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A SEARCH FOR ORGANICS IN HYDROLYSATES OF LUNAR FINES*

CHARLES W. GEHRKE**, ROBERT W. ZUMWALT***, WALTER A. AUE§, DAVID L. STALLING§§ AND JAY J. RASH§§§
University of Missouri, Columbia, Mo. 65201 (U.S.A.)
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SUMMARY

Lunar fines from the Apollo 11 and 12 missions have been analyzed for amino acids and a wide range of other derivatizable organic compounds by gas–liquid chromatography (GLC). A minimum of 4–6 p.p.b. of *each* amino acid would have been detected, but there were no indications of the presence of amino acids or other organics in the samples. However, a number of GLC peaks were found by the same methodology and proved to be dimethylpolysiloxanes by mass spectrometry (MS). They also appeared in the analysis of two meteorites and the terrestrial materials peridotite and basalt, while these compounds were not detected in numerous chemically related samples. It was established through various experimental approaches, that substances of unknown structure present in the above named samples caused the breakdown and volatilization of silicone traces in GLC and GLC–MS units. These substance(s) were stable to pyrolysis at 1000° in air, soluble in organic solvents, and similar to or stronger than hydrochloric acid in their capability to liberate siloxanes. Nine major and five minor elements present in the Lunar samples were not responsible for the chromatographic peaks.

INTRODUCTION

In our first paper[1] on the analysis of hydrochloric acid hydrolysates of the Apollo 11 lunar fines, we described the search for amino acids with a highly sensitive gas–liquid chromatographic (GLC) method[2]. The N-trifluoroacetyl *n*-butyl ester derivatives were formed by successive esterification with *n*-butanol–HCl and subsequent acylation with trifluoroacetic anhydride. Amino acids, if present, were less than 4

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** Professor and research associate in Space Sciences, University of Missouri, Columbia, and co-investigator on returned Lunar samples, Apollo's 11 and 12.

*** National Science Foundation Predoctoral Fellow, University of Missouri, Columbia.

§ Associate Professor and research associate in space sciences, University of Missouri, Columbia.

§§ Chief chemist, Fish Pesticide Research Laboratory, U.S. Bureau of Sport Fisheries and Wildlife, Columbia, Mo.

§§§ Research assistant, University of Missouri, Columbia.

p.p.b., however, the chromatograms showed that other types of organic material were present.

Since numerous blanks gave no indication of similar materials, we concluded that they were not artifacts of the analytical method. Combined gas chromatography–high and low resolution mass spectrometry (GLC–MS) showed all major peaks to contain the dimethylpolysiloxane structure, $[R(OSi[CH_3]_2)_n]^+$.

In view of the extensive use of silicones on earth and in the space program, contamination of the Apollo 11 sample was considered highly likely. Concerted studies conducted over an 8 month period were made to elucidate the source of this material. Earlier analyses[1] showed clearly that the lunar sample was *not* contaminated with silicones. Furthermore, while all terrestrial materials then studied concurrently with the Apollo 11 sample failed to yield any of the siloxane peaks, another extraterrestrial material — Pueblito de Allende meteorite — gave essentially the same chromatographic peaks as the lunar fines.

This present paper describes our efforts to define the substances which produced the prominent siloxane peaks in GLC and to determine their origin. Three working hypotheses were considered: (a) siloxanes occur in extraterrestrial materials, (b) siloxane precursors occur in extraterrestrial materials and form polymethylsiloxanes in one or more steps of the analytical procedure employed, and, (c) some inorganic substance(s) that are present in extraterrestrial material (but not in blanks) cause siloxanes that are always present in traces in the GLC–MS instrument systems, to break into smaller fragments and show up on the chromatograms.

To test these hypotheses, the analytical procedure was modified in several key aspects to define the chemistry necessary for obtaining the siloxanes. At various points in the method, pyrolysis at 1000° was used to destroy any organic material present, and esterification was conducted with both deuterated and fluorinated alcohols to label the compounds for later analysis by mass spectrometry. Also, an earlier study had shown, that it was impossible to obtain chromatographic peaks (similar to those generated by the lunar material) from commercial methyl and phenyl polysiloxanes by hydrolysis, esterification and/or acylation procedures.

However, all gas chromatographs and associated instrumentation contain traces of silicones. Indeed, even in the unlikely event that silicone-coated (or silylated) supports and substrates had never been used, silicone septa and O-rings would have introduced some contamination into the GC and MS systems. Since silicones are nonvolatile and usually remain stationary, they are not detected in chromatograms, thus, hardly anyone notices their presence. In earlier studies it was shown that such silicones could be detected both by flame ionization and by mass spectrometry, when hydrochloric acid or hydrochloric acid–alcohol mixtures were injected onto polyester chromatographic columns. These silicones were stripped by the acid reagent from the instrumental system or packing. Although this procedure damages most column materials when frequently exercised, we used it to completely free the system of the last traces of silicones prior to analyses by GLC–MS for final confirmation of silicones in the samples.

In investigating the three possible theories for observing dimethylpolysiloxanes, a number of other terrestrial and extraterrestrial samples were chosen (for obvious reasons) and analyzed: Apollo 12 fines, Pueblito de Allende and Murray meteorites, obsidian, peridotite, tektite, silicon carbide, silicic acid and two samples of basalt.

To evaluate possible effects of the high concentrations of inorganic material on the derivatization and GLC analysis of organic compounds of various functionality, the 1 *N* HCl hydrolysate of lunar fines was spiked with an alcohol, an amino acid, an amine, a fatty acid, and a dicarboxylic acid.

EXPERIMENTAL

A. Apparatus and reagents

The gas chromatographs and high resolution GC–MS system used in this study included the same basic instruments described in the previous investigations by GEHRKE *et al.*[1] on Apollo 11 samples at the Ames Research Center. In addition, a GLC–low resolution MS system incorporating a Loenco GC, a Llewellyn membrane interface, and a CEC Model 491 mass spectrometer was also used. Studies at the University of Missouri, Columbia incorporated a Packard 7300 series gas chromatograph interfaced through a Watson-Biemann type molecular separator to a CEC Model 110-B high resolution mass spectrometer which was used to obtain a "siloxane free" analytical instrumental system.

The amino acid standards, *n*-butanol, anhydrous HCl, trifluoroacetic anhydride, and dichloromethane were of the same reagent quality as in ref. 1.

A stock solution was prepared containing *n*-octanol, *n*-hexylamine, valine, lauric acid, and adipic acid at a concentration of *ca.* 15 mg of each compound in 50 ml of *n*-butanol–3 *N* HCl. Ethyl acetate was obtained from Mallinckrodt Chemical Works, and was of "Nanograde" purity. The silicic acid was purchased from Bio-Rad, Inc., and was a Bio-Sil HA, Control No. 6383, 325 mesh. Silicon carbide was obtained from K&K Laboratories, Catalog No. 18268. The micro reaction vials were obtained from Analytical Biochemistry Laboratories, Columbia, Mo.

