STUDY OF THE GAS CONTENTS OF ROCKS - AN APPROACH TO THE EVOLUTION OF ATMOSPHERES ON THE EARTH AND PLANETS

A PROGRESS REPORT

Dr. Colin Barker

University of Tulsa

May, 1972

INTRODUCTION

This progress report covers activities carried out under NASA Grant NGR 37-008-002 during the period May 1, 197 , to April 31, 1972. This was mainly a period of construction during which a high vacuum system was built for extracting volatiles from rocks either by heating or by crushing. The volatiles could then be analyzed mass spectrometrically. This system is now essentially complete and preliminary analyses have been made for selected basalts and granites.

EXPERIMENTAL

The current apparatus and experimental procedures are described in Appendix I. In developing these techniques two major experimental problems were encountered.

(a) Water: Water is a polar compound which even in high vacuum systems adhers tenaciously to surfaces at room temperature. By operating the vacuum system in an oven at 120° C adsorption problems were eliminated. At first water was determined by condensing it in a trap cooled with liquid nitrogen and then evaporating it into a stream of helium which swept it through a calibrated thermal conductivity detector. It was found that some of the water was lost from the trap while the pressures were being equilibrated and it also proved to be very difficult to distinguish between the detector response for water and the effects of pressure transients due to valve switching. As an alternative procedure the condensed water vapor was evaporated into a calibrated volume where the pressure could be measured by a mechanical gauge. This system is still available for large water samples but it has been found that with the high temperature inlet system to the mass spectrometer water can be determined just like any other gas. Water is now routinely measured with the mass spectrometer and no additional problems are anticipated.

(b) Internal standard: Neon was originally selected for the internal standard because of its inertness, suitable atomic weight and low abundance in natural materials. However light noble gases are not pumped well by ion pumps and problems with regurgitation from the pump became severe. The neon was replaced by argon and this has behaved in a much more satisfactory way. Argon has the added advantage that it can be condensed onto cooled activated charcoal. This is important because it normally takes several hours for the internal standard and the gas sample to mix whereas by condensing them onto charcoal and then re-evaporating them mixing can be effected in a few minutes.

RESULTS

Several dozen granites and basalts have been investigated in order to define our limits of detection, refine the operating procedures, establish a frame of reference for interpreting data from lunar basalts and show any gross differences in gas content and composition with age or rock type. The granites were chosen rather arbitrarily from North America but the basalts were carefully selected to give a wide geographic spread. Chemical analyses and radiometric ages were available for the basalts.

1. GRANITES

Chemical analyses of the volatiles released by the heated granites are given in Appendix II. Results given in this form are not very meaningful since reactions occurring during the high temperature, low pressure extraction process severely modify the composition. Because of this compositions are recalculated as atom percentages of the elements. Carbon, hydrogen and oxygen predominate so the data can be conveniently displayed on a C-H-O ternary diagram. Figure 1 shows such a diagram for the granites analyzed. All the points lie in the H_2O-CO_2-CO field and there appears to be no significant difference in

composition between the pre-Cambrian samples (full circle) and younger samples (open circles). However the quantities of gas evolved are greater for the older rocks than the younger ones (Figure 2). This trend is consistent with the data of Chamberlin (1908); Damon and Kulp (1958) and Wlotzka (1964). Unfortunately it is not conclusive since weathering is a time dependent process which introduces volatiles into rocks. Also the number of samples analyzed is rather small, the ages rather vague and very young granites are not represented. This data is sufficiently encouraging to justify a more detailed study. This will be done by analyzing quartz samples separated from radiometrically dated granites and granodiorites covering as wide an age range as possible. Quartz is unaffected by weathering and so one of the major uncertainties will be eliminated.

2. BASALTS

Chemical analyses of the volatiles released by the heated basalts are given in Appendix II. The samples had been chemically analyzed and/or petrologically described and were selected to provide wide geographic coverage. All the gas analyses plot in the H_2O-CO_2-CO triangle on a C-H-O ternary diagram (Figure 3). The total amounts of gas show a sharp break between oceanic and continental basalts (Figure 4). The continental sample from the Columbia River Plateau gave the greatest amount of gas but is thought to be weathered. It is not possible to relate the amount of gas to age because all the basalts used were young and it becomes increasingly difficult to get fresh material as age increases.

A few olivine nodules and eclogites have been analyzed but they show no regular trends. This is probably because it is not possible to melt them in quartz tubes and some components, especially hydrogen, diffuse out preferentially.

DISCUSSION

All the gas compositions obtained can be considered as water-carbon dioxide mixtures with small additions of either carbon monoxide, hydrogen, or methane. This composition is very different from the hydrogen-rich atmosphere postulated to have been present at the time of the earth's formation, particularly since methane and not carbon dioxide is the stable carbon compound under the generally accepted conditions. There are three possible explanations:

(i) The hydrogen-rich rocks are inaccessible (core, mantle) or are represented by rock types not yet analyzed.

(ii) Any hydrogen associated with the accreting earth has been lost.

(iii) No hydrogen was associated with the accreting earth.

Although it is difficult to eliminate (i), (ii) seems to be the most likely explanation. Initially any carbon dioxide in the atmosphere will be reduced to methane by the large excess of hydrogen

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

However as the earth heats up due to accretion, heating by radioactive elements and possibly core separation, two things happen. First the equilibrium constant for the reaction changes and increasingly favors the formation of carbon dioxide. Second, and more important, is the increasing loss of hydrogen from the earth's atmosphere. Reduction of hydrogen partial pressure favors carbon dioxide formation at the expense of methane. Rates of loss fall in the sequence $H_2 \gg CH_4 \approx H_2O > CO_2$ if all species are gaseous. However at moderate temperatures both carbon dioxide and water can be retained in solid phases. This is not possible for hydrogen and methane. Since the earth's atmosphere is

secondary and has come from outgassing the only compounds available would have been water and carbon dioxide. The volatiles remaining in the rocks, as shown by the analyses given above, reflect this composition.

CONCLUSIONS

Experimental methods have been developed for extracting and analyzing the volatiles in rocks. Preliminary analyses of granites and basalts have shown the following:

1. All the analyses lie in the H_2O-CO_2-CO triangle on a C-H-O ternary diagram.
2. The compositions of the volatiles released from granites and basalts plot in distinct, but overlapping, areas of the C-H-O diagram (Figure 6 of Appendix I).
3. Pre-Cambrian granites have a higher volatile content than younger granites. (It is not known whether this is a real effect or due to weathering.)
4. Continental basalts have a higher volatile content than oceanic basalts. (This trend is based on very few samples and must be considered tentative.)

APPENDIX I

This appendix describes the apparatus and experimental procedures as they were in April, 1972. They are, of course, subject to modification and refinement. The text is taken from a paper "Mass spectrometric analysis of the volatiles evolved from heated or crushed rocks", which will be presented at the ASTM Symposium 'Analytical Methods Developed for Application to Lunar Science Analysis', in June, 1972.

