Release and analysis of gases from geological samples

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Abstract

A system has been developed for the qualitative and quantitative analysis of gases released from geologic samples upon crushing. The system includes a hydraulically-operated stainless-steel crusher through which helium flows. The released gases are fed directly into a gas chromatograph equipped with dual columns and helium ionization detectors. The chromatographic system is capable of separating and detecting H_2, Ar, O_2, N_2, CO, CO_2, light hydrocarbons, and water. Samples ranging in size from 5mg to 1000mg can be crushed and the released trapped gases analyzed. The crushing pressure (up to 32 kbar) allows efficient release of trapped gases. Depending on the nature of the sample, 85 to 100 percent of the trapped gases in the crushed sample are released. The newly-developed crushing technique eliminates previously identified problems associated with gases generated by the crusher and adsorption of the released gases by the newly generated surfaces of the crushed sample. The analytical system has a wide range of potential uses. To date meteorites, lunar rocks and soils, basalts, glasses, and minerals with both fluid and gas phase inclusions have been analyzed. Selected examples of experimental results are presented.

Introduction

Most solid materials contain trace amounts of trapped gases which have been retained since their formation from a fluid phase. These gases may be physically adsorbed on surfaces, chemically bound within the solid (such as carbon dioxide in limestone), dissolved in the solid (such as H_2, N_2, CO_2, and SO_2 in steel), or trapped in fluid inclusions. Most analyses of gases in solid materials have focused on the releasing of gases by heating or acid dissolution. However, both of these methods provide total gas content without distinguishing between the different forms in which the gases are contained in the sample. The heating method suffers from interferences resulting from pyrolysis products. For example, H_2, CO, and CO_2 could be produced at elevated temperature in reactions such as $H_2O + Fe^{2+} \rightarrow Fe^{3+} + H_2$; $CH_4 +$ $2H_2O \rightarrow CO_2 + 4H_4$; and $CH_4 + H_2O \rightarrow CO + 3H_2$ (Piperov and Penchev, 1973). Acid dissolution may give rise to gases produced by reactions such as $C + H_2O \rightarrow CO + H_2$ or $Fe_3C + 4H^+ \rightarrow CH_4 + 3Fe^{2+}$ (Funkhouser *et al.*, 1971).

The analysis of gases trapped in pores is of special interest in investigating lunar materials, meteorites, and terrestrial volcanic rocks and minerals, because these gases may represent the magmatic environment present during crystallization or formation of these materials (Gibson and Andrawes, 1978). Organic gases, if present, may represent earlier epochs in the formation of organic matter under reducing conditions (Kvenvolden and Roedder, 1972). Gases trapped in pores, fluid inclusions, and cavities can be released by crushing the sample followed by analysis of the evolved gases by either gas chromatography or mass spectrometry. However, there are many difficulties involved with crushing experiments. Some of these difficulties are: (1) The concentration of trapped

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CRUSHING APPARATUS
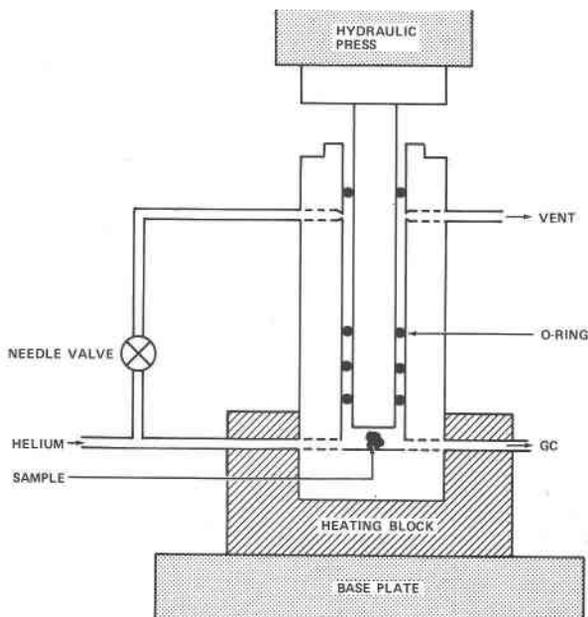
Fig. 1. Crusher; the piston is 1cm diameter and 8cm long.

gases varies widely from rock to rock and even within a single specimen; this is caused by the opening of different types of internal surfaces and cavities within the samples. (2) Trapped gases may undergo subsequent chemical reactions. (3) Trapped gases may be adsorbed on the new surfaces generated by crushing. (4) The crushing experiment, if not carefully designed, may allow gases to be generated during the crushing process. Frictional heat can generate hydrocarbons; for example, methane is commonly produced in steel crushers merely by grinding. (5) The concentration of trapped gases, if any, is low (*e.g.* some lunar materials contain gases only in the ppb range), since most of the original trapped magmatic gases have leaked from the sample along grain boundaries within the rock and/or microfractures produced by micrometeorite impacts. At this low level of concentration, only mass spectrometers or helium ionization detectors can be used to detect the gases evolved from crushing. (6) Analysis of inorganic gases with the helium detector is often cumbersome because of the appearance of anomalous negative signals (Parkinson and Wilson, 1965).