B. Chromatographic columns

Both 1 m × 4 mm I.D. and 2.5 m × 2 mm I.D. glass columns of OV-17 and ethylene glycol adipate (EGA) chromatographic phases were prepared in the manner reported earlier[1]. Also, a 300 ft. capillary column coated with OV-17 was used for introduction of the sample into the CEC Model 110-B mass spectrometer.

In an effort to obtain chromatographic columns entirely free of silicone contamination, four new glass columns were exhaustively washed with methanolic KOH, chromic acid cleaning solution, acetone, *n*-butanol–3 *N* HCl, and benzene. The "empty glass columns" were checked for organics by placing the columns in the GLC–MS system, and monitoring the effluent after the repeated injection of solvents, including *n*-butanol–3 *N* HCl. The columns were then removed from the instrument, filled with 80/100 mesh A.W. Chromosorb W, and checked again for siloxanes. They were again removed, the Chromosorb coated with 0.65 % EGA, and again placed in the GC oven for conditioning and analysis. The level of siloxane contamination present was determined by GLC–MS using both oscillographic recording and photoplate detection. Also, the *transfer lines* and *molecular separator* were checked for siloxane contamination by introducing *n*-butanol–3 *N* HCl directly into the transfer line.

C. Hydrolysis of samples (with 1 N HCl)

The following samples (1 to 2 g each) were hydrolyzed under reflux for *ca.* 15 h with (5 to 10 ml) 1 *N* HCl. The Apollo 12 lunar fines (1.2 g) were extracted with triple

distilled water (6 ml) under reflux for 15 h prior to the 1 *N* HCl extraction procedure.

Apollo 12 Lunar Fines	ARC 12023.04
Basalt	NASA 040270
Basalt	NASA 080669
Pueblito de Allende Meteorite	NASA 31-4A
Murray Meteorite	NASA 040870
Tektite	NASA 040770
Obsidian	NASA 041170
Peridotite	NASA 043070
Silicic acid	
Silicon carbide	
Sand monitor	

The sand monitor was received from the Lunar Receiving Laboratory, Houston, Texas, for the purpose of evaluating possible contaminants that might have originated in that facility.

The acidic hydrolysates were transferred to centrifuge tubes and centrifuged at *ca.* 2700 r.p.m. for 3 to 4 min. The clear solutions were decanted for further sample treatment and analysis.

D. Analytical method[2]

Aliquots of the acidic hydrolysates from (C), equivalent to 0.25 to 1.0 g of the samples, were placed in 10-ml beakers and evaporated to *ca.* 0.5 to 1 ml under an infrared (IR) lamp, then transferred to the pear-shaped reaction vials. Alternatively, an aliquot of the 1 *N* HCl hydrolysate was extracted with ethyl acetate (3 × with 5 ml (a)), leaving the bulk of inorganic salts in the 1 *N* HCl phase. Then both the ethyl acetate and acidic phases were evaporated and taken through the esterification and acylation steps. The evaporations were completed in the micro reaction vials after washing the 10 ml beakers with 1 ml aliquots of 1 *N* HCl.

After completion of evaporation, samples were allowed to cool, *n*-butanol–3 *N* HCl was then added (200 μl/0.25 g of sample), the vials were closed with teflon-lined caps, followed by ultrasonic mixing for 30–60 sec, then esterified at 100° for 30 min. The *n*-butanol was removed by evaporation under an IR lamp, 100 μl of a dichloromethane–trifluoroacetic anhydride mixture (0.5 μl TFAA/100 μl CH_2Cl_2) were added, then the closed vial was heated at 100° for 10 min. The "derivatized" samples were then analyzed by GLC, GLC–MS (high resolution) and direct probe-MS. All other details for a "nanogram method for amino acids" by ZUMWALT AND GEHRKE are described elsewhere[2].

E. Other experiments

A recovery experiment of the five compounds with various functional groups was carried out by adding *ca.* 1 μg of each compound to 0.5 g equiv. of the 1 *N* HCl hydrolysate of Apollo 11 lunar fines. The sample was then derivatized in accordance with the analytical method described above, and analyzed by GLC.

Labeling experiments were conducted using 1 *N* DCl in D_2O as the hydrolysis medium, and both C_2D_5OD–3 *N* DCl and $C_3F_7CD_2OD$–3 *N* HCl were used in place of the *n*-butanol–3 *N* HCl. Pyrolysis experiments of the acidic hydrolysates were carried out in platinum crucibles in an electric muffle furnace at 1000°. Direct der-

ivatization of 1 mg amounts of OV-17 substrate with *n*-butanol–3 *N* HCl was made by heating at 100°, 30 min, evaporating the alcohol, then adding CH_2Cl_2 prior to GLC analysis. Also, a parallel OV-17 sample was analyzed in this manner by pyrolysis at 975° for 15 h followed by derivatization. In addition, each reagent used in the derivatization was investigated with a basalt sample hydrolysate to determine its