INTRODUCTION

Naturally occurring silicate melts ('magmas') contain volatile components which profoundly influence their behavior. The viscosity, freezing range, crystallization sequence, and composition and texture of the mineral products all depend on the amount and composition of the volatiles. In spite of their importance very little is known about them. This is due in part to the insurmountable problem of sampling magmas directly but several indirect methods are available. For example, the volatiles released during volcanic activity are derived from a magmatic source. Unfortunately these volatiles are almost certainly contaminated with ground water and atmospheric gases and also suffer from the more serious objection that they correspond to the composition of magmatic volatiles at only one point in geologic time and can provide no data for the volatiles released in the past. An alternative approach is to study the rocks which crystallized from the magmas since these solid products can trap small samples of the volatiles associated with the parent melt. Although there are some difficulties in relating the composition of the volatiles in rocks to those present in the melt at the time of crystallization this does provide a potential method for estimating the composition of the volatiles associated with magmas generated up to about 3.5 billion years ago. This approach is equally valid for terrestrial and lunar samples.

APPARATUS

Introduction:

The volatiles trapped in rocks and minerals can be released either by heating or by crushing. Heating is much more efficient and it is generally assumed that melting a rock

in vacuum will quantitatively degas it after a relatively short time. Crushing however has a distinct advantage for vesicular samples. Preliminary analyses (1,2,3) have shown that the volatiles in rocks are composed mainly of water and carbon dioxide with smaller amounts of hydrogen, carbon monoxide, methane, nitrogen and noble gases. The total amount varies widely up to a maximum of over 100 ml/g. Vacuum extraction with subsequent mass spectrometric analysis of the evolved volatiles was selected as the analytical procedure. The high vacuum system and experimental procedures are described below.

High Vacuum System:

The high vacuum gas-handling system (Figure 1) was constructed of stainless steel and assembled using copper-gasketed Varian ConFlat flanges. The valves were either Varian 3/4 in. all-metal valves or teflon sealing packless Hoke valves. The system was completely free from mercury, grease or volatile organic materials and was evacuated by a sorption pump and a 30 liter/sec Varian Noble Vaclon pump. The former proved to be very inconvenient to use and the main line was usually evacuated through the calibration line by a rotary pump. This was connected to the high vacuum system through a molecular sieve trap. The whole of the gas handling system was enclosed in an oven at 120° C to minimize problems due to adsorption of polar compounds, particularly water. This section is shown enclosed by a dashed line in Figure 1.

Furnace:

Rock or mineral samples were heated in a quartz sample tube (5 cm. x 0.8 cm. diam.) resting inside a larger vertical quartz tube. This larger tube was attached to a Varian 1.33 in. ConFlat flange through a quartz-stainless steel graded seal. Quartz imposes an upper temperature limit of 1200° C, although this could be extended by using ceramic

tubes. The quartz tubes were heated by a nichrome-wound resistance furnace operated from two variable voltage transformers. It took approximately one hour to reach maximum temperature.

High Vacuum Crusher:

Samples could be crushed in the high vacuum system using the device shown in Figure 2. When current was passed through the coils they acted as solenoids and lifted the mild steel weight. Interrupting the current let the weight fall onto the sample (4,5). By using the coils in different combinations the weight could be dropped from various heights. The available options are listed in Table 1. The sequencing was carried out automatically by a set of motor-driven switches which completed a cycle once every 3 seconds. The number of drops, which was displayed on a counter, could be preset with an accuracy of $\pm$ 1 drop using a built-in timer. In 150 drops the crusher could reduce fifty percent of a quarter-gram quartz sample to greater than 200 mesh from starting material of roughly 3 mm cubes. Typical crushing efficiency curves for quartz, fluorite and basalt are given in Figure 3. The crusher was mounted inside an oven so that it could be operated at 120° C.

Mass Spectrometer:

The volatiles evolved by heating or crushing the rock samples were analyzed with an E.A.I. QUAD 1110 quadrupole mass spectrometer which has a mass range 1-300 and unit resolution throughout the range. It includes a secondary election multiplier as an integral unit but since large gas samples were available and the spectrum was not being scanned rapidly it was desirable to by-pass it. This was done by taking the output from the first dynode and amplifying it with an Applied Physics Corporation, Model 30M

vibrating reed electrometer. The mass spectrometer was always operated dynamically and gas samples were introduced through a Granville-Phillips leak valve.

In order to get accurate gas compositions the mass spectrometer had to be calibrated both for the cracking patterns of individual gases and for relative sensitivities. Samples of pure gases were provided in a 'calibration line' for this purpose and could be introduced into the mass spectrometer individually or as mixtures of known composition. The mixtures were made by admitting a tap-to-tap volume of the first gas into the calibration line and measuring the pressure, V_1, with the oil manometer. A tap-to-tap volume of the second gas was then added and the new total pressure measured, V_2. The ratio of the components is then $V_1/(V_2 - V_1)$ (since the increase in volume due to the second tap-to-tap volume is negligible). Because the gas analysis is performed in two stages (described below) it was necessary to have values for absolute amounts. A convenient way of achieving this was to add an accurately known quantity of internal standard. Neon was originally used as the standard because of its inertness, low abundance in natural materials and suitable atomic weight. Unfortunately the lighter noble gases are not pumped well by ion pumps and problems with regurgitation and high memory effects were severe. It became necessary to use argon instead since this behaved in a much more satisfactory way. Aliquots of this were taken from a stainless steel reservoir, located in the oven, using a tap-to-tap procedure in the same way that argon-38 aliquots are obtained in potassium-argon dating (6). Even though the tap-to-tap volume was small compared with the volume of the reservoir the size of the aliquot decreases exponentially as aliquots continue to be withdrawn. In order to define the curve volumes of the internal standard were calibrated at intervals. These calibrations were carried out using weighed amounts

of cadmium carbonate which decompose on heating to give accurately known amounts of carbon dioxide. Then, knowing the relative sensitivities for carbon dioxide and argon, the absolute amount of argon follows directly. In practice the relative sensitivity of argon was put equal to one and the other gases referred to this. Table 2 summarizes the calibration data used.

Water Determination:

With the heated inlet system water could be handled in the same way as other gases and determined mass spectrometrically. However for samples rich in water an alternative procedure was available. The water could be condensed into a trap cooled with solid carbon dioxide and then evaporated into a calibrated volume where the pressure was registered by a stacked diaphragm gauge. The response of this gauge is independent of the nature of the gas. Known quantities of water for calibrating the volume or for calibrating the relative sensitivity of the mass spectrometer were obtained by thermally dehydrating weighed amounts of barium chloride dihydrate ($BaCl_2.2H_2O$).

ANALYTICAL PROCEDURE

Extraction of Volatiles:

Samples of approximately 0.1 g were weighed into the quartz sample tubes. These were then put into the larger tubes and reconnected to the high vacuum system via the ConFlat flange. Atmospheric gases were pumped out through the backing line and the final evacuation effected by the ion pump. Samples to be crushed were loaded into the bucket at the bottom of the crusher by removing the 2-3/4 in. ConFlat flange. Sample

size was normally in the range 0.2 to 0.5 g. The volatiles were then released from the samples either by operating the crusher or by bringing the furnace up to temperature.

Analysis of Volatiles:

The volatiles extracted from rocks were separated into two fractions - those that condensed at liquid nitrogen temperatures and those that did not. The condensable volatiles were mainly carbon dioxide and water and by separating these major components the determination of the minor components was simplified and the accuracy improved. For example, the contribution of carbon dioxide at m/e = 28 accounted for most of that peak, the balance being nitrogen and carbon monoxide. A small error in the calibration data for the 28/44 ratio for carbon dioxide would have had a very large effect on the apparent contribution of nitrogen and carbon monoxide to the mass-28 peak and produced large errors in the determination of these gases. Also there was a second problem in determining trace and major components together because the dynamic range of the mass spectrometer is limited. The separation by fractional freezing is shown schematically in Figure 4. Separate argon internal standards were used for condensable and non-condensable fractions.