Analysis of released gases by mass spectrometry or helium ionization detectors has been investigated. Heymann and Yaniv (1971) used vacuum crushing followed by mass-spectrometric analysis of the abundances and isotopic composition of the noble gases in a 117mg breccia sample from Apollo 11. Their crushing system was a stainless-steel cylinder and plunger. To crush a sample, the plunger was dropped on the sample about 6000 times. They estimated their method of crushing released 50 percent of the noble gases. Abell *et al.* (1970) applied vacuum crushing and mass spectrometry to analyze the abundances and isotopic composition of the organogenic elements in lunar soils. They crushed 2–5g samples by subjecting them to intermittent shaking in a stainless-steel capsule with a stainless-steel ball. Carbon monoxide and low-molecular-weight hydrocarbons were detected in lunar materials, but comparable amounts were detected also in their blanks. Kvenvolden and Roedder (1971) crushed a 7.0g quartz sample with fluid inclusions from South-West Africa in a rotating pyrex ball mill for 20 hours. Part of the evolved gases was expanded into the inlet system of mass spectrometer; another part was analyzed by gas-chromatography flame ionization detector system. Both inorganic and organic gases were detected in their analysis. Funkhouser *et al.* (1971) described a crushing system with helium ionization detectors. The samples (100–500mg) were crushed by extending a steel ram against a base plate. The crusher was in line with a gas chromatograph. A similar system operating under vacuum was used for additional analyses by mass spectrometry. They analyzed 26 lunar samples, a few meteorites, and terrestrial samples. Active and inert gases were detected in their work.

Barker and Sommer (1973) and Barker and Torkinson (1975) have used a vacuum crushing and mass spectrometry system similar to that described by Heymann and Yaniv (1971). These authors have found that, under certain experimental conditions, the gases released upon crushing are adsorbed by the freshly generated surfaces of the sample. Piperov and Penchev (1973) used a grinding vacuum system in which a mill loaded with steel balls was used to grind the sample under vacuum. They used mass spectrometry to analyze the gases released from micro-inclusions in allanite and found that the surfaces generated upon grinding would adsorb CO_2 and H_2O under their experimental conditions.

We have developed a system in which samples ranging from 5 to 1000mg can be crushed and the gases in the samples analyzed both qualitatively and quantitatively. The system neither adsorbs any of the released gases nor does it generate significant amount of gases that might interfere with the analysis.

Experimental

A Varian Aerograph Model 1700 gas chromatograph equipped with dual columns and helium ionization detectors was used. The detectors operate on the principle that the helium atoms within the carrier gas will be excited from the ground state to a metastable state by high-energy beta particles. The metastable helium will ionize all other gases (except neon) upon collision when they elute from the chromatographic column. As a high voltage is applied to the anode of the detector, the ions formed are collected, providing a current which is amplified and fed into a recorder. The helium detector is ultrasensitive to leakage of air. This was carefully considered in the design of the crusher, and all the connections were checked for leakage. Connections were silver-soldered wherever possible.

A Valco 8-port gas-sample injection valve equipped with $100\mu l$ sample loops was adapted to the gas chromatograph. Hydrogen at concentration levels of 1 to 5 ppm was added to the ultra-high-purity helium carrier gas (99.9999 percent purity) by permeation tube technique. The addition of hydrogen to the carrier gas provides positive response to all analyzed gases (Andrawes and Gibson, 1978). Water was removed from the carrier gas by passing it through a Matheson Hydrox purifier (Matheson, La Porte, Texas). This is a particularly important step when analyzing for water. For calibration, a glass exponential dilution flask (Varian Aerograph) was used. The dilution flask generated different concentrations of the calibration gas, which was introduced to the flask by a gas-sample injection valve.

The chromatographic columns were stainless steel tubes: 2 and 6 meters of 3.2mm O.D. and 2.1mm I.D. were packed with molecular sieve 5A 80/100 mesh. Two-meter columns were used to separate H_2, Ar–O_2, N_2, CH_4, and CO. A six-meter column was used to separate Ar and O_2. The molecular sieve columns were conditioned at 300°C with He flow of 60ml/min for 48 hours. Carbon dioxide and light hydrocarbons were separated on 3-meter columns of 3.2mm O.D. and 2.1mm I.D. packed with Porapak-Q 80/100 mesh. This column was conditioned at 200°C with He flow of 60ml/min for 48 hours. Detectors were operated at 400 volts and at room temperature. Chromatograms were obtained on Varian A-25 strip-chart recorder operating at 1/2 millivolt full scale. The Spectra Physics SP-4000 data system was used to integrate peak areas. Detection limits (in ng) for gases were found by calibration to be: H_2 0.04; N_2 0.6; CH_4 0.05; O_2 0.4; CO 0.6; Ar 0.7; CO_2 0.05; C_2H_2 0.03; C_2H_4 0.03; C_2H_6 0.04; C_3H_8 0.03.