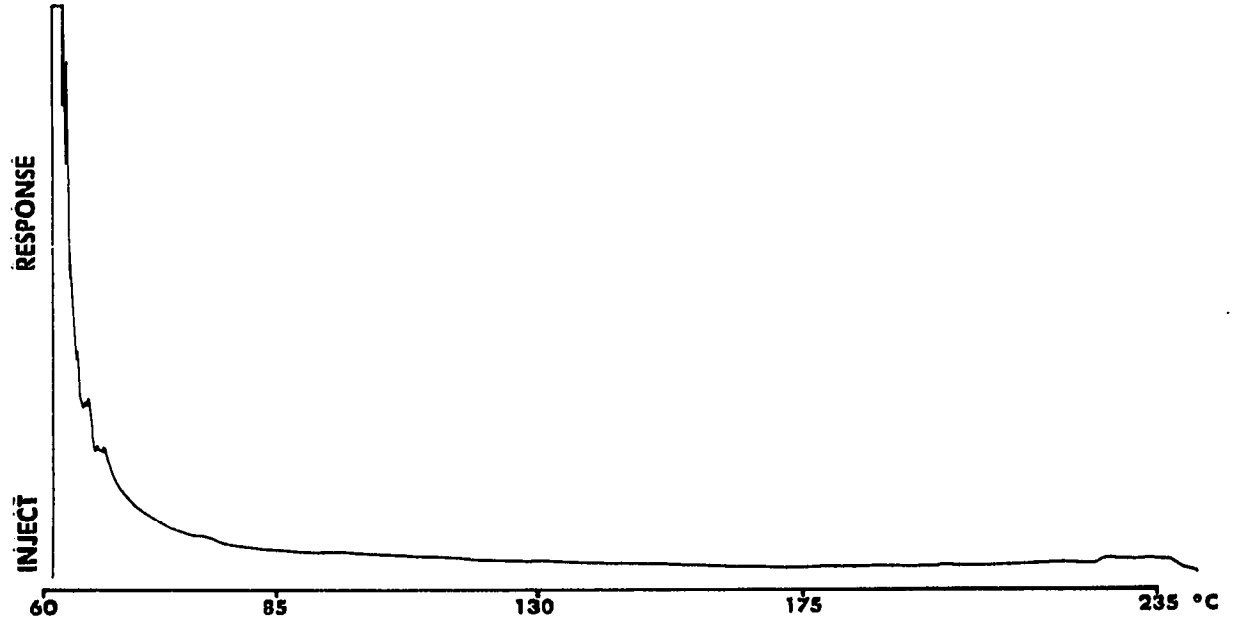

Fig. 1. Reagent blank. 25 ml of ethyl acetate; final volume: 100 μl; injected: 6 μl; attenuation: 8×10^{-11} a.f.s.; initial temperature: 60°; initial hold: 4 min; program rate: 4°/min; final temperature: 235°; column: 1.0 w/w% OV-1 on 80–100 mesh H.P. Chromosorb G, 1 m × 4 mm I.D. glass.

contribution to the formation of siloxanes. In addition, a study was designed to determine the possible effects of some metal chlorides on the chromatographic system. Mixtures of chloride salts of Fe(III), Ti(II), Al(III), Mg(II), Na(I), Cr(III), Cu(II), Rb(I), Zn(II), K(I), Co(II), Cd(II), Ca(II), and Ni(II) were taken through the entire derivatization method then analyzed on an OV-17 column.

RESULTS AND DISCUSSION

The chromatographic results from the initial analyses of the 1 *N* HCl extracts of the Apollo 11 lunar fines and PDA meteorite prompted further study of the meteorite prior to the Apollo 12 investigations. Typical chromatograms obtained for the complete reagent blank and PDA sample are presented in Figs. 1 and 2. The prominent chromatographic peaks at retention temperatures of 69, 77, 99, and 109° show ion fragments typical of methylpolysiloxanes with the general formula $[R(OSi[CH_3]_2)_n]^+$ as reported earlier[1].

The Apollo 12 lunar fines then were studied using the same analytical methods, with the exceptions as presented in the EXPERIMENTAL section. Fig. 3 shows the chromatogram obtained from the ethyl acetate extract of the Apollo 12 1 *N* HCl hydrolysate. The chromatogram obtained from the remaining aqueous HCl phase of Apollo 12 is presented in Fig. 4; the same major mass spectrometric peaks were found.

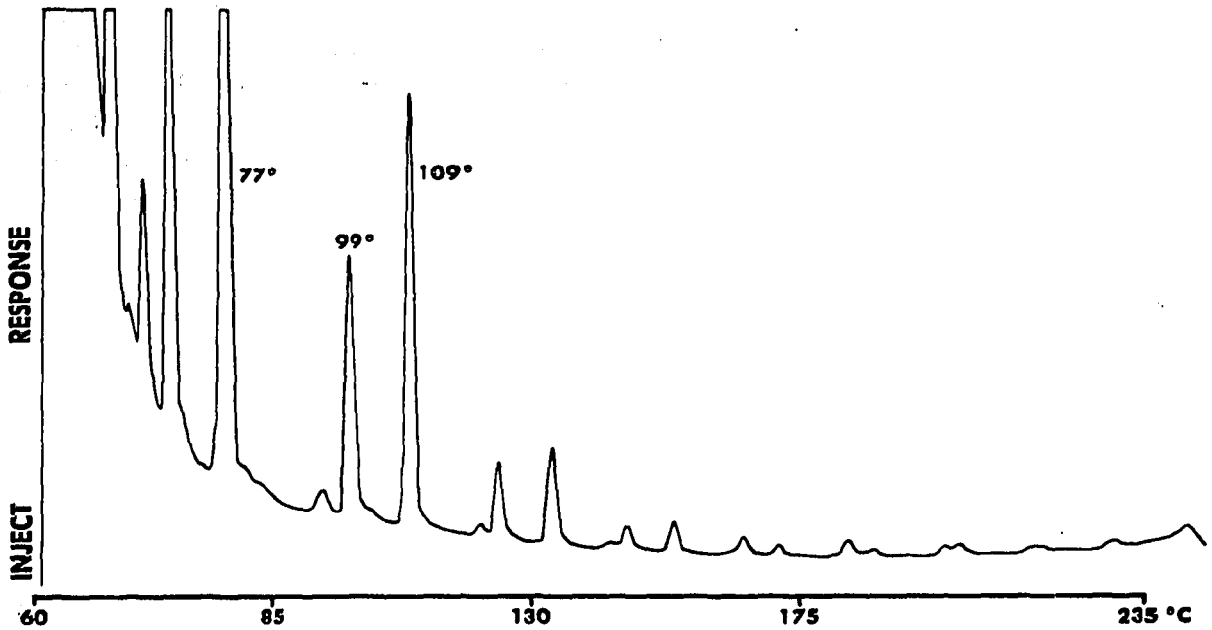

Fig. 2. Ethyl acetate extract of 1 *N* HCl hydrolysate of PDA meteorite. Sample: 0.3 g equiv., 3 ml of 1 *N* HCl; 25 ml of ethyl acetate; final volume: 100 μl; injected: 6 μl; attenuation: 8×10^{-11} a.f.s.; initial temperature: 60°; initial hold: 4 min; program rate: 4°/min; final temperature: 235°; column: 1.0 w/w% OV-1 on 80–100 mesh H.P. Chromosorb G, 1 m × 4 mm I.D. glass.

Both samples were again studied by GLC–MS, and the peaks were characterized as siloxanes. Corresponding reagent blanks revealed no evidence of the siloxane peaks as seen in Fig. 5.