The usual procedure involved adding the first argon internal standard during the gas extraction so that efficient mixing with the volatiles occurred. At the end of the gas extraction either the sample tube or an adjacent tube was cooled with liquid nitrogen for fifteen minutes and during this time the background in the mass spectrometer was scanned and recorded. Then the mixture of argon and non-condensable gases was introduced into the mass spectrometer by opening the leak valve until the pressure in the mass spectrometer (as registered by the gauge on the ion pump) was about 8×10^{-7} torr. The mass spectrum was scanned every 300 sec (nominal) and the peak areas measured by the digital integrator.

These values, together with the time from the start of the analysis, were printed on a teletype. Three or four scans of the spectrum were normally made and during this time peak areas fell about five percent. When the scans were completed the gas sample was pumped away, a second argon internal standard introduced into the system and the liquid nitrogen coolant removed. The condensable gases were left for one hour to mix with the standard and were then analyzed in the same way as the non-condensables. The mixing could be accelerated by condensing the gases onto activated charcoal cooled with liquid nitrogen and subsequently releasing them by heating.

DATA HANDLING

The mass spectrometric procedures outlined above generated well over a hundred peaks. Measuring these by hand would be time-consuming and introduce the possibility of errors in transcribing data. For these reasons some alternative method of data handling was needed. The system finally selected used a Vidar Autolab 6300T digital integrator to measure peak areas. Although designed to operate with the output from a gas chromatograph this instrument performed excellently with the output from the vibrating reed electrometer. When used directly with the electron multiplier some preamplification of the signal was necessary. A Speedomax W strip chart recorder operated in parallel with the digital integrator and gave a permanent record of the analysis. A permanent record of the peak areas was printed by the teletype, each number being identified by the time in seconds from the start of the analysis. The teletype also punched a paper tape which could subsequently be read over a telephone line to the University's Computer facility. The data handling system is shown schematically in Figure 5.

The computer program was written in FORTRAN IV for a Xerox Sigma 6 digital computer. Times and peak areas were read in and separated into individual scans on the basis of time. Since the scan time was 259 sec the program accepted the first peak, at time t, as m/e = 2 and then looked at the interval $t + (259 \pm 2)$. A peak in this range with an area within ten percent of the first mass 2 peak was accepted as the first peak in the second scan. Then using the time for this peak the process could be repeated to identify the first peaks in succeeding scans. Mass-to-charge ratios within each scan were also assigned on the basis of time since this was linearly related to accelerating voltage and quadrupole mass spectrometers have a linear relationship between mass-to-charge ratio and accelerating voltage. In the mass spectra of the non-condensable gases there was no (or insignificant) overlap at peaks with m/e = 2, 15, 34 and 40 so that these peaks could be used directly for hydrogen, methane, hydrogen sulfide and argon respectively. Oxygen could be determined from the m/e = 32 peak after correcting for any hydrogen sulfide contribution. Nitrogen and carbon monoxide both have parent peaks at m/e = 28 but can be determined separately using the 12 and/or 14 peaks after they have been corrected for any methane contribution. Absolute amounts of the various gases were found by reference to the argon-40 peak, making due allowances for differences in relative sensitivities. The mass spectrum of the condensable gases could be handled in an analogous manner and combined with the composition of the non-condensable gases to give the composition of the total gases evolved from the rock or mineral sample.

Gas compositions expressed in terms of the various chemical compounds probably have little significance since reactions occurring during the high temperature, low pressure extraction will radically alter the composition of the volatiles originally present in the rock. For this reason compositions are better expressed in terms of the numbers of atoms

of each element. Carbon, hydrogen and oxygen account for 98% or more of the volatiles evolved from rocks and so compositions can be conveniently plotted on carbon-hydrogen-oxygen ternary diagrams after normalizing these three elements to 100%.

RESULTS

Typical analyses of the volatiles evolved from heated rocks are given in Table 3. In the analyses performed so far water and carbon dioxide have always been present in major amounts together with lesser amounts of hydrogen, carbon monoxide, methane, nitrogen and noble gases. Hydrogen sulfide has been absent from all the analyses and may have been removed by reaction with the copper gaskets. Gold plating the gaskets would eliminate this problem. A plot of the data on a C-H-O ternary diagram (Figure 6) has shown that for all the rocks analyzed the compositions of the volatiles lie in the triangle defined by carbon dioxide, carbon monoxide and water. In general basic rocks are slightly richer in the CO_2-CO component. The amount of volatiles released varied from less than 1 ml/g to over 100 ml/g and depended very strongly on rock type.

Duplicate determinations for a basalt sample are given in Table 4 and show satisfactory agreement for compositions expressed either as individual compounds or as atom percentages of carbon, hydrogen and oxygen. On the normal ternary diagram the points plot extremely close to one another. The absolute amounts of gas show a rather large difference. It is difficult to be certain that the material is the same in both analyses since variations between samples of the same rock are potentially large. Differences can be minimized by taking aliquots from one finely crushed sample. Other possible sources of error include (i) sample tube outgassing, (ii) errors in the volume of the internal

standard and (iii) inaccuracies in the calibration data. The volatiles contributed from the sample containers can be minimized by a preliminary high temperature outgassing since this reduces the volatiles from the tubes to much less than one percent of the volatiles released by the rocks. The volume of the internal standard varies very little between successive aliquots so that its effect on the gas composition is negligible, but absolute quantities will be in error by the same percentage as the error in the argon volume. Since the major components (H_2O, CO_2, H_2) are determined from peaks at mass-to-charge ratios which show no overlap with other compounds cracking patterns are of secondary importance in calculating carbon-hydrogen-oxygen percentages. Relative sensitivities are important however and introduce errors of approximately $\pm$ 5%.

CONCLUSIONS

The experimental methods developed for analyzing the volatiles released from heated or crushed rocks have been successfully applied to terrestrial samples. Since adequate data for the amount and composition of the volatiles in rocks was not previously available it was essential to establish a frame of reference before analyzing lunar samples. The analyses of the volatile components of lunar rocks obtained so far (7) has shown that they fall well within the capabilities of the system described above.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of the National Aeronautics and Space Administration who through Grant NGR 37-008-002 made this study possible. We would like to thank the many people who supplied samples, and also B. E. Torkelson, J. J. Hayes and C. C. Dodd for their invaluable assistance.

REFERENCES

1. Chamberlin, R.T., "The Gases in Rocks", Carnegie Institute, Washington, 1908.

2. Shepherd, E.S., "The Gases in Rocks and Some Related Problems", Amer. J. Sci., Vol. 35A, 1938, pp. 311-351.

3. Barker, C.G., "Mass Spectrometric Analysis of the Gas Evolved From Some Heated Natural Minerals", Nature, Vol. 205, 1965, pp. 1001-1002.

4. Naughton, J.J., "Possible Use of Argon-39 in the Potassium-Argon Method of Age Determination", Nature, Vol. 197, 1963, pp. 661-663.

5. Barker, C.G., "The Quantitative Determination of Some of the Volatile Constituents Evolved by Rocks and Minerals on Heating", D.Phil. Thesis, Oxford University, 1965.

6. Lanphere, M.A. and Dalrymple, G.B., "Simplified Bulb Tracer System for Argon Analyses", Nature, Vol. 209, 1966, pp. 902-903.