After the system was calibrated (*via* the exponential dilution flask and the gas sampling valve), the crusher was connected directly to the dual-column gas chromatograph. The crusher (Fig. 1) was constructed from stainless steel and hardened by heat treatment. The crusher piston is 1cm in diameter and 8cm long. Silicon-rubber O-rings were used to seal the crusher. The two stainless-steel tubes in the lower part of the crusher are for the helium carrier gas. The upper two tubes serve two functions: (1) to replace the air at the dead volumes with helium, and (2) to permit operation of the crusher under a helium atmosphere by having a continuous flow of purified helium between the upper two O-rings. This procedure eliminates the possibility of atmospheric gases leaking into the crusher during movement of the piston. Some features which were incorporated in the design of the crusher are: (1) the use of the silicon-rubber O-rings on the piston to seal the crusher. A continuous flow of helium in the upper part of the crusher assures complete seal to atmosphere. The silicon-rubber O-rings do not outgas any volatiles that interfere with the analysis. (2) The sample is crushed in a small dead volume which allows fast introduction of the released gases to the analytical column. (3) The crusher is made from heat-treated stainless steel and permits the sample to be exposed to high pressures. (4) The hydraulic press allows application of uniform and high force to all samples crushed. These conditions are required in order to provide quantitative analysis of released gases. Figure 2 shows the schematic diagram for the entire system.

After the sample is loaded in the crusher, the piston is slowly inserted until it approaches the sample. Purified helium flows through the crusher during insertion. This normally takes about a half hour to assure complete removal of the air between the O-ring baffles. The helium carrier gas flows through the crusher into the chromatographic columns at 60 ml/min (as measured at the outlet of the detectors). To purge the air in the system, the helium carrier gas was allowed to flow in the system overnight before the sample was crushed. Meanwhile, purified helium flows through the upper part of the crusher continuously at a rate of 20 ml/min. All samples were crushed at room temperature except when samples were analyzed for water, when the crusher was heated to 150°C. The sample was crushed by applying a hydraulic press to the piston.

When water is trapped along with other gases in
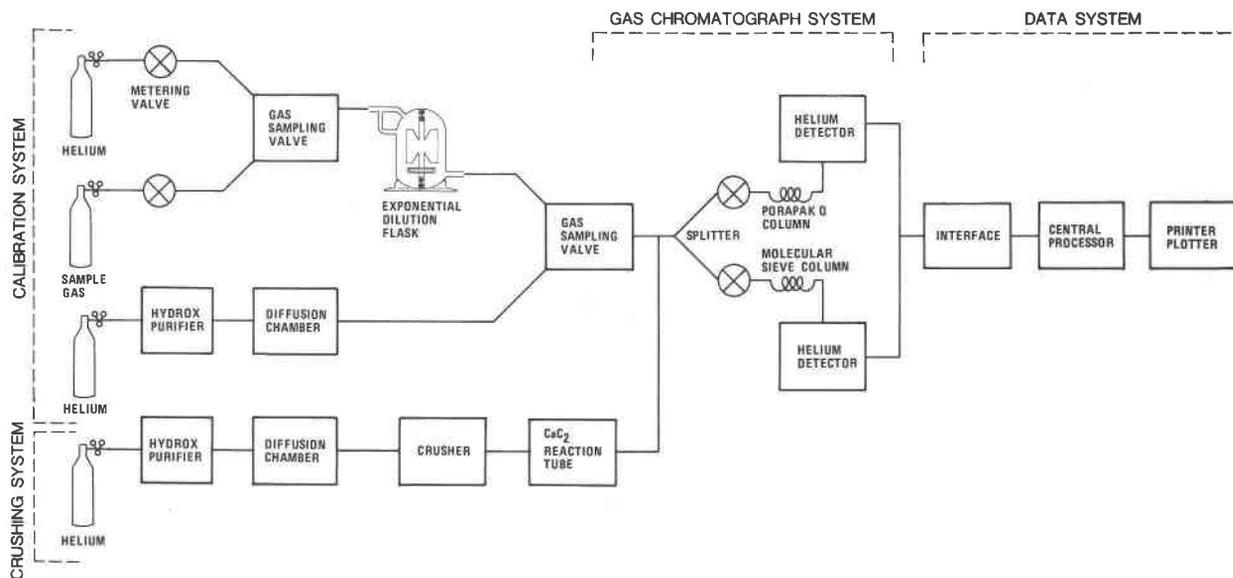
Fig. 2. Diagram of the crushing system.

vesicles, fluid inclusions, or melt inclusions, it cannot be detected by the method described above. Water is a polar compound, and at room temperature it will be removed from the sample and pass through the analytical system too slowly for effective detection. It can be detected indirectly by allowing it to react with calcium carbide and measuring the acetylene produced. For water determination the crusher was heated to 150°C, and the effluent from the crusher (containing water vapor) was passed directly to a CaC_2 reaction tube. The reaction tube was a stainless-steel bulkhead union packed with 100mg CaC_2 (100 mesh). The reaction tube containing the CaC_2 was heated to 100°C with an external heater.

Results and discussions

Applying the chromatographic technique to the analysis of gases released from geologic samples upon crushing involves two basic problems. The first concerns the design and efficient use of the crushing system to provide qualitative and quantitative analysis. The second involves the use of the helium ionization detectors in line with the crushing system to provide positive and linear response to all gases released.

The helium ionization detector is the only chromatographic detector capable of detecting permanent gases at the ppb concentration level. The mechanism by which this detector operates is not completely understood. One major problem associated with the helium detector is that its response to H_2, Ar, O_2, and N_2 can be either positive or negative, depending upon the composition of the helium carrier gas. Recently, we have investigated the influence of the helium carrier gas composition on the detector response (Andrawes and Gibson, 1978) and found that high-purity helium with 1–5 ppm H_2 provides positive and linear response to all gases. Two important factors have to be considered if the helium detector is to be properly used in the crushing experiment. (1) The crusher and the entire chromatographic system must be leak-free. Atmospheric leaks in the system will either prevent the operation of the detector or will change the response of the detector. (2) The helium detector response depends on a number of factors, one of which is the flow rate of the helium carrier gas. Any change in the flow rate of helium during the crushing experiment will give results that are either obscure or misleading.