Extensive analyses conducted on a tektite, an obsidian sample, silicic acid,

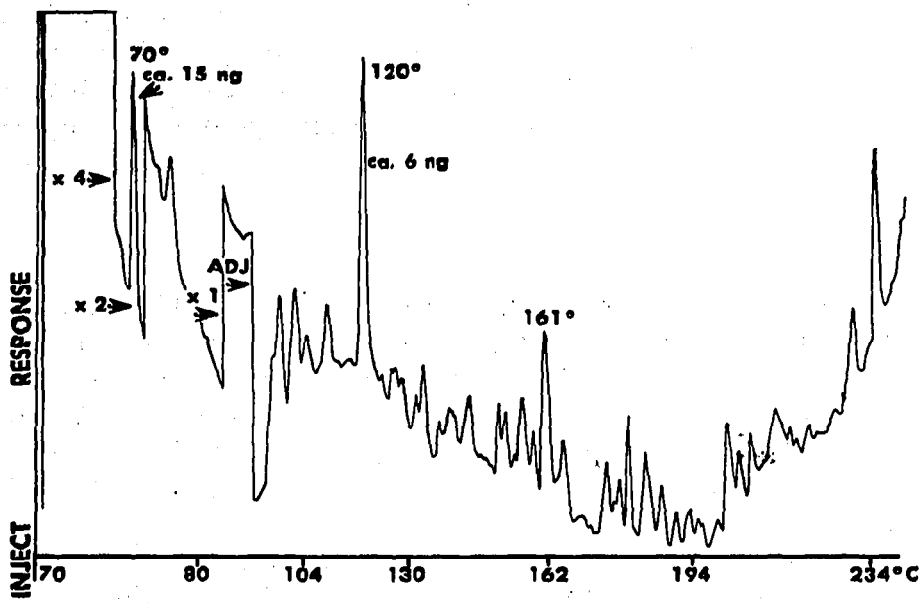

Fig. 3. Apollo 12 lunar fines, ethyl acetate extract of 1 *N* HCl hydrolysate. 1 g equiv.; final volume: 100 μl; injected: 5 μl; attenuation: 4×10^{-12} a.f.s. = × 1; initial temperature: 70°; initial hold: 6 min; program rate: 4°/min; final temperature: 235°; column: 1.0 w/w% OV-17 on 80–100 mesh H.P. Chromosorb G, 2.5 m × 2 mm I.D. glass.

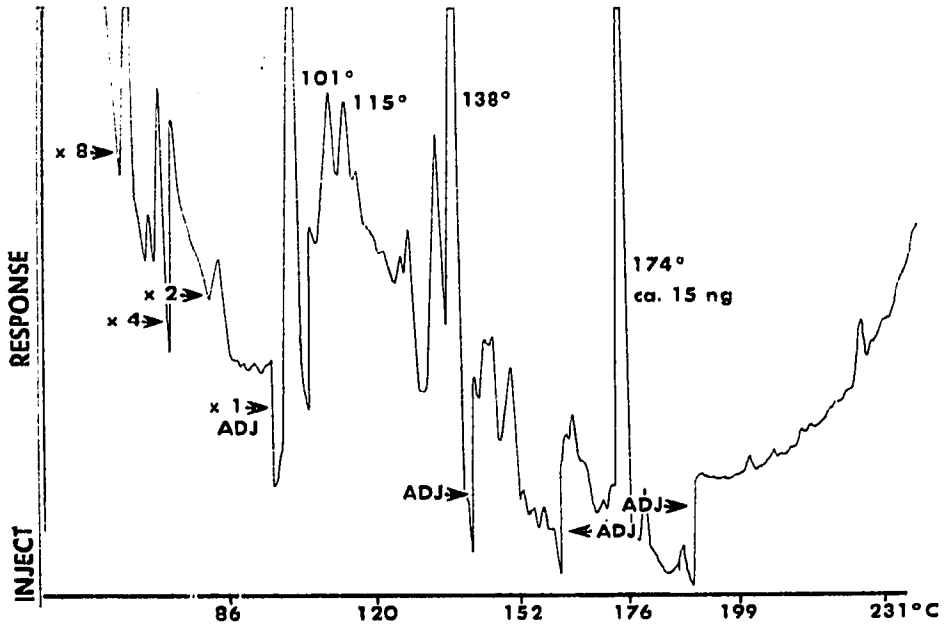

Fig. 4. Apollo 12 lunar fines 1 *N* HCl hydrolysate (after ethyl acetate extraction). 1 g equiv.; final volume: 250 μl; injected: 5 μl: attenuation: 4×10^{-12} a.f.s. = × 1; initial temperature: 70°; initial hold: 6 min; program rate: 4°/min; column: 1.0 w/w% OV-17 on 80–100 mesh H.P. Chromosorb G, 2.5 m × 2 mm I.D. glass.

sand monitor from the Houston Lunar Laboratory, and silicon carbide resulted in no significant chromatographic peaks.

Although every effort has been made to select as "blank" samples which simulate lunar materials in physical or chemical properties, it should perhaps be stressed at this point that no true "blanks" of extraterrestrial materials exist.

The situation would, of course, be different if the compounds of interest were known and the lunar sample itself could be used for spiking experiments.

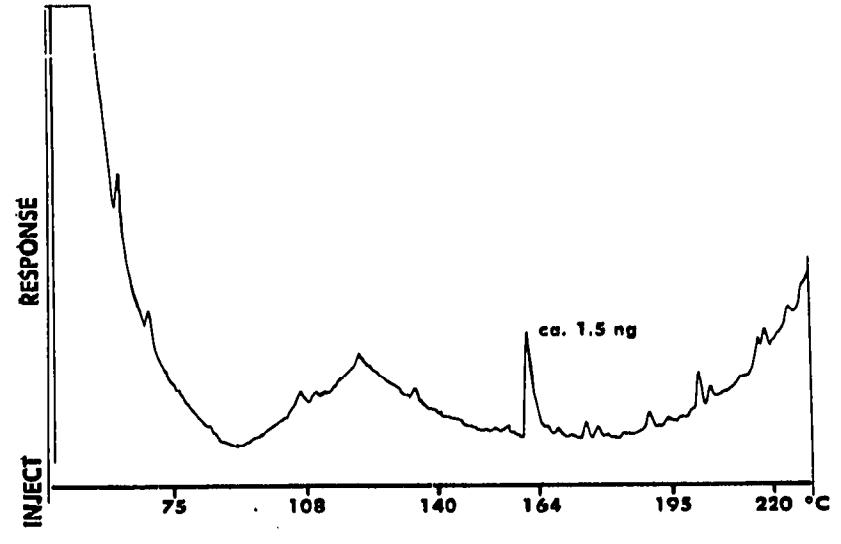

Fig. 5. Reagent blank. Ethyl acetate extract of 5 ml of 1 *N* HCl; final volume: 100 μl; injected: 5 μl: attenuation: 4×10^{-12} a.f.s.; initial temperature: 70°; initial hold: 6 min; program rate: 4°/min; final temperature: 228°; column: 1 w/w% OV-17 on 80–100 mesh H.P. Chromosorb G, 2.5 m × 2 mm I.D. glass.

