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## GAS CHROMATOGRAPHIC ANALYSIS OF VOLATILES IN FLUID AND GAS INCLUSIONS

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### SUMMARY

Most geological samples and some synthetic materials contain fluid inclusions. These inclusions preserve for us tiny samples of the liquid and/or the gas phase that was present during formation, although in some cases they may have undergone significant changes from the original material. Studies of the current composition of the inclusions provide data on both the original composition and the change since trapping.

These inclusions are seldom larger than 1 millimeter in diameter. The composition varies from a single major compound (*e.g.*, water) in a single phase to a very complex mixture in one or more phases. The concentration of some of the compounds present may be at trace levels.

We present here some analyses of inclusions in a variety of geological samples, including diamonds. We used a sample crusher and a gas chromatography-mass spectrometry (GC-MS) system to analyze for organic and inorganic volatiles present as major to trace constituents in inclusions. The crusher is a hardened stainless-steel piston cylinder apparatus with tungsten carbide crushing surfaces, and is operated in a pure helium atmosphere at a controlled temperature.

Samples ranging from 1 mg to 1 g were crushed and the released volatiles were analyzed using multi-chromatographic columns and detectors, including the sensitive helium ionization detector. Identification of the GC peaks was carried out by GC-MS. This combination of procedures has been shown to provide geochemically useful information on the processes involved in the history of the samples analyzed.

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## INTRODUCTION

Samples with large fluid inclusions were first described in the eleventh century. The interest in these rare samples continued, and in the early eighteenth century, some of these inclusions were analyzed, and the data obtained were used to support the Neptunist theory of the formation of minerals and rocks from water. Early and recent workers in the field recognized the potential of these inclusions for revealing significant scientific information, such as geological thermometric data, evaluation of mineral and ore deposits, and information about the evolution of the earth itself. Since inclusions represent actual samples — the only samples we have — of former fluids existing at some time in the history of the Earth, they are important clues in understanding the geological operants. In spite of the considerable interest in fluid inclusions, most of the earlier reports were only descriptive in nature, and were made without the benefit of modern techniques and instruments.

Destructive methods of analysis included breaking the inclusions while submerged in a liquid such as glycerol, followed by transfer of the gas bubble to different reagents and measurement<sup>1</sup>. Crushing in various fluids can be used to obtain qualitative composition<sup>2</sup>. These methods can be extremely sensitive in qualitative terms, but generally they are insensitive and tedious, and they can be conveniently used only for inclusions that are about 200  $\mu\text{m}$  in diameter, unless the gas is highly compressed. Most inclusions however, are much smaller, and they may contain a complex mixture that cannot be analyzed by these methods.

Other powerful, destructive techniques used included gas chromatography (GC), mass spectrometry (MS), or GC-MS. Several workers in the field have adapted a crushing device to GC or MS. The crushing device is the most important step in such analyses; if it is not carefully designed, it can introduce contaminating volatiles in significant amount. On the other hand, some of the volatiles released from the sample can be adsorbed on the newly generated surface of the crushed sample and thereby be excluded from analysis.

One method reported in the literature for the extraction of volatiles prior to GC or MS involves stepwise heating of the sample until the inclusions decrepitate<sup>3</sup>. A considerable portion of such released volatiles may be generated from either thermal decomposition or chemical reaction. For example:  $\text{H}_2\text{O} + \text{Fe(II)} \rightarrow \text{Fe(III)} + \text{H}_2$ ;  $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$ ;  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ .

Another method commonly used is grinding the sample in a sealed container with metal or ceramic balls, followed by sampling the atmosphere inside the container for the released gases<sup>4,5</sup>. However, this method is flawed by the generation from the crushing material of gases that are not indigenous to the samples (including  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ ) and the resorption of some of the released gases takes place on the newly generated surfaces of the ground sample<sup>6</sup>.

Gentle crushing has been reported, in which the sample is crushed by dropping a moderately heavy steel weight on the sample several times, with the aid of an external magnet<sup>7,8</sup> or by pressing a steel ram against a base plate<sup>9</sup>. Even such gentle crushing generates some gases, especially  $\text{H}_2$  and  $\text{CH}_4$ , by merely grinding two stainless-steel plates together<sup>9</sup>. While this method releases less contaminating gases, it will not open all small inclusions. Even diamonds have been crushed in this manner<sup>10</sup>, in a stainless-steel chamber, by using a tungsten carbide piston. Crushing was ac-

complished by tapping the head of the device with a hammer. The head piston sometimes fragmented, and some gases were detected in blank runs.

All the methods mentioned above were used in the past for the analysis of permanent gases. Analysis of fluid inclusions containing complex organic mixtures have not received the same attention, except for a report by Murray<sup>11</sup>, and Kvenvolden and Roedder<sup>12</sup>. Samples with organics are generally analyzed in two steps: (1) grinding in a sealed container, followed by the analysis of the vapor phase for the detection of permanent gases, and (2) solvent extraction for the detection of organic compounds. Compounds with intermediate volatiles, such as C<sub>5</sub> to C<sub>10</sub> hydrocarbons, are often lost in this processes<sup>12</sup>.

