with a capacitance manometer and mass spectrometer. In Lunar and Planetary Science XVI, pp. 801-802. Lunar and Planetary Institute, Houston.

Sommer M.A., and Gibson E.K. (1986) Volatile determinations of individual fluid inclusions within the 3.4 B.Y. North Pole barites from the Warrawoona group, Northwestern Australia. In Lunar and Planetary Science XVII, pp. 815-816. Lunar and Planetary Institute, Houston.

Zolensky M.E., McKay D.S., Schramm L.S., VerPloeg K.L., Warren J.L., and Watts L.A. (1986) Cosmic Dust Catalog 8, 1. JSC 22425, NASA Johnson Space Center, Houston.