Previous studies of the 1 *N* HCl extract of a basalt sample had not generated chromatographic peaks when a 1 h hydrolysis was used[1]. However, when the hydrolysis time was prolonged to 15 h, chromatograms as seen in Figs. 6 and 7 were obtained

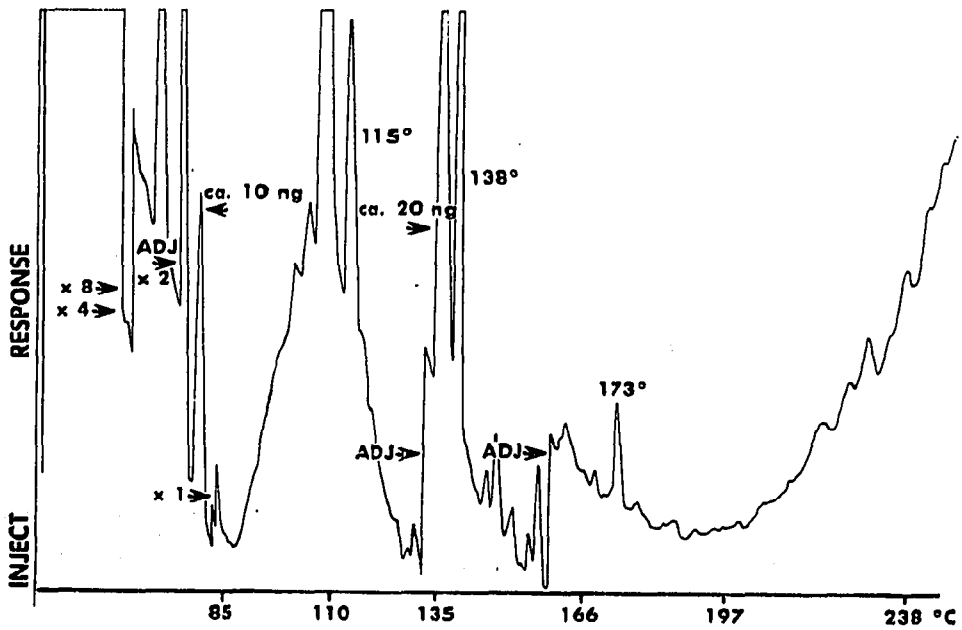

Fig. 6. Basalt; ethyl acetate extract of 1 *N* HCl hydrolysate; 1 g equiv.; final volume: 100 μl; injected: 5 μl; attenuation: 4×10^{-12} a.f.s. = 1; initial temperature: 70°; initial hold: 6 min; program rate: 4°/min; final temperature: 245°; column: 1 w/w% OV-17 on 80–100 mesh H.P. Chromosorb G, 2.5 m × 2 mm I.D. glass.

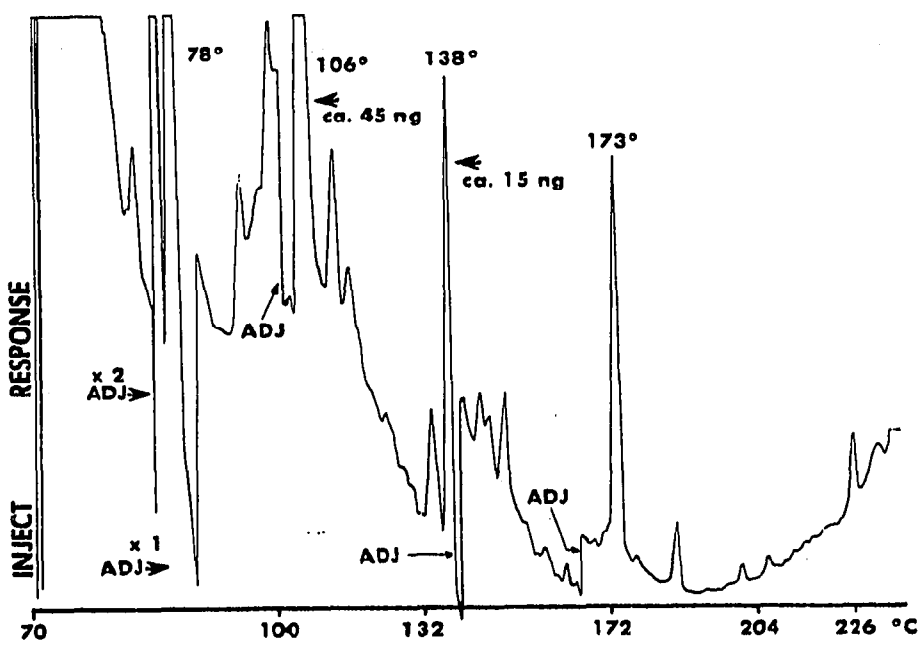

Fig. 7. Basalt 1 *N* HCl hydrolysate (after ethyl acetate extraction); 1 g equiv.; final volume: 250 μl; injected: 5 μl; attenuation: 8×10^{-12} a.f.s. = × 1; initial temperature: 70°; initial hold: 6 min; program rate: 4°/min; final temperature: 228°; column: 1.0 w/w% OV-17 on 80–100 mesh H.P. Chromosorb G, 2.5 m × 2 mm I.D. glass.

for the ethyl acetate and HCl fractions, respectively. After the many negative results obtained from a variety of geological and other material, this was the first time that a *terrestrial* sample had given rise to chromatographic peaks similar to those found for the lunar and meteorite samples. Again, GLC–MS identified these peaks as siloxanes, similar to those found in the Apollo 11, 12, and PDA experiments. Analyses were repeatedly performed on two basalt specimens to confirm these results.

Concurrent studies on the Murray meteorite also resulted in the generation of pronounced chromatographic peaks as seen in Fig. 8. Some of these peaks were also confirmed to be siloxanes by GLC–MS.

It is evident from the chromatograms presented that peaks observed in the above experiments represented quantities of siloxanes approaching 100 ng/peak in some instances, thus differing markedly from the reagent blanks and "blank" samples which did not exhibit this unusual characteristic.