Recently, a hydraulically operated hardened stainless-steel crusher has been reported for the analysis of lunar materials<sup>13,14</sup>. This crusher, which has a piston and cylinder (Fig. 1) was operated in a pure helium atmosphere. The released volatiles are detected with the sensitive helium ionization detector. This system generates minimal amounts of H<sub>2</sub> and CH<sub>4</sub>, which are corrected for on the basis of blank runs. The hydraulic press allows crushing under stepwise increasing pressure to assure that most cavities are opened. In the work reported here, we used the modification of the piston cylinder crusher used previously in ref. 13. This modification allowed crushing hard samples between two discs of tungsten carbide, as shown in Fig. 1. The crusher design eliminates or drastically reduces sources of contamination. Samples as hard as diamonds can easily be crushed. Samples as small as 1 mg were crushed, and the released volatiles were analyzed by using multiple chromatographic columns and detectors. Samples included diamonds, basalts, quartz, and olivine.

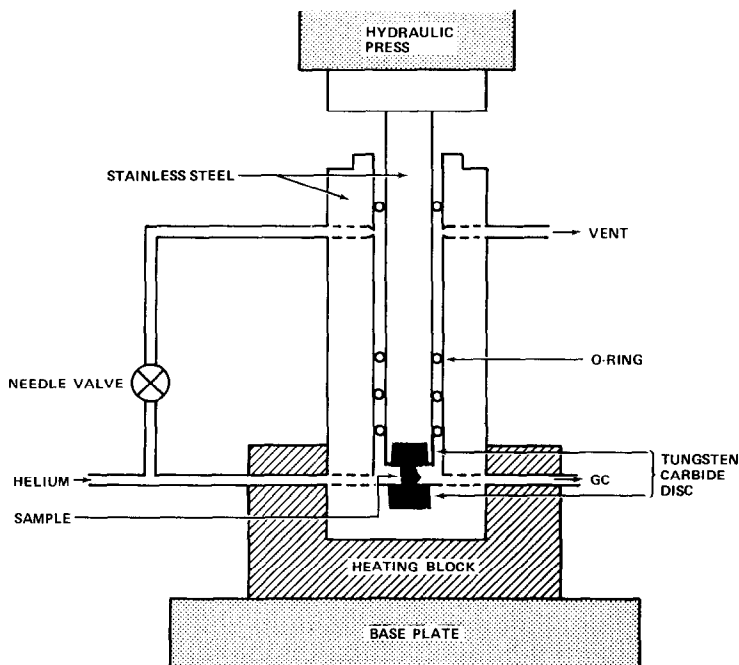


Fig. 1. Crushing apparatus.

## EXPERIMENTAL

In this work we used: (1) a Varian 1700 gas chromatograph with dual columns and helium ionization detection (HID); (2) a Perkin Elmer Sigma 2 gas chromatograph with flame-ionization detection (FID) and flame photometric detection (FPD); and (3) a DuPont DP1 gas chromatograph in combination with a mass spectrometer.

HID was used as previously reported<sup>15</sup> for the analysis of gaseous samples only. FID and FPD were used according to normal operating conditions. The GC-MS was used to identify the organic compounds present. Each detector was interfaced with a Spectra Physics data system SP-4000 to integrate peak areas. Chromatograms were obtained on a Houston Instrument strip chart recorder or on a Spectra Physics printer plotter SP-4050.

The columns used were:

(1) Molecular Sieve: stainless-steel tubing, 2 m  $\times$  3.2 mm O.D.  $\times$  2.1 mm I.D., packed with Molecular Sieve 5 Å, 80–100 mesh. This column was conditioned at 200°C with helium at a flow-rate of 60 ml/min; the column was used to separate H<sub>2</sub>, Ar + O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO; detection by HID.

(2) Porapak N: stainless-steel tubing 2 m  $\times$  3.2 mm O.D.  $\times$  2.1 mm I.D., packed with Porapak N, 80–100 mesh, and conditioned at 200°C with helium at a flow-rate of 60 ml/min. This column separates CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>8</sub>; detection by HID.

(3) Durapak: PTFE tubing, 2.5 m  $\times$  3.2 mm O.D.  $\times$  1.6 mm I.D., packed with Durapak phenylisocyanate-Porasil C, 80–100 mesh. The column was conditioned at 70°C with helium at a flow-rate of 30 ml/min. This column was used with FID to separate C<sub>1</sub> to C<sub>6</sub> hydrocarbons.

(4) Chromsil: PTFE tubing 3 m  $\times$  3.2 mm O.D.  $\times$  1.6 mm I.D., packed with Chromsil 310, 80–100 mesh, and conditioned at 70°C with helium at a flow-rate of 60 ml/min. This column was used with FPD to separate sulfur-containing compounds.