7. Proceedings of the First, Second and Third Lunar Science Conferences.

TABLE 1. - OPTIONS AVAILABLE FOR THE OPERATION OF THE HIGH VACUUM CRUSHER

	Height of drop	Sequence
1.	Center of coil 1	Coil 1, on off
2.	Center of combined coils 1 and 2	Coils 1 and 2, on off
3.	Center of combined coils 1, 2 and 3	Coils 1, 2 and 3, on off
4.	Center of coil 3 (accelerated down to coil 1, then free fall)	Coils 1, 2 and 3, on Coil 1, off Coil 2, off Coil 3, off; coil 1, on Coil 1, off

TABLE 2. - SUMMARY OF CALIBRATION DATA

	Relative Sensitivity (Argon = 1.00)	Cracking pattern
Hydrogen	4.80	
Methane	1.38*	14/15 = 0.173; 12/15 = 0.025
Water	2.56	
Carbon monoxide	1.03	12/28 = 0.078
Nitrogen	1.00	14/28 = 0.120
Carbon dioxide	3.57	

* referred to mass 15 peak

TABLE 3. - TYPICAL GAS ANALYSES

	1	2	3	4
Hydrogen	6.00	3.21	3.23	0.23
Methane	0.00	0.11	0.31	0.11
Water	69.70	63.40	60.00	78.26
Carbon monoxide	1.42	4.64	3.01	2.11
Nitrogen	1.36	3.88	0.35	0.20
Hydrogen sulfide	0.00	0.00	0.00	0.00
Carbon dioxide	21.52	24.76	33.10	19.07
Total (ml/g)	46.06	21.09	36.19	36.84

1 Granite, pre-Cambrian: Monarch Pass, Colorado

2 Granite, Mississippian: Rockport, Massachusetts

3 Basalt, Miocene: Baja, California

4 Basalt, Eocene: S.E. Australia

TABLE 4. - DUPLICATE ANALYSIS FOR CRUSHED BASALT

	PERCENT	
	#1	#2
Hydrogen	1.86	2.69
Helium	0.06	0.05
Methane	0.05	0.07
Water	80.22	76.29
Carbon monoxide	3.89	5.43
Nitrogen	3.14	4.39
Hydrogen sulfide	0.00	0.00
Carbon dioxide	10.79	11.08
Carbon	5.17	5.95
Hydrogen	57.73	56.77
Oxygen	37.10	37.28
Total (ml/g)	86.94	59.85

FIGURE CAPTIONS

FIGURE 1 Schematic diagram of the high vacuum system.
The dashed line encloses all units normally operated at 120° C.

P - Pressure gauge
V - Calibrated volume
M - Molecular sieve trap
C - ConFlat flange
G - Stainless steel - quartz graded seal

FIGURE 2 High vacuum crusher

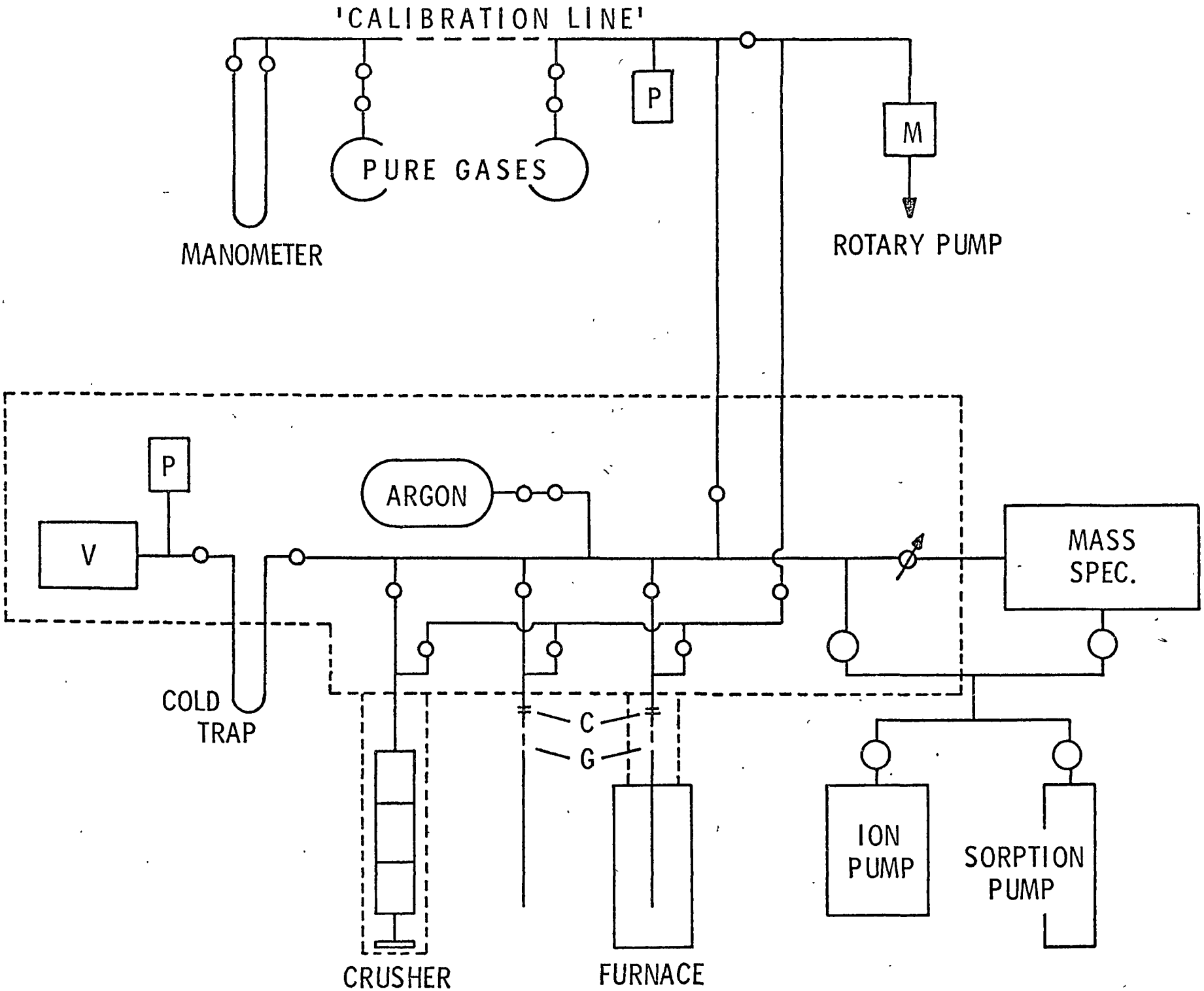
FIGURE 3 Efficiency curves for the high vacuum crusher. All samples were initially angular pieces with largest dimension about 3 mm.