The analysis of the five component performance mixture of *n*-octanol, *n*-hexylamine, valine, lauric acid, and adipic acid revealed each of these types of compounds were susceptible to GLC detection under the derivatization and chromatographic conditions used. The analysis of this standard mixture is presented in Fig. 9. Fig. 10 presents a chromatogram obtained on analysis of the 1 *N* HCl hydrolysate of lunar fines *spiked* with the standard mixture. *n*-Hexylamine, valine, and lauric acid were recovered, indicating these types of compounds would have been derivatizable and therefore amenable to detection by GLC–MS, were compounds of these types present in the lunar fines. *n*-Octanol and adipic acid were not recovered, with loss of *n*-octanol

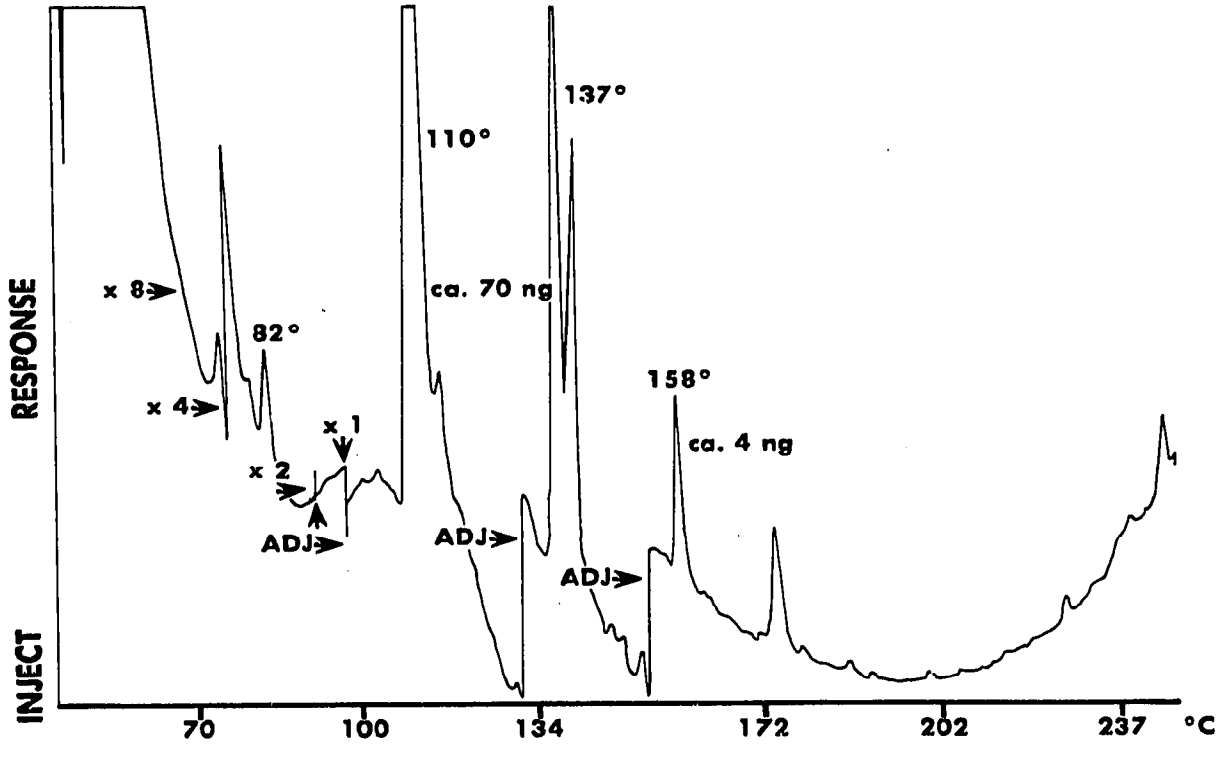

Fig. 8. Murray meteorite 1 *N* HCl hydrolysate (after ethyl acetate extraction). Final volume: 250 μl; injected: 5 μl; initial temperature: 70°; initial hold: 6 min; program rate: 4°/min; final temperature: 245°; attenuation: 8×10^{-12} a.f.s. = × 1; column: 1.0 w/w% OV-17 on 80–100 mesh H.P. Chromosorb G, 2.5 m × 2 mm I.D. glass.

occurring during the evaporation steps of the derivatization procedure. The subsequent pyrolysis experiments were then devised to trace the origin of the siloxane chromatographic peaks. The acidic basalt extract, which had yielded prominent GLC peaks before, showed the same peaks after pyrolysis at 700° for 15 h. It was considered highly unlikely that organic molecules could have remained intact at this temperature. However, the results were reconfirmed in another experiment using a pyrolysis temperature of 1100° for 15 h. These experiments clearly demonstrated that chromatographic siloxane peaks still occurred after subjecting the sample to conditions which should have *totally destroyed* any siloxanes indigenous to the sample.

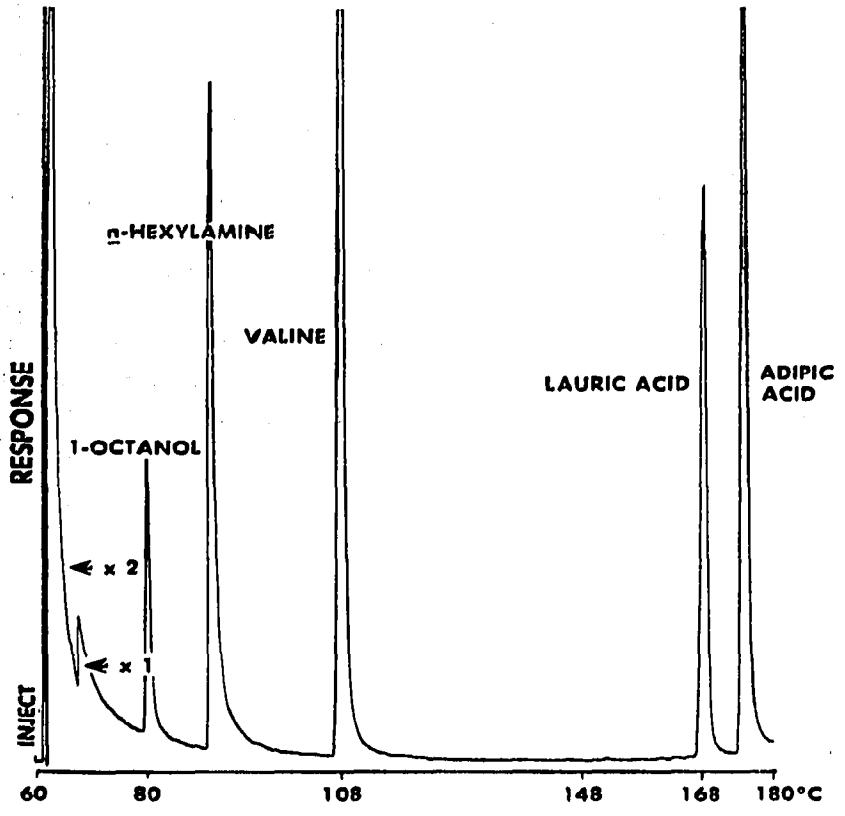

Fig. 9. Performance and chromatographic standard. Derivatization and GLC analysis of a five-component mixture. Sample injected: *ca.* 1 μg of each; attenuation: 2×10^{-10} a.f.s. = × 1; initial temperature: 60°; program rate: 6°/min; final temperature: 180°; injection port: 280°; 3.0 w/w% OV-17 on 80–100 mesh H.P. Chromosorb W, 1.5 m × 4 mm I.D. glass.