(5) Glass capillary column, 50 m  $\times$  0.25 mm I.D., coated with SE 30, film thickness 0.4  $\mu$ m, purchased from Chrompack. The column was conditioned at 280°C and operated between 40°C and 240°C with helium at a flow-rate of 3 ml/min. This column was used for the analysis of organic compounds in inclusions.

The crusher used in this work is shown in Fig. 1. The crusher piston is 1 cm in diameter and 8 cm long. The tungsten carbide discs were incorporated in the crusher by heat shrinking. The silicone rubber O-rings were lubricated with a thin layer of silicone lubricant high-vacuum grease. The O-rings sealed the crusher from the surrounding atmosphere. This was particularly important when HID was used. The samples were crushed in a stepwise manner by means of a hydraulic press. The numbered sequence of "crushings" of a given sample refers to stepwise increases in the piston pressure. The base of the crusher is seated in a heating block permitting operation  $\leq$  300°C.

The crusher was connected to the gas chromatograph directly, but when HID was used, the crusher was connected to the gas chromatograph via a four-way switching valve (Valco Instrument) to avoid opening the helium ionization detector to the atmosphere when loading samples. A gas sampling valve was connected to the four-way valve for gaseous calibration (Valco Instrument, 100- $\mu$ l sample loop). The detector response was calibrated after each sample was crushed.

Prior to crushing, samples were ultrasonicated in clean acetone, dried and placed in the crushing device at 200°C for about 2 h with helium flowing through to remove adsorbed gases. The crusher was then cooled to room temperature, and the helium flow through the crusher was switched so that it flowed to the chromatographic columns. The sample was then ready to be crushed.

For the analysis of samples containing organic mixtures, inorganic gases and light hydrocarbons, samples were crushed with the crusher in line with the gas chromatograph. For the analysis of higher-molecular-weight compounds, the sample was crushed with the crusher heated to 120°C, and the effluent of the crusher was connected with a short, pre-column capillary tube immersed in liquid nitrogen. The collection time was 40 min, after which the pre-column was connected to the front end of the gas capillary column, and the liquid nitrogen was removed.

## RESULTS AND DISCUSSION

### *Crushing device*

In order to release volatiles trapped in solids by the crushing method, special care has to be taken, especially for the analysis of trace volatiles. Most crushing devices will contribute some volatiles, so a blank determination is essential. Blank experiments should be carried out with samples having the same hardness and dimension as those of the samples to be crushed, but devoid of any volatiles. For many samples, these criteria are difficult to meet.

The formation of volatiles in any crushing device results from localized heat generated from pressing two objects together or from the plastic deformation of the samples and the crusher. This heat might be high enough to release some of the volatiles adsorbed on the surfaces of the crushing device or the sample itself. For example, in a stainless-steel crusher, such as the one used in this work, if the piston touches the body of the crusher or if the O-ring is too tight, any small movement of the piston will generate significant H<sub>2</sub> and CH<sub>4</sub>, as shown in Fig. 2. In the crushing procedure used, we minimized the generation of heat by lubricating the piston and by providing enough clearance between the piston and the body of the crusher to avoid any physical contact. Adsorbed volatiles on sample and crusher were minimized by heating the sample in the crusher with helium flow before crushing.

Of the several samples that were crushed as blanks, the most important were synthetic inclusion-free quartz and ceramic alumina. On the Knoop hardness scale (k100), synthetic quartz rated 820, and ceramic alumina 1700. Most geological samples we analyzed have a hardness less than that of quartz except for the diamond samples, which have a hardness between 6500 and 10,000. The tungsten carbide discs between which the samples were crushed have a hardness of 1800. Fig. 3 shows the blank obtained from crushing synthetic inclusion-free quartz (93 mg), along with the detector response to a standard mixture of gases. The standard contained 1.3 ng O<sub>2</sub>, 0.88 ng N<sub>2</sub>, 0.28 ng CH<sub>4</sub>, 0.69 ng CO, 0.43 ng CO<sub>2</sub>, 0.27 ng C<sub>2</sub>H<sub>6</sub>, 0.29 ng C<sub>2</sub>H<sub>4</sub>, 0.26 ng C<sub>2</sub>H<sub>2</sub> and 0.92 ng C<sub>3</sub>H<sub>8</sub>. Neither moving the piston nor crushing the inclusion-free quartz generated any gases. On the other hand, crushing geological samples much harder than quartz proved to be quite different. Fig. 4 shows the chromatograms obtained from crushing 400 mg ceramic alumina. Initial crushing (*i.e.* at low pressure) resulted in the detection of N<sub>2</sub> and CH<sub>4</sub>. With greater applied force on the

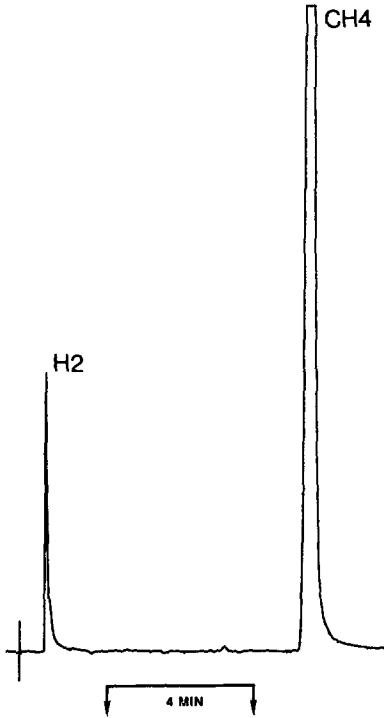


Fig. 2. Hydrogen and methane generated from the stainless-steel crusher, when the piston touches the body of the crusher, or O-rings are too tight. Column, Molecular Sieve 5Å; detection by HID.