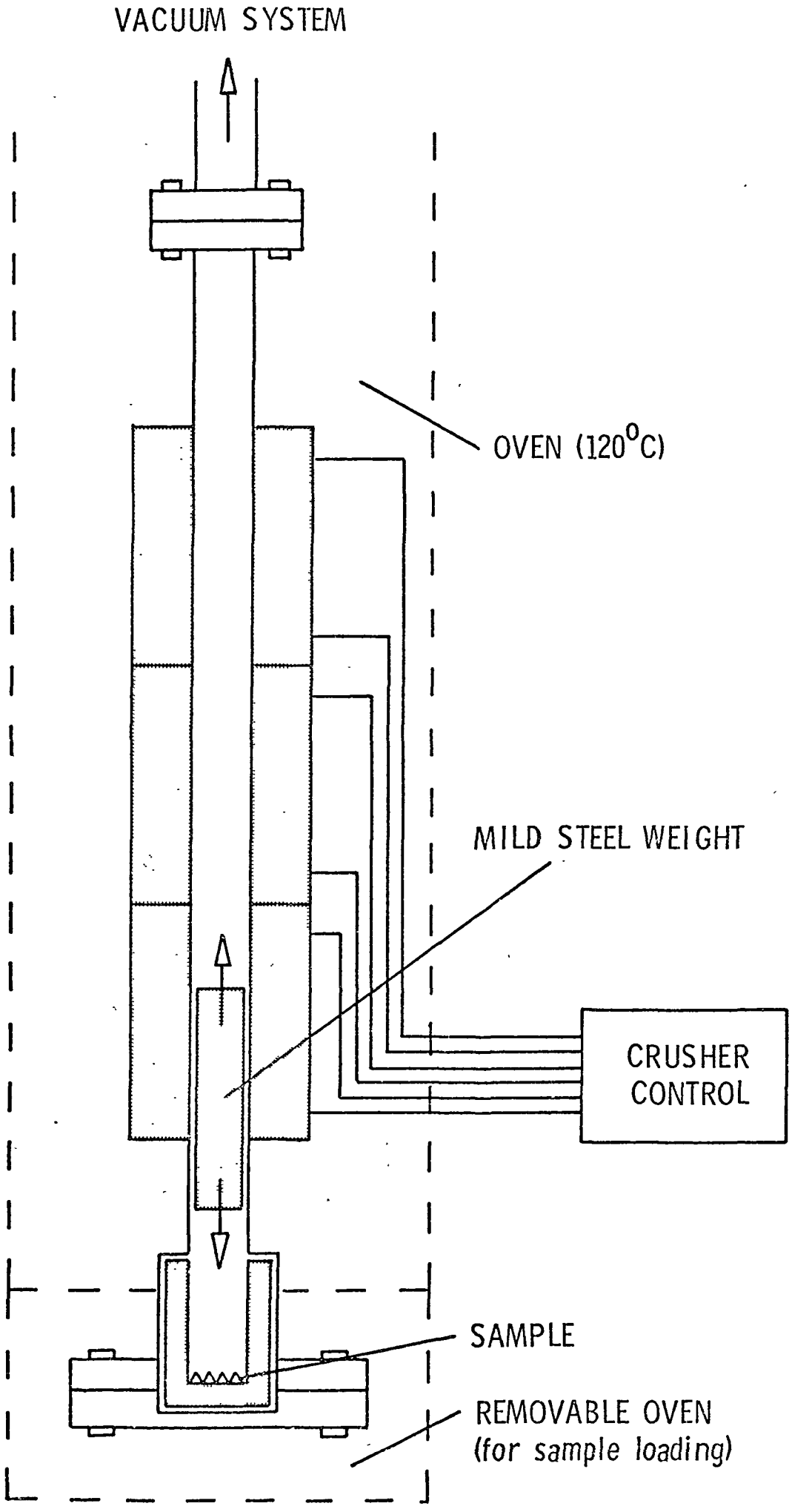
1 200 mesh
2 60-200 mesh
3 20-60 mesh
4 20 mesh

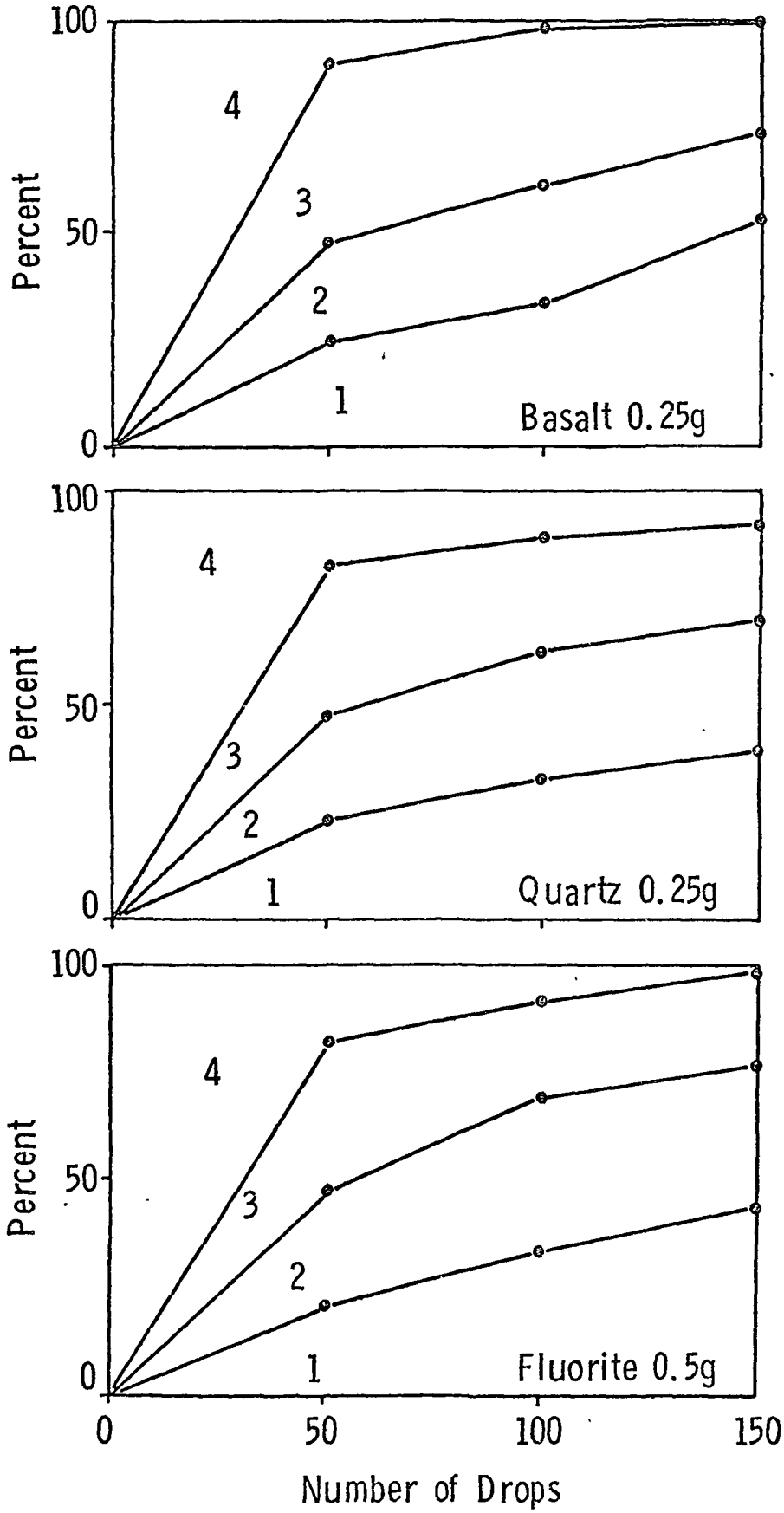
FIGURE 4 Schematic representation of the analytical procedure.