To exclude the possibility that the siloxanes were the product of an unusual synthetic process occurring during sample preparation, labeling experiments were conducted with fluorine and deuterium containing alcohols. Neither experiment resulted in an apparent mass shift of the siloxane fragments studied by GLC–MS. The obvious conclusion, therefore, was that the siloxanes were not being synthesized in the analytical method, nor were they indigenous to the samples. Rather, they may have originated in the gas chromatographic system, as the result of a particular characteristic of, or material(s) contained in and unique to the sample itself.

At this point in time, peridotite, a granitoid igneous rock composed of ferromagnesium minerals, principally chrysolite, $(Fe,Mg_2)SiO_4$, was included in the stud-

ies. Chromatographic peaks, again identified as siloxanes on analysis of this material were observed.

This finally substantiated the earlier findings on basalt, that the appearance of siloxane peaks was not exclusively limited to extraterrestrial materials.

With some of the possibilities for siloxane formation excluded, a comprehensive study was now undertaken to demonstrate that the siloxanes originated indeed from the GLC–MS instrumental analytical system itself.

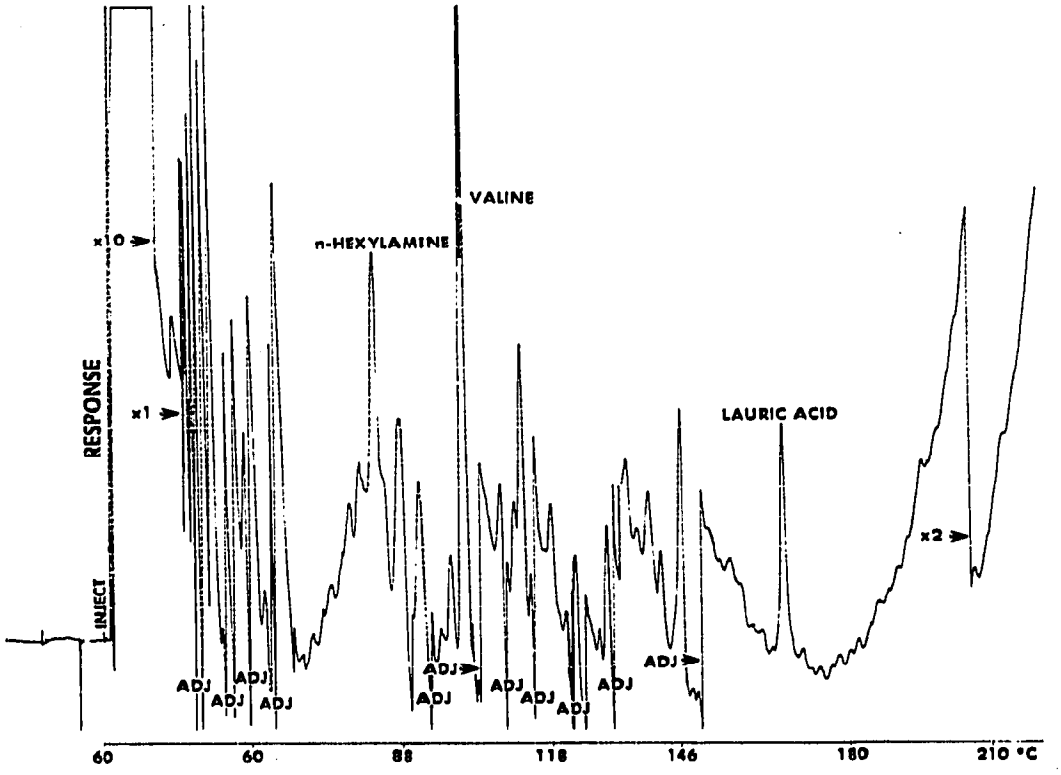

Fig. 10. Apollo 11 1 *N* HCl hydrolysate five component mixture *spike*; sample: 0.5 g equiv. of lunar fines, *spiked* with *ca.* 1 μg of each; 200 μl *n*-butanol–3 *N* HCl; 100 μl TFAA–CH_2Cl_2 (0.5 μl/100 μl); final volume: 100 μl; injected: 5 μl; initial temperature: 60°; initial hold: 6 min; program rate: 4°/min; final temperature: 210°; attenuation: 1×10^{-11} a.f.s. = × 1; injection port: 280°; column: 1.0 w/w% OV-17 on 80–100 mesh H.P. Chromosorb G, 2.5 m × 2 mm I.D. glass.

High resolution–direct probe mass spectrometry of the derivatized hydrolysate of the basalt sample using photoplate detection was used to bypass the GLC system. No evidence of siloxanes was observed. However, introduction of the sample by direct probe is a less efficient method of sample introduction than by GLC. Therefore, the GLC–MS system had to *be freed* of any siloxanes which had a reasonable chance to influence the results. At the trace levels detectable by MS and GLC, this task was formidable. It would not have been possible, in fact, to be confident in the success of the cleaning procedures without the earlier information from solvent studies which had shown that gas chromatographic or silicone columns would generate siloxane peaks upon injection of hydrochloric acid (3 *N*) or HCl dissolved in *n*-butanol. Obviously, it is not a common practice to inject hydrochloric acid into a gas chromatograph. Nor had butanol–3 *N* HCl (which is used in the analytical procedure) ever

been injected — as demonstrated by the repeated blanks. The butanol–HCl used in the analytical method had been totally removed in the evaporation. Thus, *n*-butanol–3 *N* HCl was chosen to evaluate the GLC–MS combination with regard to the preparation of an instrumental system entirely free from silicone contamination.

After rigorously cleaning all GLC parts that would come in contact with an injected sample, a new, cleaned *empty* glass column was placed in the instrument. On injection of *n*-butanol–3 *N* HCl and C_2D_5OD–3 *N* in DCL, traces of siloxanes were detected mass spectrometrically, but diminished on repeated injections. This technique was continued until a chromatographic column of 0.65 w/w % EGA on 80/100 mesh A.W. Chromosorb W exhibited either "extremely low" or "undetectable levels" of siloxane contamination. This "silicone free" instrumental system was then used to study carefully the acidic extracts of the basalt and PDA meteorite. Deuterated reagents were used to prepare both the basalt and PDA sample hydrolysates using 1 *N* DCl in D_2O, and C_2D_5OD–3 *N* in DCl. On analysis of these samples by GLC–MS using the EGA column, no significant chromatographic peaks were observed, nor were siloxanes apparent in the MS oscillographic recording, although prominent peaks were produced when the same samples were injected on an OV-17 column. However, some siloxane fragments were noted by the more sensitive photoplate detection when the labeled derivatized basalt and PDA samples were chromatographed on the EGA system, but again no shift in mass number was observed, ruling out completely the possibility of a synthesis process involving $-CD_3$ during sample preparation or chromatography.