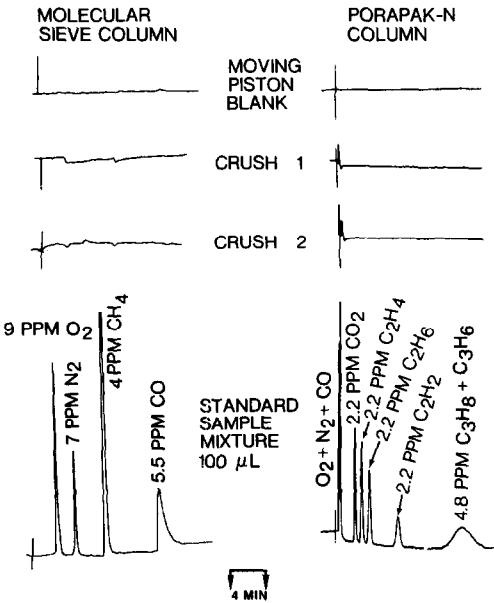


Fig. 3. Blank from crushing 93 mg synthetic inclusion-free quartz, and detector response to a standard gas mixture. Detection by HID.

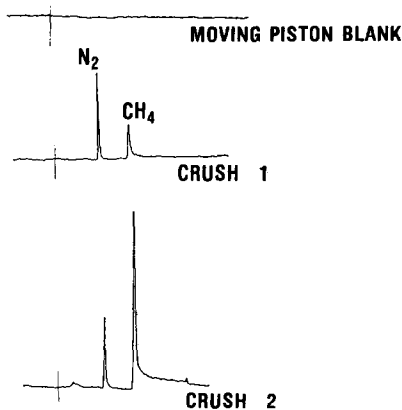


Fig. 4. Blanks obtained from stepwise crushing of ceramic alumina (400 mg). Column and detector as in Fig. 2.

crusher the amounts of  $\text{CH}_4$  detected were much higher than those produced on the initial crushing. These results suggest that at least some, if not all, of the methane detected was generated in the crusher. On the other hand, the nitrogen was probably released from the ceramic alumina upon crushing. Light crushing a small ceramic alumina ball (50 mg) generated a blank similar to that shown in Fig. 3, but hard crushing (30,000 to 40,000 pound per in.<sup>2</sup>) produced detectable quantities of methane.

#### *Gases in diamond*

During the course of this work, we crushed five samples of diamond, each of which was under 30 mg; the final pressure on each sample was about 20,000 pound per in.<sup>2</sup>. The measurement of the composition of the gases evolved from diamonds may provide useful data on the nature of the environment in which diamonds were formed. The gases present in diamonds represent one of the few available direct "samples" of the volatiles present in the Earth's deep interior. Diamonds occur in kimberlite pipes and certain other rocks believed to originate from below the crust of the Earth. They require high temperatures and pressures (1200°C, 45 kbar, equivalent to a depth of 150 km) for formation in thermodynamic equilibrium with graphite. For this reason, rocks containing diamonds are thought to originate in the mantle of the Earth. Because diamonds are associated with kimberlite pipes which have large concentrations of carbonate, it has been suggested that the gases present in diamonds are carbon-containing species (*e.g.*,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$ ).

Most of the work of analyzing impurities in diamond has focused on non-volatile components<sup>16</sup>, but gases in diamond have been reported by various workers<sup>17</sup>. Nitrogen was detected in Type I and II diamond using para-magnetic spin resonance<sup>18</sup>, and was also detected by mass spectrometry after heating the sample to 2000°C<sup>19</sup>. Melton and Giardini<sup>10,20</sup> have reported most of the available data on volatiles released from diamond by crushing or by graphitization at high temperature. The species detected included significant amounts of  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , ethyl alcohol and butene<sup>10,20</sup>. Roedder<sup>21</sup> has noted that Melton and Giardini's data result in  $\text{H}_2/\text{H}_2\text{O}$  volume ratios ranging from 6.0 to 0.01 and  $\text{CO}/\text{CO}_2$  ratios ranging from 23 to 0. More importantly, he found that no correlation exists between these