To crush a sample the ram of the hydraulic press is pumped. This will move the piston 0.3mm into the crusher. We will designate pumping the ram one time "Crush 1," pumping the ram the second time "Crush 2," and so on. The sample can be crushed by two different techniques. In the first technique, the sample is crushed by pumping the ram several consecutive times until a force of 25 tons (pressure 32 kbar) is applied. In this case, one analysis will be obtained. The second method of crushing the sample involves a stepwise procedure. The ram can be pumped one time (Crush 1) and then the released gases analyzed. After the analysis is completed, it will be followed by Crush

2 and so on. This will be repeated multiple times until the forces applied to the sample are ultimately 25 tons. The sum of the analyses (Crush 1 + Crush 2. . . .) will provide the total quantities of the gases released. To evaluate both crushing techniques, some samples were crushed by each method. Initial results have prompted us to adopt the stepwise crushing technique because of the following disadvantages associated with the one-step method: (1) The time required for all released gases to reach the analytical column will be relatively long (slow sample introduction to the analytical column), with the result that the separation between different gases is reduced and the peaks on the chromatogram will be overlapping and broad. Peak areas are not as accurately calculated if they are broad and overlap. (2) Crushing the sample in one step might change the gas flow across the sample and hence in the column. This will change the background current of the detector (the base line) which in turn could obscure the results. (3) The one-step crushing will generate higher frictional heating than that generated by the stepwise method. The frictional heat generates light hydrocarbons (*e.g.* CH_4) which interfere with the analysis.

In initial experiments, it was found that simply moving the piston in the crusher generates considerable amounts of hydrogen and methane if the base of the piston comes in contact with the crusher. By adjusting the dimensions of the bottom of the piston to minimize any physical contact between the piston and the wall of the crusher, the amount of hydrogen and methane released was minimized but not completely eliminated; however, the amount generated was minute (0.12ng H_2 and 0.15ng CH_4), caused very little interference, and can be accounted for in the analysis blank. Figure 3 shows the analysis of a sample containing no trapped gases; this could be considered a blank analysis.

The pressure applied by the hydraulic press allows efficient breaking of the sample. At 25 tons pressure on Pele's Tears volcanic glass (45mg), 50 percent of the sample became $<100\mu m$. The efficiency of the crushing has also been evaluated by crushing selected samples multiple times. After the sample was crushed the first time, it was removed from the crusher, disaggregated, and recrushed. The results are shown on Figure 4. The initial crush removes between 85 and 100 percent of the releasable gases within a sample. The efficiency of the crushing system in releasing gases, however, depends on the nature of the sample and sample size. In most cases, 15–30mg of material will allow for efficient crushing, but large sample size
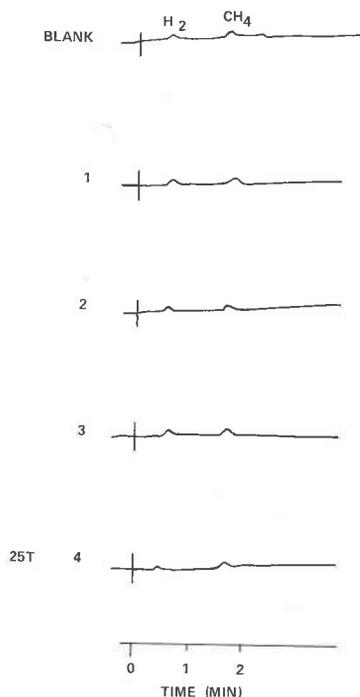
Fig. 3. Typical chromatogram for blank analysis (*e.g.*, the sample contained no releasable gases). The blank sample was the immature lunar soil 61221,11.

may be required in the case of samples with vugs and vesicles larger than 0.5mm. The large sample size may also be required in order to obtain a representative sample.