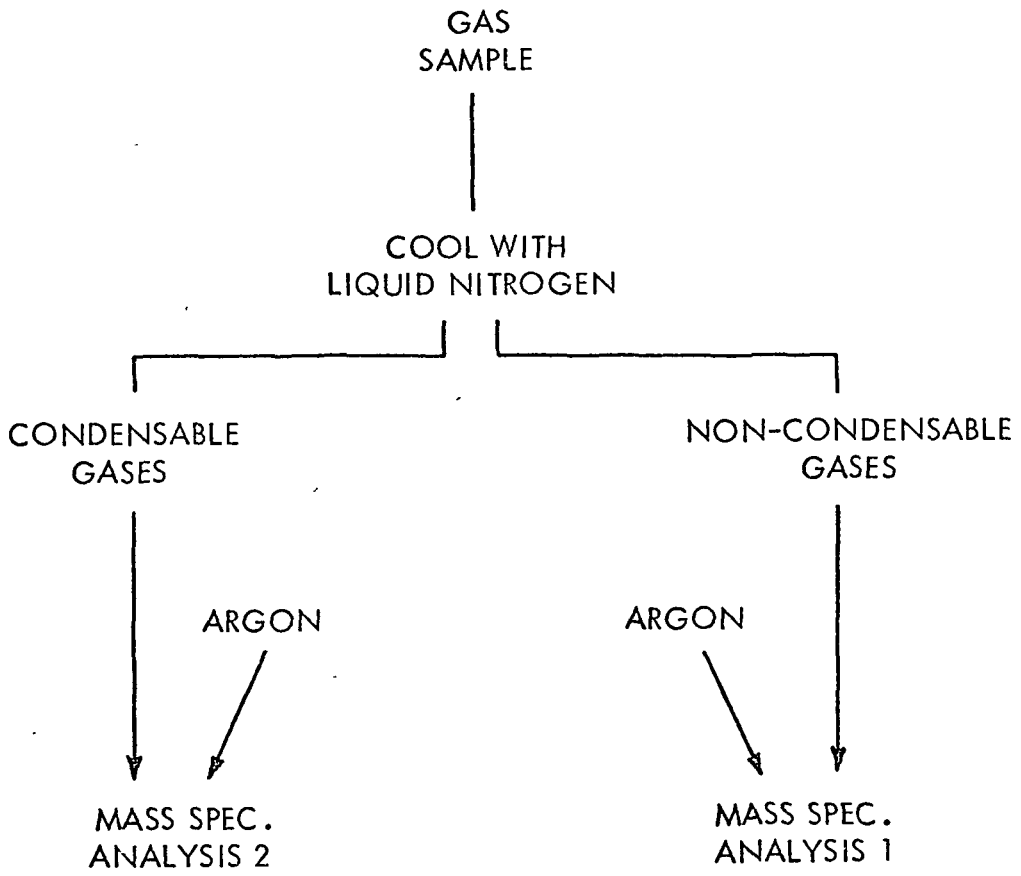
FIGURE 5 Block diagram of the data handling system

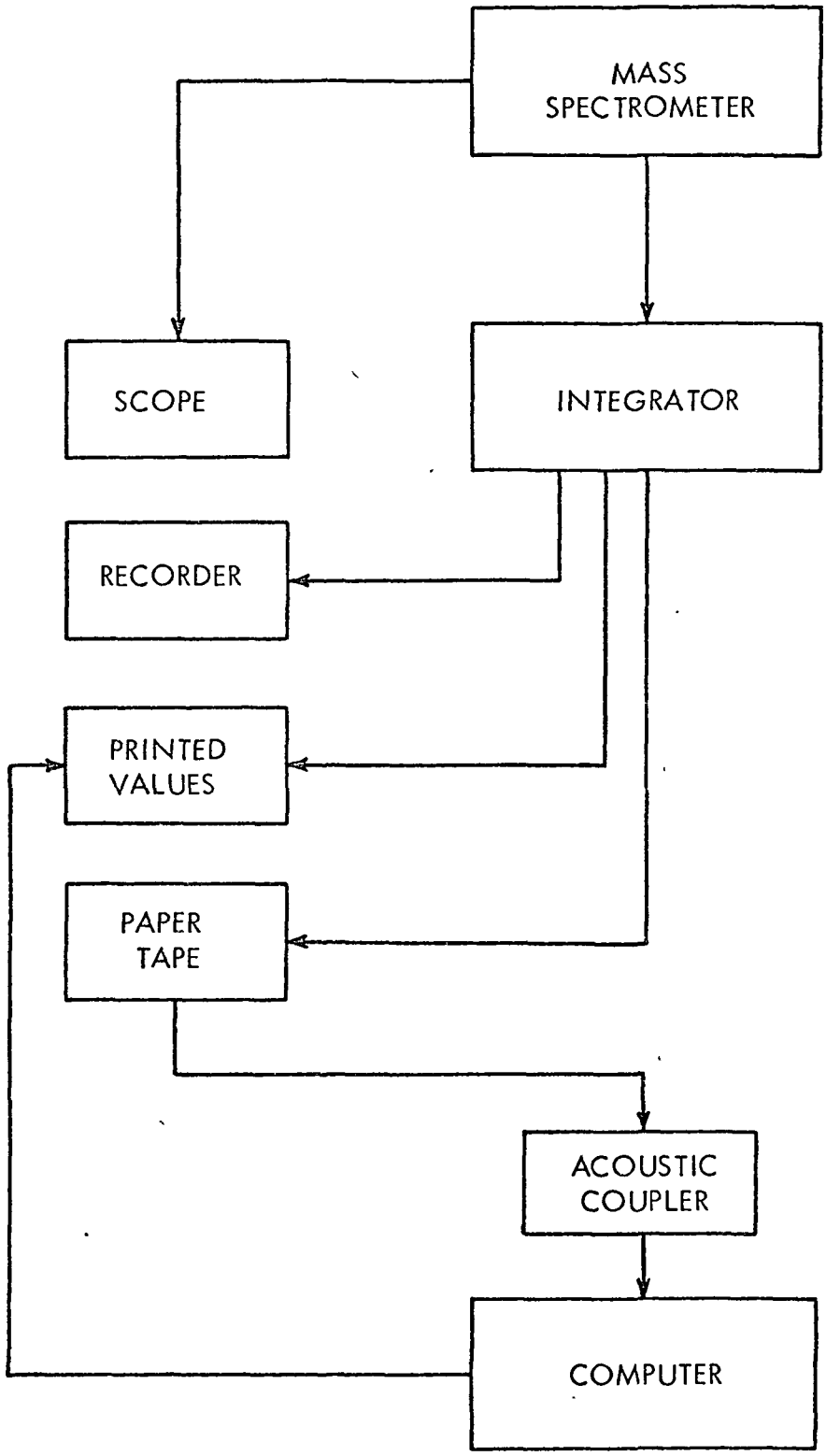
FIGURE 6 Carbon-hydrogen-oxygen ternary diagram showing the fields for basalts (10 samples) and granites (25 samples).