two ratios, and the ratio  $(\text{H}_2/\text{H}_2\text{O}):(\text{CO}/\text{CO}_2)$  ranges from 52 to 0.008, such ratios mutually contradictory evidence for  $f_{\text{O}_2}$ . We crushed five samples of type II diamond from Southwest Africa. Each was about 2.5 mm  $\times$  4 mm, yellow in color, and contained several dark spots which may be graphite. The samples were crushed at 20°C and the effluent of the crusher was split between the Molecular Sieve and Porapak N columns. Fig. 5 shows a typical series of chromatograms, obtained from crushing a 20-mg diamond sample. Steps 1 through 6 involved crushing the sample in 6 increments of pressure. Only  $\text{CH}_4$  and  $\text{CO}_2$  were detected, and the amounts of  $\text{CO}_2$  detected in the diamond samples were less than  $3 \times 10^{-9}$  ml, *i.e.* about 3 orders of magnitude less than those reported by Melton and Giardini<sup>10,20</sup>. Moreover, we did not detect any other gases. The pattern of increasing  $\text{CH}_4$  with increasing pressure as seen in Figs. 4 and 5 and reported by Andrawes and Gibson<sup>13</sup> indicate that most, if not all, the methane detected was a contaminant produced during crushing. The amount of  $\text{CH}_4$  detected from crush 1 is more than that detected from crush 2, due to the fact that relatively greater force is applied to smaller surface area in crush No. 1. The difference between the results reported here and those of Melton and Giardini<sup>10,20</sup> is very significant, and more work is required to corroborate or refute the data reported by Melton and Giardini.

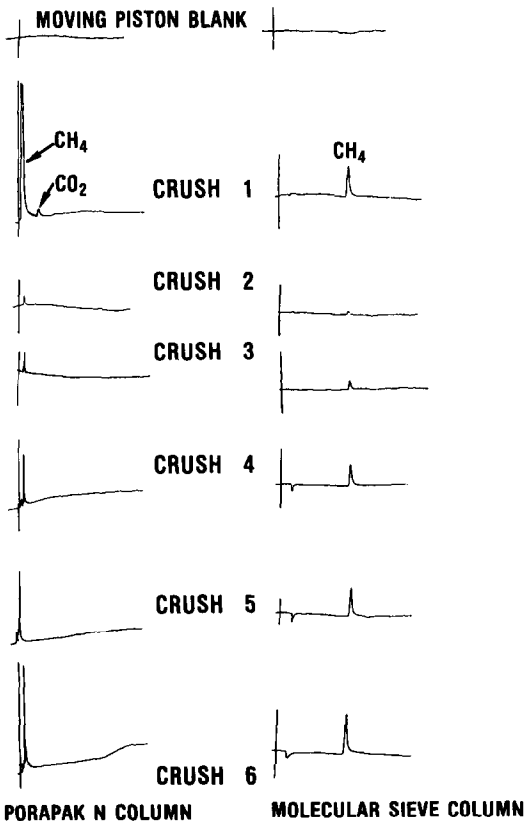


Fig. 5. Chromatograms from stepwise crushing of diamond sample. Detection by HID.



*H<sub>2</sub>S in quartz*

A fetid quartz sample from Brazilian pegmatite was analyzed on Porapak N and Molecular Sieve columns, coupled to two helium ionization detectors. The gases were also analyzed independently on a Chromosil 310 column with FPD. Fig. 6 shows typical chromatograms obtained with HID. Only H<sub>2</sub>S was detected in significant amounts ( $60 \times 10^{-3}$  ml). These results were also confirmed by the FPD data. Much smaller amounts (<1%) of CO<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub> were also detected, as shown in Fig. 6.

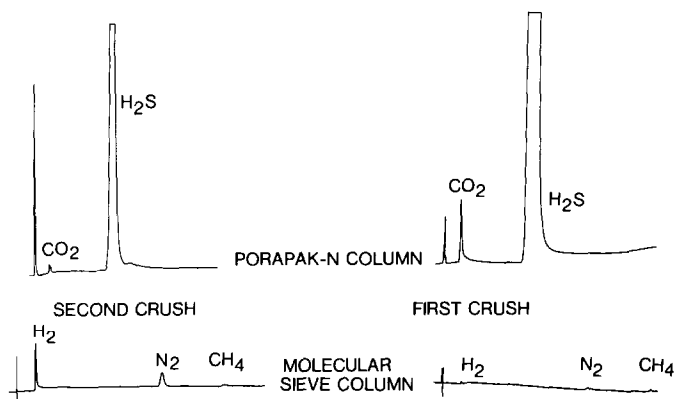


Fig. 6. H<sub>2</sub>S and other trace gases released from Brazilian pegmatitic quartz. Detection by HID.