The question of whether the newly-opened internal surfaces of the crushed sample would adsorb any of the released gases was examined by performing the following experiment. (1) The crusher without a sample is placed in line between the gas sampling valve and the analytical columns. (2) A known quantity of gas sample standard mixture is injected in the system passing through the crusher and analyzed, and peak areas are integrated. The gas sample was 100 μl helium containing (ppm) 9 H_2, 9.5 O_2, 17 N_2, 4.7 CO_2, 4.7 CH_4, 4.8 C_2H_2, 4.3 C_2H_4, and 4.7 C_2H_6. (3) The sample to be examined for adsorption is loaded in the crusher and crushed as described above. (4) After the gases released from the sample are analyzed, the gas sample mixture is injected into the system passing through the newly-crushed samples, the standard sample is analyzed, and peak areas are integrated. (5) The analyses from steps 2 and 4 are compared. If the crushed sample adsorbs any of the gases in the gas sample, step 4 will indicate either the absence or decrease in peak area of the adsorbed gas
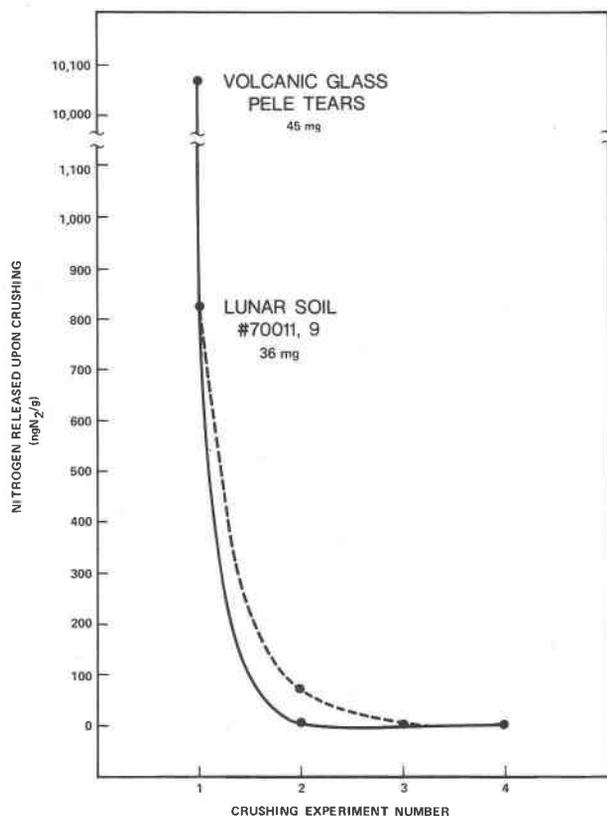
Fig. 4. Efficiency of the crushing.

when compared with the analysis of step 2. In our work there was no evidence of gases adsorbed by the sample. However, if adsorption appears to be a problem for a specific sample, the sample can be heated inside the crusher prior to crushing to a temperature at which the sample would not adsorb any gases.

Selected examples

Several examples of typical analytical results from a variety of samples using our analysis technique will be discussed.

Lunar soil agglutinates. Lunar soils contain a variety of components which reflect the history of each soil. Agglutinates, which are constructional glass particles found in soils, reflect the maturity of the regolith at the site of collection. As a lunar soil matures, its agglutinate content increases (McKay *et al.,* 1972). Previous studies (Gibson and Andrawes, 1978) have shown that the lunar soils contain inorganic gases which can be released upon crushing. The quantity of gas released is directly related to the history and maturity of the soils as measured by their fine-grained iron abundances (Morris, 1976). In order to determine the actual sites from which the gases are released, mineral separates have been prepared and

analyzed. A lunar soil (69961,33) was sieved, and agglutinate particles were hand-picked from the $>90\mu$m fraction. Analysis of 4.6mg of agglutinates is shown in Figure 5. The sample was crushed in four stages. The gases released were nitrogen and methane. The total nitrogen abundance measured from the four crushes was 150ng N_2/g. Methane abundances were 70ng CH_4/g. Most of the gases was released from the sample during the first and second crushes, as seen from the decrease in nitrogen and methane abundances (peak heights) between stages 2 and 3. Exposing the sample to a force of 25 tons depleted most of the releasable gases. Increasing the crushing force above 25 tons generates methane from the crusher; therefore this was the upper limit on the force applied to all samples crushed. To date, about 30 lunar soils and rocks have been crushed and the results reported (Gibson and Andrawes, 1978). Argon, nitrogen, and methane have been detected in mature lunar soils. Immature soils and lunar basalts do not contain any releasable gases other than nitrogen at greater than 2.5ng/g levels.

Pele's Tears—volcanic glass. Volcanic glasses known as Pele's Tears, obtained from the 1973 erup-
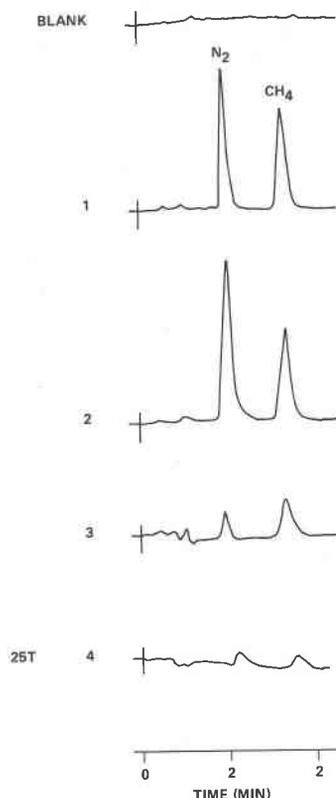
Fig. 5. Gases released upon crushing a separated 4.6mg agglutinate from lunar soil 69961,33. Column 2-meter molecular sieve 5A; temperature 25°C.