The next step was to reconfirm the findings of the earlier pyrolysis experiments using both an OV-17 column and the "silicone free" EGA column–MS system. Both basalt and PDA sample hydrolysates were analyzed, another aliquot of the hydrolysate was then pyrolyzed at 975° for 15 h, derivatized, then analyzed again. The analyses with the OV-17 column before and after pyrolysis were substantially the same, with prominent chromatographic peaks being generated in each instance. However, the analyses conducted with the "silicone free" EGA GLC–MS system showed only *low levels* of siloxane fragments, and in general these did not appreciably decrease after pyrolysis. In only one instance were the siloxanes completely undetectable by MS due to the absence of even traces of these compounds in the instrumental system. It is therefore apparent that some samples, the extraterrestrial Apollo's 11 and 12, PDA and Murray meteorites, basalt and peridotite, themselves possess a unique chemistry which liberates siloxanes from the instrumental GLC–MS system. The behavior of these samples thus contrasts sharply with that of all the other terrestrial samples (except basalt and peridotite) taken through the same analytical-instrumental methodology (tektite, obsidian, silicic acid, SiC, sand monitor, quartz crystals, and method blanks).

Further studies confirmed that siloxanes formed in the derivatization from OV-17 and butanol–3 *N* HCl, were not stable as expected to pyrolysis at 1000°; no chromatographic peaks were obtained.

Some concluding experiments were designed to determine if a particular element or ion in the sample was responsible for the generation of the siloxane peaks. The metal chlorides listed in Section E were taken through the derivatization and GLC methods, but failed to produce significant GLC chromatographic peaks. Further studies to define unequivocally the substance(s) responsible for the formation of the

gas chromatographic siloxane peaks were regarded as beyond the scope of these investigations.

CONCLUSIONS

Our earlier investigations on Apollo 11 lunar fines, PDA meteorite, and several terrestrial samples by a multistep GLC method designed to detect amino acids, had shown that extraterrestrial samples cause methylsiloxane peaks in the chromatograms. This investigation on Apollo 12 and many other samples traced the origin of these siloxanes. Three working hypotheses had been formulated (a) siloxanes occur in extraterrestrial material, (b) siloxane precursors occur in extraterrestrial material and form polymethylsiloxanes in one or more steps of the analytical procedure employed, and, (c) some unidentified substance(s) that are present in extraterrestrial material (but not in blanks) cause siloxanes that are always present in traces in the GLC–MS instrument systems, to break into smaller fragments and show up on the chromatograms.

It was established through use of labeled reagents, pyrolysis at 1000°, use of "siloxane free" substrates, supports and "siloxane free" GLC–MS instruments, and a number of other experiments, that exhaustive acid hydrolysis (1 *N* HCl for 15 h) yield substance(s) from the samples. These substances are stable to pyrolysis at 1000°, soluble in organic solvents, and liberate organosiloxanes from the ubiquitous traces of silicone ever present in analytical instrumentation. In all of our experiments, major attention and importance was always focused on using representative blanks. However, in experiments on extraterrestrial material, as lunar or meteorite samples, a true blank does not exist. The effect of the sample itself cannot be excluded nor simulated.

It was strikingly apparent that the extraterrestrial samples (Apollo's 11 and 12, PDA and Murray meteorites) and terrestrial basalt and peridotite possess a unique chemistry or contain unidentified substance(s) which free siloxanes from the instrumental GLC–MS system. This unique behavior of these samples contrasts sharply with that of all the other terrestrial samples taken through the same analytical-instrumental methodology, *i.e.*, tektite, obsidian, silicic acid, SiC, sand monitor, quartz crystals, reagent method blanks, and OV-17 hydrolyzed, derivatized and pyrolyzed.

To determine if a particular major or minor element or ion in the samples were responsible for the generation of siloxane peaks, experiments were designed to investigate the effect of Fe(III), Ti(II), Al(III), K(I), Mg(II), Ca(II), Na(I), Cr(III), Cu(II), and trace elements, Ni(II), Zn(II), Co(II), Cd(II), and Rb(I). All failed to give significant GLC peaks above background.

Of the three "working hypotheses" considered to explain the source of the methylsiloxane peaks, our experiments have shown conclusively one to be correct. Unidentified substances present in Apollo's 11 and 12, PDA and Murray meteorites, basalt, and peridotite cause the emergence of siloxanes from the GLC–MS instrumentation analytical systems. The chemical nature of the substance(s) present in these samples responsible for the formation of siloxane peaks remains an interesting problem.

GLC–MS results from the Apollo's 11 and 12 and meteorite studies clearly point out that the analysis for trace organics in inorganic matrices, in particular analysis of

extraterrestrial samples, presents a complex and extremely difficult problem. A true reagent-sample blank is not available, and the conclusions can only be drawn after a rigorously safe-guarded experimental design with cross checking at every step. Apollo's 11 and 12 experiments demonstrate that chromatographic peaks can be generated by materials in the samples whose nature is unknown. Organic solvent extracts may contain substance(s) that form GLC peaks from chromatographic substrates, supports, reagents, or the trace organics present in the instrumental system itself.

Therefore, the fact that samples show prominent GLC peaks, whereas various blanks do not, could have been extremely misleading in this and other investigations in the nanogram sensitivity range. It is to be expected that similar possibilities for erroneous data interpretation will be encountered from the analysis of other extraterrestrial samples, where the ultimate in GLC–MS-sensitivities are being used.

In summary this study has resulted in several conclusions: (1) The lunar material does not contain any appreciable amounts of organic material (2 to 20 p.p.b. level) which would have been detected directly or as derivatives under these experimental conditions. The gas chromatographic techniques used would have shown a very wide range of organic structures ($-NH_2$, –OH, –COOH, –SH, etc.).

(2) Several extraterrestrial — and two of many analyzed terrestrial — materials contain substances which lead to the liberation of siloxane peaks from the silicone traces in GLC instrumentation. A common denominator of these samples may perhaps be the fact, that all of them are igneous materials, formed at high temperature under anaerobic conditions, which contain iron magnesium silicates.

(3) From a general point of view in regard to trace analysis of organic compounds in complex inorganic matrices, there exist severe possibilities for error inherent in GLC–MS instrumentation at sensitivities in the nanogram range. These possibilities have generally gone unnoticed.

(4) The current controversy: tektite, terrestrial or extraterrestrial? may be enriched by an indication pointing to its terrestrial origin. All extraterrestrial materials examined up to now caused prominent siloxane peaks, whereas tektite failed to do likewise.

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