The inclusions in the quartz sample had previously been examined with a microscope and found to contain liquid water solution, a vapour bubble, and an immiscible liquid droplet which was tentatively identified as liquid H<sub>2</sub>S at 3 to 4 atmospheres pressure<sup>5</sup>. Examination of the same sample by Raman microprobe spectrometry confirmed the presence of H<sub>2</sub>S in the vapor bubble, but it was impossible to identify the immiscible droplet, because no spectra could be obtained for this phase<sup>22</sup>. As most of the immiscible droplets persisted above the critical temperature of H<sub>2</sub>S, they could not be pure H<sub>2</sub>S liquid, but the authors speculated that the droplet might consist of liquid hydrocarbons plus H<sub>2</sub>S. Our results, however, failed to detect any hydrocarbons or other volatiles.

*CO<sub>2</sub> in olivine*

Naturally occurring olivines with inclusions containing CO<sub>2</sub> are not uncommon. Carbon dioxide is probably the most important fluid component in geological systems other than water. The sample we analyzed was from Hualalai, Hawaii. Previous investigation of this sample<sup>2,3</sup> showed that CO<sub>2</sub> was readily detected by several techniques, including infrared absorption, but other components were not detected. This sample was formed during basaltic volcanism, and hence it would be highly desirable to know what other gases, such as He, Ar, and Xe might be present in the inclusions. Also the equilibrium between CO<sub>2</sub> and ferrous silicates and perhaps water at high temperature should result in the formation of some CO and CH<sub>4</sub> in the inclusions.

We analyzed this sample on Porapak N and Molecular Sieve columns. The

two columns were connected to two helium ionization detectors, and were capable of separating  $H_2$ , Ar,  $O_2$ ,  $N_2$ ,  $CH_4$ , Xe,  $CO_2$  and  $C_2$  hydrocarbons. Because the concentration of  $CO_2$  in this sample was high, only 1.23 mg was crushed. In the initial work, the hydraulic pressure was maintained on the sample after crushing. This caused continuous cracking and opening of additional small inclusions and resulted in a chromatogram with continuously eluted peaks, all of which were from  $CO_2$ . This result was also observed with some other samples as well and can be avoided by releasing the pressure after each crushing to allow a complete elution of the volatiles released prior to the next crushing. Fig. 7 compares the chromatograms obtained when keeping the pressure on the sample and when the pressure is released. Several samples were analyzed, but no other gases were detected by either HID or FPD.

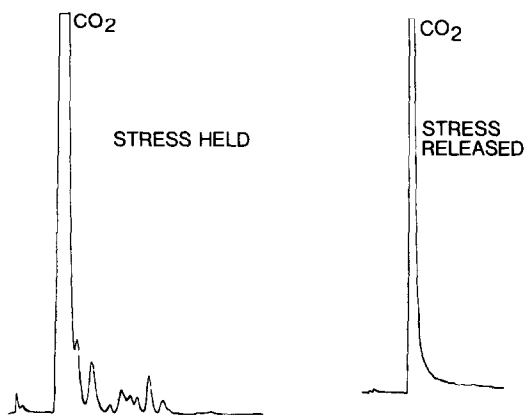


Fig. 7.  $CO_2$  released from 1.23-mg sample of Hawaiian olivine.

### *Hydrocarbons in fluorite*

Very few detailed analysis of the hydrocarbons in oil inclusions have been reported<sup>11,12</sup>. We analyzed a series of fluorite samples from the Hill Mine, N.E. corner, 725 Level, in the southern illinois fluorite-lead-zinc district<sup>24,25</sup>. These samples contain a yellow-brown oil, opaque black oil, or a combination of both. In this work we investigated the composition of organic and inorganic matter present in samples with yellow-brown oil only. A comprehensive study is underway to examine all samples, including those containing opaque black oil.

Because of the complexity of the composition of these samples, they were analyzed on Molecular Sieve, Porapak N, Durapak phenylisocyanate, and SE 30 glass capillary columns. FID, HID, and GC-MS were used for detection and identification. With the combination of 4 columns and 3 detectors useful and comprehensive information was obtained about the composition of these samples. Connecting the effluent of the crusher directly to the analytical columns assured a complete analysis for both highly volatile and less volatile compounds. GC-HID separated and identified  $H_2$ ,  $N_2$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$  and  $C_3H_8 + C_3H_6$ . GC-FID separated and detected  $C_1$  to  $C_6$  hydrocarbons with the Durapak column, and  $C_6$  to  $C_{31}$  hydrocarbons with the SE30 capillary column. GC-MS identified some of the compounds present between  $C_5$  and  $C_{31}$  hydrocarbons.