tions of Mauna Ulu, Hawaii, were analyzed for their trapped gases. Initially, two chromatographic columns were used, a 2-meter molecular sieve column to separate H_2, O_2–Ar, N_2, CH_4, and CO, and a 3-meter Porapak-Q column to separate CO_2 and light hydrocarbons. Figure 6 shows the analyses of the released gases with a 2-meter molecular sieve column. The analysis on the Porapak-Q column indicated the presence of CO_2, but no light hydrocarbons were detected. Concentrations of the released gases were 192μg O_2–Ar/g, 558μg N_2/g, and 187μg CO_2/g. The methane concentrations were almost identical to the blank values, suggesting that methane results from the piston pressing on the cylinder and wall and is not released from the sample. Figure 6 indicates no systematic changes in the gases released during successive crushes. Crush 2 released much less gas than Crush 1, while Crush 3 released more than Crush 2. Crush 4, 8, and 9 did not release any Ar–O_2, while Crush 1, 2, 3, 5, 6, 7 did. Figure 6 shows that only the sum total of 10 crushes will provide qualitative and quantitative analysis of the gases in the sample. The ratio of Ar/O_2 is of special importance in determining the contribution of atmospheric gases to the gases released from the glass. The 2-meter molecular sieve column in Figure 6 does not provide Ar and O_2 separation. The separation can be achieved with a 6-meter column (Fig. 7). The ratio of Ar/O_2 in this sample was found to be 0.043, which is close to the atmospheric ratio of 0.045 for these two gases. Thus, we concluded that the Ar and O_2 measured in the glass sample are from atmospheric air. Muenow (1973) reported on the nature of the gases released from Pele's Tears during high-temperature studies. He showed that gases were released at low temperatures ($<700°$C) by a rate-limiting diffusion mechanism, and at temperatures in the softening range of the glass by bursting of bubbles trapped near the vaporizing surface of the sphere-like particles. A portion of the gases measured in his work was generated by reactions occurring at elevated temperatures. In the newly-developed crushing technique, gases trapped within the glass are released, avoiding the production of additional species generated by heating. Thus the combination of Muenow's method and our analytical technique will produce invaluable information on the nature of gases present in volcanic products.

Meteorite analysis. Analysis of the volatile-rich carbonaceous chondrites has intrigued workers for many years, as they searched for the original ingredients from which these primitive objects were formed. Analysis of the trapped gas phases within the carbonaceous chondrites may provide information
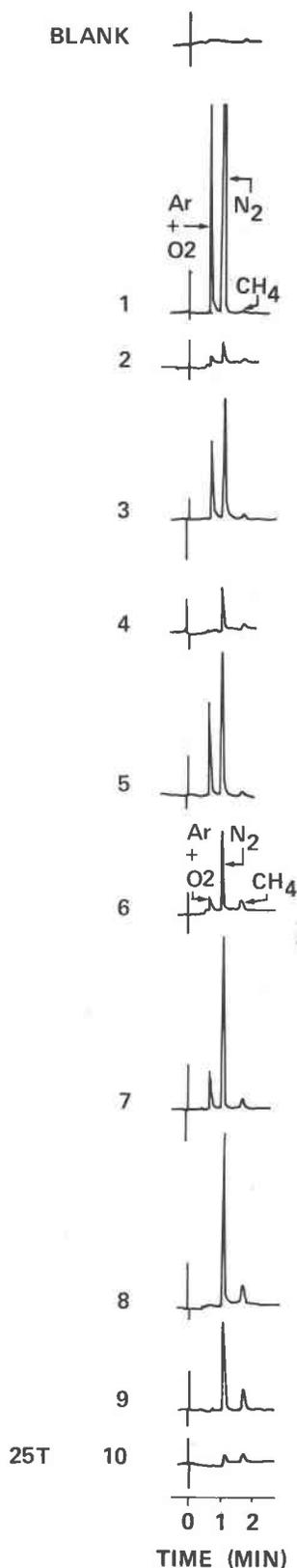
Fig. 6. Gases released upon crushing a 45mg sample of Pele's Tears volcanic glass. Column 2-meter molecular sieve 5A; temperature 60°C.
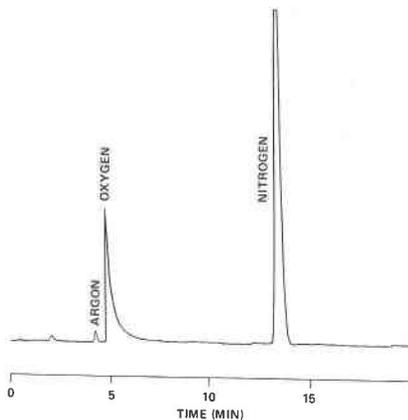
Fig. 7. Gases released upon single crush (Crush 1) of 53mg Pele's Tears volcanic glass. Column 6-meter molecular sieve 5A; temperature 25°C.

on the nature of the volatiles present at the time of their formation. To date, there have been numerous studies of total elemental abundances for the light elements (*e.g.* C, N, S, rare gases, *etc.*), along with their isotopic compositions (Gibson *et al.,* 1971; Belsky and Kaplan, 1970; Kung and Clayton, 1978; Mazor *et al.,* 1970). However, little work has been carried out on the analysis of the trapped inorganic gases in carbonaceous chondrites.

The Murchison (C2) carbonaceous chondrite (133mg interior sample) was examined for its volatiles released upon crushing (Fig. 8). The 2-meter molecular sieve column was used, whereby analysis for H_2, N_2, O_2–Ar, CH_4, and CO could be carried out. The initial crushing of the meteorite (steps 1–5) revealed that methane was the major gas phase released. Trace amounts of nitrogen and hydrogen were released throughout the crushing. Carbon monoxide evolution was noted from steps 3–9; major release of trapped CO occurred with step 7. The variation in gases released with increasing pressures reflects the opening of different sites within the meteorite where the volatiles have been stored. The sum of all nine crushing steps provides the total amount of gases measured during the complete crushing study. The nature of the released gases reflects the reduced nature of the gases at the time of incorporation into the meteorite. The absence of atmospheric oxygen and carbon dioxide is particularly noteworthy. The concentration of gases (in $\mu g/g$) was 0.03 H_2, 3.57 N_2, 3.1 CH_4, and 6.8 CO.