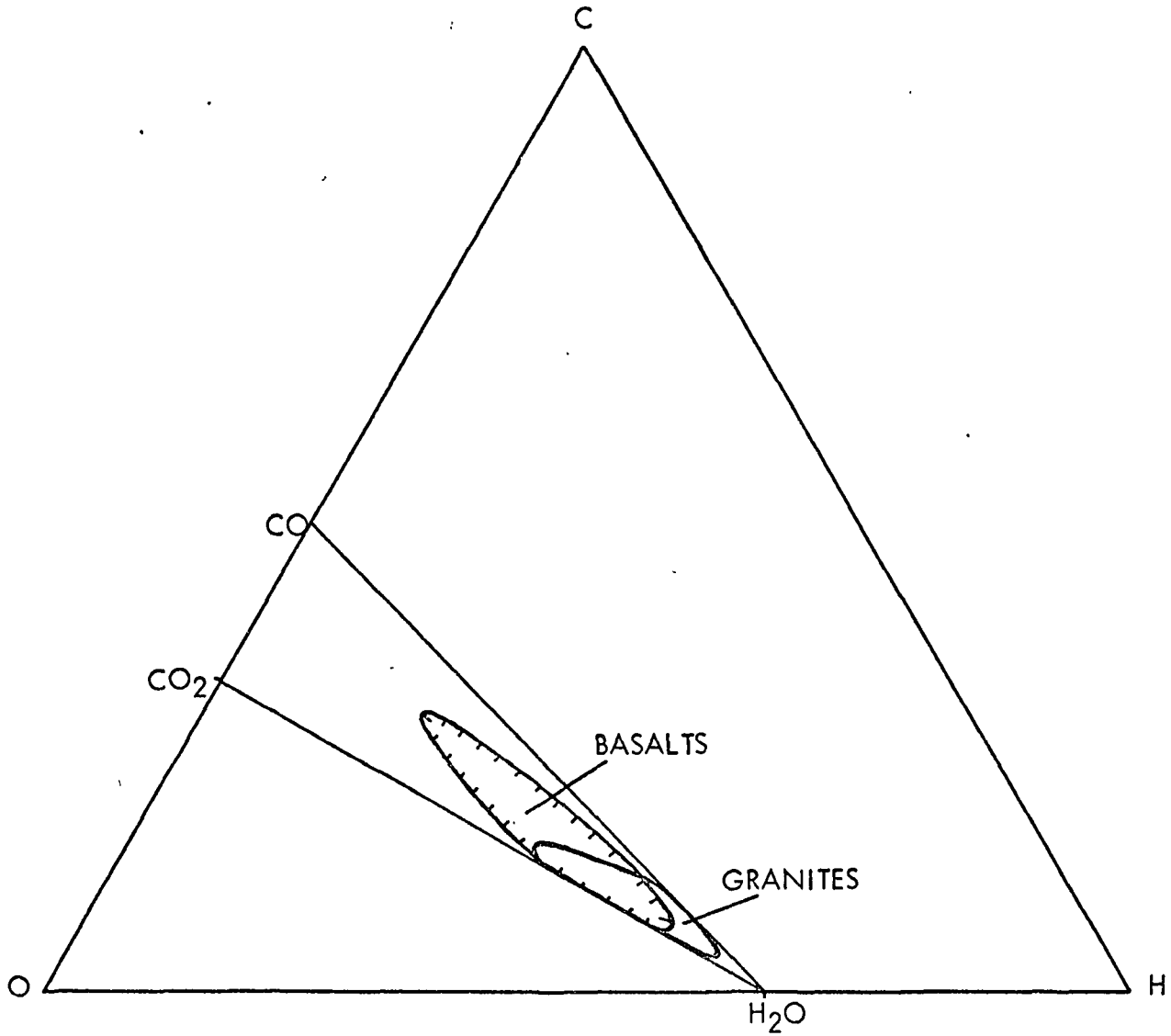

'CALIBRATION LINE'
P
M
PURE GASES
MANOMETER
ROTARY PUMP
P
V
ARGON
MASS
SPEC.
COLD
TRAP
C
G
ION
PUMP
SORPTION
PUMP
CRUSHER
FURNACE


VACUUM SYSTEM
OVEN (120°C)
MILD STEEL WEIGHT
CRUSHER CONTROL
SAMPLE
REMOVABLE OVEN
(for sample loading)


100
50
0
Percent
4
3
2
1
Basalt 0.25g
Quartz 0.25g
Fluorite 0.5g
0
50
100
150
Number of Drops


GAS
SAMPLE
COOL WITH
LIQUID NITROGEN
CONDENSABLE
GASES
NON-CONDENSABLE
GASES
ARGON
ARGON
MASS SPEC.
ANALYSIS 2
MASS SPEC.
ANALYSIS 1


MASS SPECTROMETER
SCOPE
INTEGRATOR
RECORDER
PRINTED VALUES
PAPER TAPE
ACOUSTIC COUPLER
COMPUTER


C
CO
CO_2
BASALTS
GRANITES
O
H
H_2O

APPENDIX II

RESULTS

Table II.1: Percentage composition of the gases evolved on heating selected granitic rocks

Sample	1	2	3	4	5	6	7	8
Hydrogen	.15	11.95	1.74	.39	2.09	1.82	7.53	5.58
Helium	.48	2.13	.35	.22	.33	.30	1.41	.70
Methane	.00	.00	.00	.00	.00	.00	.00	.00
Water	86.64	54.41	67.50	74.29	38.93	54.44	70.68	73.86
Carbon Monoxide	.98	10.85	1.94	.75	6.98	3.62	5.26	4.48
Nitrogen	.00	.00	.00	.00	.78	.00	.00	.00
Hydrogen Sulfide	.00	.00	.00	.00	.00	.00	.00	.00
Argon	.00	.00	.00	.00	.00	.00	.00	.00
Carbon Dioxide	11.74	20.66	28.48	24.35	50.91	39.83	15.12	15.38
Total Volume of Gas (ml/gm)	46.80	55.26	29.67	40.81	35.99	71.24	57.11	27.95

Table II.1: Continued

Sample	9	10	11	12	13	14	15	16
Hydrogen	2.51	4.60	7.35	5.99	9.83	5.04	4.85	8.82
Helium	.44	.52	.57	.10	1.02	.66	1.09	1.22
Methane	.00	.00	.00	.00	.00	.00	.00	.00
Water	59.47	83.17	74.42	69.66	59.24	78.15	75.38	52.39
Carbon Monoxide	2.63	1.29	3.63	1.41	6.53	1.72	2.27	12.08
Nitrogen	.00	.00	.00	1.35	1.32	.00	.00	1.31
Hydrogen Sulfide	.00	.00	.00	.00	.00	.00	.00	.00
Argon	.00	.00	.00	.00	.00	.00	.00	.00
Carbon Dioxide	34.96	10.43	14.02	21.50	22.06	14.44	16.41	24.18
Total Volume of Gas (ml/gm)		32.60	33.11	46.06	24.95	50.45	36.23	25.35

Table II.1: Continued

Sample	17	18	19	20	21
Hydrogen	7.04	3.19	9.92	5.01	5.15
Helium	1.92	.65	1.77	.84	.55
Methane	.00	.11	.00	.00	.08
Water	66.21	62.99	50.50	69.54	65.52
Carbon Monoxide	3.16	4.61	9.27	3.77	4.22
Nitrogen	.00	3.85	1.18	.78	.71
Hydrogen Sulfide	.00	.00	.00	.00	.00
Argon	.00	.00	.00	.00	.00
Carbon Dioxide	21.67	24.60	27.36	20.07	23.77
Total Volume of Gas (ml/gm)	19.95	21.09		32.84	34.44