TABLE I  
COMPOUNDS, IDENTIFIED IN OIL INCLUSIONS OF FLUORITE SAMPLE

<i>Substance</i>	<i>Formula</i>	<i>Substance</i>	<i>Formula</i>
C <sub>5</sub> -Cycloalkane	C <sub>5</sub> H <sub>10</sub>	<i>n</i> -Pentylcyclohexane	C <sub>11</sub> H <sub>22</sub>
C <sub>6</sub> Alkane (br)*	C <sub>6</sub> H <sub>14</sub>	Naphthalene	C <sub>10</sub> H <sub>8</sub>
<i>n</i> -Hexane	C <sub>6</sub> H <sub>14</sub>	<i>n</i> -Dodecane	C <sub>12</sub> H <sub>26</sub>
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	C <sub>13</sub> -Alkane (br)	C <sub>13</sub> H <sub>28</sub>
Benzene	C <sub>6</sub> H <sub>6</sub>	<i>n</i> -Hexylcyclohexane	C <sub>11</sub> H <sub>24</sub>
Hexene	C <sub>6</sub> H <sub>6</sub>	C <sub>5</sub> -Alkylbenzene	C <sub>11</sub> H <sub>16</sub>
C <sub>7</sub> -Alkane (br)	C <sub>7</sub> H <sub>16</sub>	Methylnaphthalene	C <sub>11</sub> H <sub>10</sub>
C <sub>7</sub> -Cycloalkane	C <sub>7</sub> H <sub>14</sub>	<i>n</i> -Tridecane	C <sub>13</sub> H <sub>28</sub>
<i>n</i> -Heptane	C <sub>7</sub> H <sub>16</sub>	2,6,10-Trimethyl-dodecane	C <sub>15</sub> H <sub>32</sub>
Methylcyclohexane	C <sub>7</sub> H <sub>14</sub>	<i>n</i> -Tetradecane	C <sub>14</sub> H <sub>30</sub>
Heptene	C <sub>7</sub> H <sub>14</sub>	2,6,10-Trimethyltridecane	C <sub>16</sub> H <sub>34</sub>
C <sub>8</sub> -Cycloalkane	C <sub>8</sub> H <sub>16</sub>	<i>n</i> -Pentadecane	C <sub>15</sub> H <sub>32</sub>
Toluene	C <sub>7</sub> H <sub>8</sub>	<i>n</i> -Hexadecane	C <sub>16</sub> H <sub>34</sub>
C <sub>8</sub> -Alkane (br)	C <sub>8</sub> H <sub>18</sub>	<i>n</i> -Heptadecane	C <sub>17</sub> H <sub>36</sub>
<i>n</i> -Octane	C <sub>8</sub> H <sub>16</sub>	Pristane	C <sub>19</sub> H <sub>40</sub>
Ethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	<i>n</i> -Octadecane	C <sub>18</sub> H <sub>38</sub>
Octene	C <sub>8</sub> H <sub>16</sub>	Phytane	C <sub>20</sub> H <sub>42</sub>
C <sub>9</sub> -Cycloalkane	C <sub>9</sub> H <sub>18</sub>	<i>n</i> -Nonadecane	C <sub>19</sub> H <sub>40</sub>
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	<i>n</i> -Eicosane	C <sub>20</sub> H <sub>42</sub>
<i>m,p</i> -Xylene	C <sub>8</sub> H <sub>10</sub>	2,6,10,14-Tetramethylnonadecane	C <sub>23</sub> H <sub>48</sub>
C <sub>9</sub> -Alkane (br)	C <sub>9</sub> H <sub>20</sub>	<i>n</i> -Heneicosane	C <sub>21</sub> H <sub>44</sub>
<i>o</i> -Xylene	C <sub>8</sub> H <sub>10</sub>	<i>n</i> -Docosane	C <sub>22</sub> H <sub>46</sub>
<i>n</i> -Nonane	C <sub>9</sub> H <sub>20</sub>	4,8,12,16-Tetramethylheneicosane	C <sub>25</sub> H <sub>52</sub>
C <sub>3</sub> -Alkylbenzene	C <sub>9</sub> H <sub>12</sub>	<i>n</i> -Tricosane	C <sub>23</sub> H <sub>48</sub>
<i>n</i> -Propylcyclohexane	C <sub>9</sub> H <sub>18</sub>	<i>n</i> -Tetracosane	C <sub>24</sub> H <sub>50</sub>
C <sub>10</sub> -Cycloalkane	C <sub>10</sub> H <sub>20</sub>	<i>n</i> -Pentacosane	C <sub>25</sub> H <sub>52</sub>
<i>n</i> -Decane	C <sub>10</sub> H <sub>22</sub>	<i>n</i> -Hexacosane	C <sub>26</sub> H <sub>54</sub>
<i>n</i> -Butylcyclohexane	C <sub>10</sub> H <sub>20</sub>	<i>n</i> -Heptacosane	C <sub>27</sub> H <sub>56</sub>
C <sub>4</sub> -Alkylbenzene	C <sub>10</sub> H <sub>14</sub>	<i>n</i> -Octacosane	C <sub>28</sub> H <sub>58</sub>
C <sub>11</sub> -Cycloalkane	C <sub>11</sub> H <sub>22</sub>	<i>n</i> -Nonacosane	C <sub>29</sub> H <sub>60</sub>
C <sub>11</sub> -Alkane (br)	C <sub>11</sub> H <sub>24</sub>		
<i>n</i> -Undecane	C <sub>11</sub> H <sub>24</sub>		

\* br = branched.