Quartz crystal with inclusions. Crushing techniques followed by a variety of methods for analyzing volatiles have been widely used to study gases present in fluid inclusions. A summary of past studies is included in the extensive review of Roedder (1972).
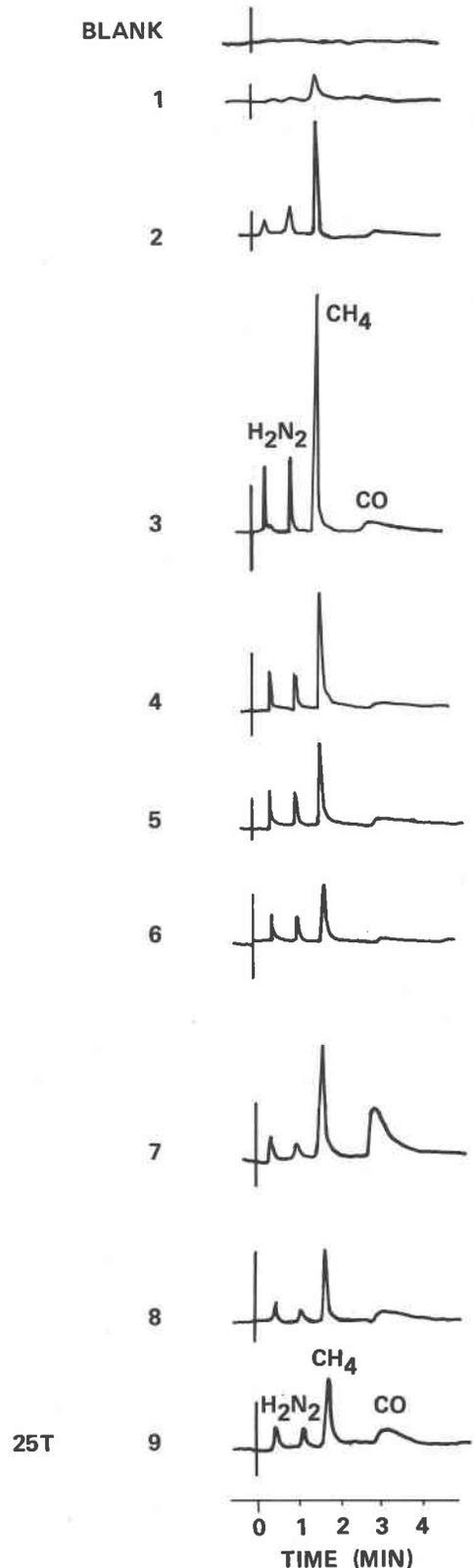
Fig. 8. Gases released upon crushing a 133mg piece of Murchison C2 meteorite. Column 2-meter molecular sieve 5A; temperature 60°C.

QUARTZ CRYSTALS
GEI AUS NO. 6
S. W. AFRICA
75 MG
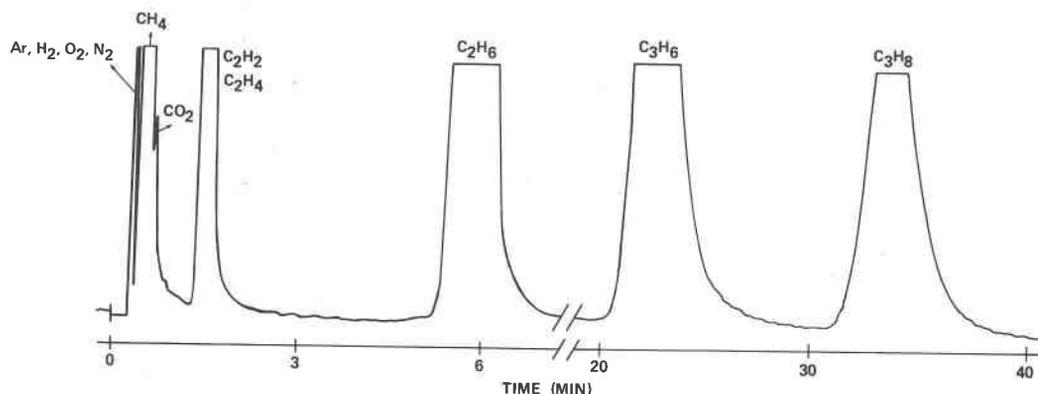
Fig. 9. Gases released upon single crush, quartz crystal with inclusion. Column 3-meter Porapak-Q; temperature 60°C.

Kvenvolden and Roedder (1971) reported the analysis of quartz crystals which contained both primary and secondary inclusions filled with one or more combinations of organic liquid, moderately saline aqueous liquid, dark-colored solids, and/or vapor. Samples of these quartz crystals from the Geiaus No. 6 locality were obtained and analyzed. Figure 9 shows the analytical results from a single crush (Crush 1) of a 75mg sample which was simply fractured. In our work we detected the presence of the low-molecular-weight gases, C_2H_2 and/or C_2H_4 (290μg/g), and C_3H_6 (130μg/g), which were not reported by Kvenvolden and Roedder. In addition, we confirmed the presence of N_2, (3.3μg/g), CH_4 (508μg/g), CO_2 (0.9μg/g), C_2H_6 (173μg/g), and C_3H_8 (114μg/g). Hydrogen and CO detected by Kvenvolden and Roedder were probably due to heating their crushing system to 150°C; we did not detect H_2.