SAMPLE LOCATIONS FOR GRANITIC ROCKS

Sample Number	
1	Epidotized Granite, Gallinas Canyon, New Mexico - Pre-Cambrian
2	Biotite Granite, Platte Canyon, Colorado - Pre-Cambrian
3	Granite, 5 miles east Llano, Texas - Pre-Cambrian
4	Red Granite, Mt. Scott, Wichita Mts., Lawton, Okla. - Pre-Cambrian
5	Granite, Odessa, Minn. - Pre-Cambrian
6	Porphyoblastic Granite, Royal Gorge, Colorado - Pre-Cambrian
7	Town Mt. Granite, 4 miles north Llano, Texas - Pre-Cambrian
8	Granodiorite, Watab, Minn. - Pre-Cambrian
9	Granite, 2 miles east of Cotapaxi, Colorado - Pre-Cambrian
10	Granite, Wind River Canyon, Wyoming - Pre-Cambrian
11	Granite, Stone Mt. Georgia - Pre-Cambrian
12	Silver Plume Granite, Monarch Pass, Colorado - Pre-Cambrian
13	Granite, Monarch Pass, Colorado - Pre-Cambrian
14	Granite, Sangre de Cristo Mts., New Mexico - Pre-Cambrian
15	St. Cloud Granite, Minn. - Pre-Cambrian
16	Granite, Fredericksburg, Texas - Pre-Cambrian
17	Granite, Monitor Pass, California - Jurassic
18	Hb. Granite, Rockport, Essex Co., Mass. - Mississippian
19	Granite Rocklin, Placer Co., California - Jurassic
20	Granite, Yosemite Park, California - Mesozoic
21	Granite, Woodburg, Vermont - Mississippian

Table II.2: Percentage composition of the gases evolved on heating selected basic and ultrabasic rocks

	14377	17678	Re69	B3A-33	B3A-33	GA2903	GAI400	B65-3	Eclog.
Hydrogen	1.39	6.64	1.86	3.18	3.12	0.23	2.00	7.26	0.48
Helium	4.64	21.32	3.32	1.46	1.65	2.13	3.58	5.69	0.61
Methane	0.28	0.41	0.35	0.31	0.41	0.11	0.36	0.08	0.03
Water	64.82	23.40	67.12	59.12	54.42	76.60	61.11	4.21	94.66
Carbon Monoxide	0.00	20.42	9.27	2.97	4.13	2.07	8.50	25.08	0.85
Nitrogen	1.06	1.48	0.67	0.34	0.54	0.20	0.74	1.68	0.10
Ethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hydrogen Sulfide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Argon	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00
Carbon Dioxide	28.28	26.34	17.41	32.61	35.72	18.67	23.72	56.00	3.27
Total Volume of Gas (ml/gm)	24.94	7.43	15.28	36.19	34.55	36.84	23.07	5.03	84.52

SAMPLE DESCRIPTIONS AND LOCALITIES FOR BASIC ROCKS

Basalts were selected for the preliminary analyses because of their close similarity to lunar rocks. At this early stage of the study it was vital to get fresh, unaltered material and so the basalts chosen are young, ranging in age from contemporary to 50 m.y. An olivine nodule and an eclogite were also run for comparison. Many people have offered rocks and those who provided the samples used in this study are acknowledged individually below:

SSW.1.1. Fine grained tholeiitic basalt Penguin Point Visokoi Island, South Sandwish Islands. Microphenocrysts plagioclase, clinopyroxene and magnetite in intergranular groundmass plagioclase, subcalcic augite and occasional olivine. Recent. (Donor: Dr. P.E. Baker, Leeds Univ., unpublished)

14377 High alumina basalt. Black Rocks St. Kitts, West Indies. Microphenocrysts of plagioclase, olivine and occasional hypersthene in a fine matrix of plagioclase clinopyroxene and magnetite. Recent. (Donor: Dr. P.E. Baker, Leeds Univ., unpublished)

17678 Hawaiite (undersaturated and almost an alkali basalt) Roiho, Easter Island. Youngest flow on the island, probably only two or three thousand years old. Intergranular to subophitic texture, with early formed rounded olivines, plagioclase (An_{65}) laths and poikilitic clinopyroxene. (Donor: Dr. P.E. Baker, Leeds Univ., unpublished)

Re69 Basalt, with scattered olivine phenocrysts, (Oceanite Series, Piton des Neiges) from roadside, Ilet Rond, entrance to Cirque de Cilaos. (Donor: Dr. W.J. Wadsworth, Manchester Univ. See 'The basalts of Reunion Island, Indian Ocean' Bull. Volc., 29 (1966) 7-24)

B3A-33 Miocene basalt, Baja California. (Donor: Dr. D. Krummenacher, San Diego State, unpublished)

GA2903 Barrington Volcano. Altitude 1184m. Fine-grained holocrystalline alkali olivine basalt, with no apparent alteration. Age (by K-Ar) 51 m.y. (Donor: Dr. I. McDougall, A.N.U., Canberra. See 'On the polar-wander path for Australia during the Cenozoic' Geophys. J.R. Astr. Soc. 18 (1969) 371-395)

GA1400 Main Range Volcanics. Mt Mitchell, 3,745' elevation. Andesine basalt. Plagioclase (? andesine) is fresh and interstitial glass is undevitrified. Age (by K-Ar) 22 m.y. (Donor: Dr. I. McDougall, A.N.U., Canberra. See 'Isotopic age determination on tertiary volcanic rocks and intrusives of South-Eastern Queensland' Proc. Roy. Soc. Queensland, 79 (1967) 79-92)

B65-3 Olivine from nodule in alkaline basalt. Formal $(Mg_{86.86} Fe_{10.54} Al_{2.38} Mn_{0.22})_2 SiO_4$. (Donor: Dr. C.J. Vitaliano, Indiana Univ. See 'Alkali basalt from Nye County, Nevada' Amer. Min., 50 (1965) 73-84)

Table II.3 Chemical analyses of basic rocks

	B3A-33	SSW.1.1	14377	17678	Re69	B65-3
SiO_2	49.73	51.04	53.30	47.79	48.45	40.55
Al_2O_3	15.19	17.12	19.00	15.88	14.71	1.62
Fe_2O_3	5.98	3.90	3.98	3.14	4.42	n.d.
FeO	2.71	6.97	5.48	8.49	7.40	10.27
MgO	8.94	5.91	4.12	7.79	6.57	47.43
CaO	10.11	11.76	9.00	9.96	11.06	n.d.
Na_2O	3.61	1.96	3.70	2.96	2.48	n.d.
K_2O	0.63	0.37	0.46	0.73	0.48	n.d.
TiO_2	0.88	0.87	0.89	2.97	2.17	n.d.
MnO	0.15	0.19	0.20	0.08	0.17	0.16
P_2O_5	0.20	0.07	0.10	0.19	0.37	n.d.
H_2O	1.75	0.31	0.23	0.22	1.27	0.06
CO_2	0.53	n.d.	n.d.	n.d.	n.d.	n.d.
TOTAL	100.41	100.50	100.63	100.24	99.80	100.09

APPENDIX III

PUBLICATIONS

'Mass spectrometric analysis of the volatiles released by heating or crushing rocks', Paper accepted for presentation at the ASTM F-7 Committee National Meeting in Los Angeles, June 1972.

'Processing of mass spectrometer output using a digital integrator, punched paper tape and time-shared computer', Paper accepted for presentation at the 1972 Oklahoma Tetrasectional Meeting of the American Chemical Society, March 1972.