A representative FID gas chromatogram on SE-30 column is shown in Fig. 8. Table I lists peaks identified by GC-MS. C<sub>10</sub> and C<sub>11</sub> hydrocarbons are the major components present, but in addition, branched alkanes, cycloalkanes, and alkylbenzenes were identified.

The chromatographic pattern of these samples is similar to but more complex than those previously found in quartz samples with oil inclusions<sup>1,2</sup>. The main difference is that the quartz sample contained *n*-C<sub>17</sub> hydrocarbons as the major component, while the fluorite samples analyzed in this work contained *n*-C<sub>10</sub>, and *n*-C<sub>11</sub> hydrocarbons as the major components. Also *n*-C<sub>4</sub> to *n*-C<sub>10</sub> were detected in the fluorite sample, but not sought for in the quartz sample. Probably, they were present but were lost during the analysis procedure used in that work.

In general, the volatile organic mixture present in these samples is similar to crude oil, but its composition is simpler. The origin of these organic substances is

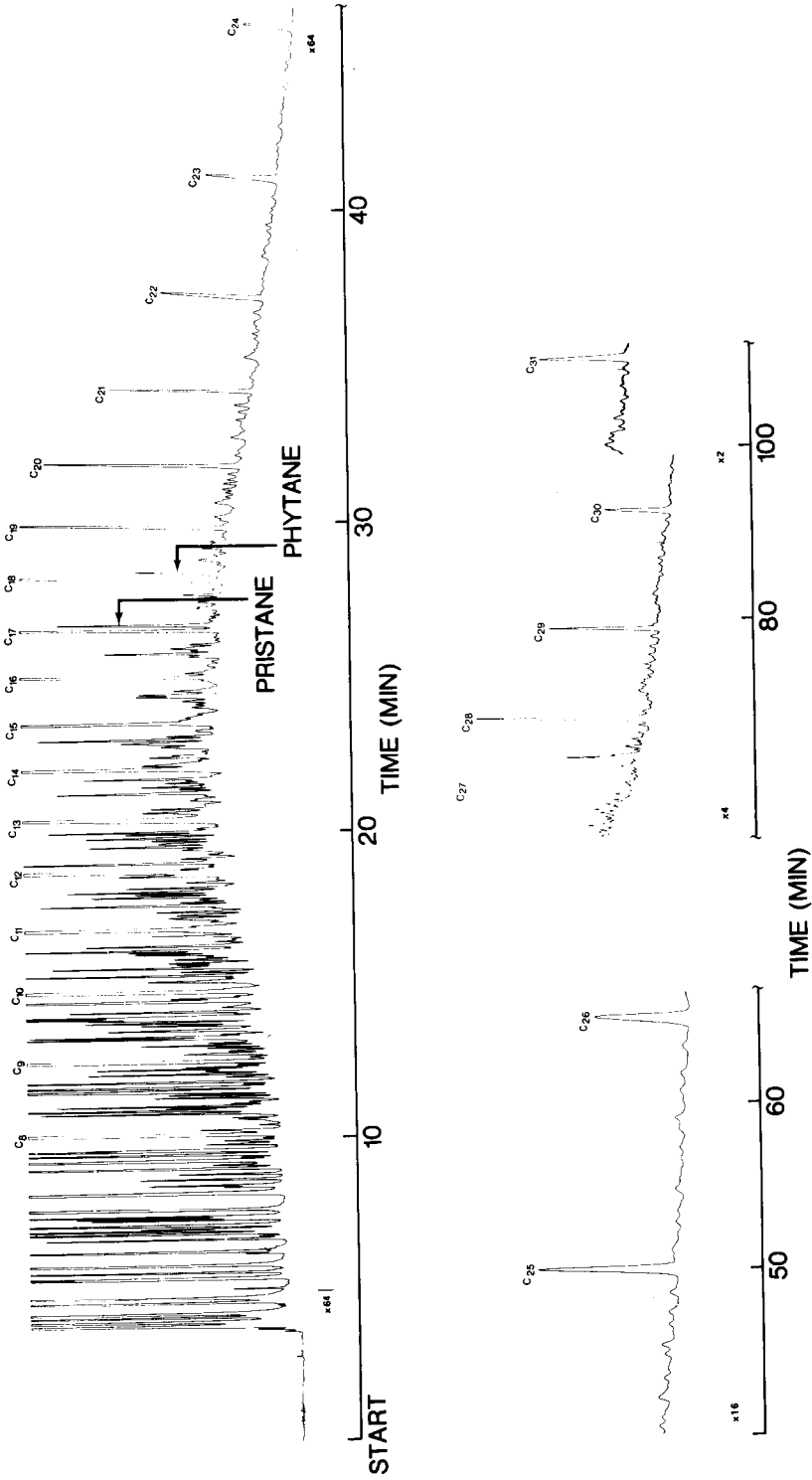


Fig. 8. FID gas chromatogram of a yellow-brown oil inclusion from fluorite sample.

believed to be biological<sup>12</sup>. Details about the origin of the oil droplets, how they were trapped, and variations in the composition of different samples will be the subject of a future report.

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