Water analysis. The determination of trace amounts of water trapped in geological samples is one of the most important and at the same time most difficult measurements to make accurately. Gas chromatography can be used to make these measurements but the direct measurement of water by gas chromatography presents two problems: (1) it is difficult to measure water levels below 100 ppm (Hachenberg, 1973, p. 133–140); and (2) water is a polar compound and not readily eluted from normal chromatographic columns. The water peak is usually asymmetrical and shows considerable tailing, which makes it very difficult to determine trace amounts. To avoid the above problems, indirect determinations of water can be made by gas chromatography. The water is converted into a nonpolar compound easily eluted from normal chromatographic columns and therefore easily detected at trace concentrations. Water can be converted to C_2H_2 by reaction with CaC_2 (Sundberg and Maresh, 1966), or to H_2 by reaction with CaH_2 or $LiAlH_4$ (Aubeau *et al.,* 1964). In our work, we have converted the water to acetylene because it can be detected with high sensitivity by the helium ionization detectors, and because it is unlikely to be present in the geological samples. Thus the acetylene measured will be due only to the presence of water. Initially, we attempted to crush the sample mixed with CaC_2. However, this arrangement has its faults because simple crushing of CaC_2 produces acetylene. The source of the C_2H_2 is not fully understood, but may be from adsorbed H_2O on the surfaces of CaC_2 reacting with fresh surfaces of CaC_2 produced by crushing. The problem was avoided by passing the released gases into a small reaction tube filled with CaC_2 attached to the exhaust line. This method of converting the water to acetylene for later measurement by the GC works satisfactorily. Figure 10a gives the analysis of water released from a sample of Pele's Tears from Mauna Ulu. The sample was crushed in a single crush, which fractured the glass sample and opened interior voids. The water released was converted to acetylene, and its elution is shown in the chromatogram. The amount of water measured (as determined by acetylene conversion) was 0.1mg H_2O/g.

Our studies have shown that analysis of other gases simultaneously with the water analysis could not be completely successful. We found that the calcium

PELE TEARS
VOLCANIC GLASS
35 MG
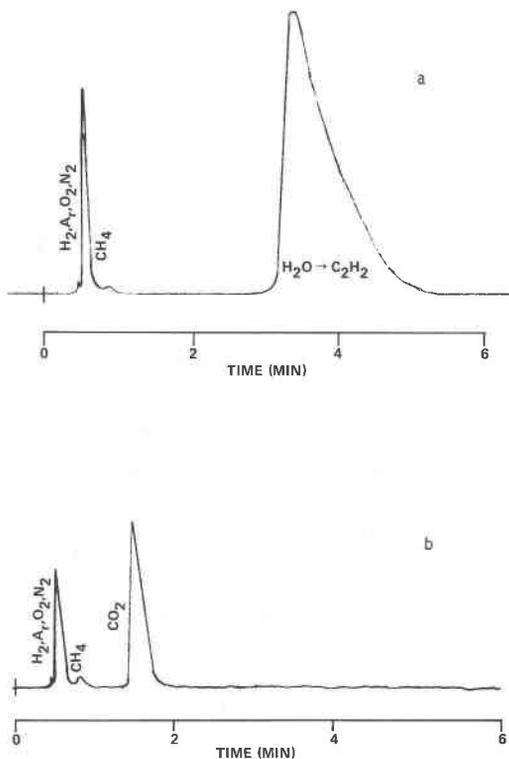
Fig. 10. Gases and water released upon crushing Pele's Tears volcanic glass. Column 3-meter Porapak-Q; temperature 25°C. (a) Analysis of water converted to C_2H_2 in CaC_2 reaction tube. (b) Analysis of the same sample bypassing the CaC_2 reaction tube.

carbide reaction tube retains CO_2. Data in Figure 10b show the evolution of carbon dioxide from the Pele's Tears sample when the CaC_2 reaction tube is not used. Figure 10a shows the absence of the CO_2 which has been retained by the reaction tube. Thus, two independent analyses should be made, one for gases and one for water.

Conclusions

An analytical system has been developed for the qualitative and quantitative analysis of volatile phases released from crushed samples. The gas chromatograph equipped with helium ionization detectors is an excellent means of analyzing trace quantities of volatiles (at the ppb level). The high sensitivity of the analysis system permits use of extremely small samples. After the proper calibration of the chromatographic system, quantitative data can be obtained from samples as small as 4–5mg. We have analyzed volcanic glass, lunar agglutinate particles,

quartz crystals with inclusions, and volatile-rich meteorite samples. The analysis method could be extended to include other gases possibly present, such as H_2S, SO_2, NO_2, F_2, *etc.*, by the proper selection of the analytical columns. Numerous other applications can be found in the areas of fluid-inclusion analysis of ore deposits, ceramics, glass manufacturing, experimental petrology studies of gas and melt inclusions, crystal-growth studies, *etc.* The newly-developed method of analysis will be applied to fluid and melt inclusion analysis and we hope for considerable progress, but the nature of the samples and extraction procedures used are the prime considerations in evaluating the precision, the accuracy, and most important, the significance of any measurements obtained.

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