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Carbon and Stable Carbon Isotopes in  
Mantle Derived Material

by

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## ABSTRACT

In this investigation, three possible forms of carbon were identified in mantle-derived material: volatile carbon (methane and carbon dioxide), residual carbon of uncertain location, and carbonate carbon. Volatiles were separated by vacuum crushing, the residuals and total carbon by vacuum fusion, and carbonate carbon by acid evolution.

Isotopic analyses of the evolved gases indicate that the residual carbon has a carbon isotope value of approximately -15‰ to -20‰, the volatile carbon gas has a value of less than -21‰, and the carbonate about -6.8‰, all values being relative to PDB.

The different isotopic values displayed by the separate forms of carbon indicate that there are several forms of carbon in the mantle. Carbon as a volatile phase may be of importance in the magmatic and intrusive processes of mantle material upward into the crust.

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## Table of Contents

Introduction	1
Field Work	4
Petrographic Analysis	9
Analytical Procedures	
Sample Preparation	12
Volatile Carbon Extraction	14
Fusion Extraction	18
Other Extraction Methods	21
Isotopic Determinations	22
Results and Conclusions	
Volatiles	26
Residuals	28
Phases of Carbon in the Mantle	30
General Conclusions	31
Appendix	
Petrographic Descriptions	33
Detailed Sample Preparation	38
Detailed Extraction Procedures	40
Bibliography	47

## INTRODUCTION

This study evaluates the forms of carbon in the mantle and their isotopic ratios as found in ultramafic xenoliths in kimberlites and basalts. By experimentally separating the different forms of carbon, volatile and residual, and then by analyzing them isotopically, differences or similarities of various types of xenoliths can be established. These differences may then be used to establish relationships between the mantle carbon and carbon in other parts of the earth.

Carbon in the mantle may occur in a variety of forms. Diamond, a high pressure form of carbon, is found in kimberlites, ultramafic intrusions interpreted as being of very deep origin (Dawson, 1972; Frick, 1972). Graphite may also account for part of the carbon in the mantle, possibly as fine particles in and around grains of other minerals. Carbonate appears to be a primary constituent in some inclusions in basalts (O'Neil et al, 1970), but thermodynamic relations seem to preclude it as a primary form in the deeper parts of the mantle (French, 1966; Skippen, 1971). Carbides may also occur in the mantle, but they would more likely be found at greater depths under low oxygen fugacities; the carbides found in meteorites suggest this association (Brett, 1967). However, carbides have been reported in certain kimberlites (Dawson, 1972).

In recent years, work has been done on defining and identifying mantle rocks at the surface. One source of mantle rocks at the surface is the tectonically implaced slices of oceanic lithosphere, mantle,

and crust, such as the Troodos and the Vourinos ultramafic complexes. Although these ultramafics are interpreted to be mantle rocks (Moore, 1969; Moore and Vine, 1971), they are often equilibrated under near surface conditions. The ideal source for mantle material would sample at great depths, and then transport the material rapidly to the surface, before any alteration or re-equilibration of the sample could occur.

This set of conditions seems to be most closely approximated in some basaltic eruptive sequences and kimberlites with included ultramafic xenoliths. Jackson and Wright (1970) proposed a type-to-depth correlation for inclusions in certain Hawaiian basaltic volcanics. They have shown that there seems to be a zonation downward of the mantle rock types, dunite being the shallowest and garnet peridotite the deepest. White (1966) did extensive investigation of the xenoliths in a wide variety of Hawaiian basalts and suggested similar conclusions. Similar type-to-depth correlations have also been suggested in kimberlite pipe areas (Dawson, 1972; Frick, 1972; McGetchin and Silver, 1972) around the world. As to the occurrence of carbon in these type of rocks, only limited investigation has been conducted. Fuex (1970) conducted a survey of carbon in igneous rocks to define some of the problems and solutions that might be expected in further work.

The materials used in this study are xenoliths from both basalts and kimberlites. In basalt, xenolithic inclusions are generally divided into three categories (after Jackson and Wright, 1970): dunite, hercynite, and garnet peridotite, in order of increasing depth. In the

SAMPLE LOCALITIES

H-1	Dunite	Hualalai 1801 Flow, Hawaii
KH-1	Peridotite	Kilbourne's Hole New Mexico
BP-1	Olivine	Buell Park, Arizona
GK-1	Dunite	Green Knobs, New Mexico
GK-2	"	"
V-3	Dunite	Vulcan's Throne, Arizona
PC-2	Peridotite	Peridot Cove, Arizona
PC-3	"	"
PC-4	"	"
PC-6	"	"
PC-7	"	"
PF-1	Vein quartz	Packsaddle Formation Llano, Texas
PF-2	"	"
PF-3	"	"
Pl.F-1	"	Palmetto Formation near Ash Meadows, Nevada

Table 1

areas where they occur, the dunite nodules are the most abundant and the eclogite nodules the least. As much as possible, dunite or olivine rich samples were used in this study to reduce possible variation in chemistry caused by the presence of other minerals. The study includes a sample of dunite from Hualalai 1801 lava flow in Hawaii, which consists mainly of magnesian olivine and only minor pyroxene and accessories. Other basalt xenoliths studied were lherzolites from Kilbourne Hole, New Mexico, Peridot Cove, Arizona, and Vulcan's Throne, Arizona. The inclusions from kimberlites were collected on the Navajo Indian Reservation in the Four Corners area of Arizona and New Mexico. These samples consisted of relatively fresh dunite nodules and loose grains of olivine and garnet. The loose olivine and garnet grains have been variously interpreted as being disaggregation products from eclogite nodules, the kimberlite itself, or both (Frick, 1972; Watson and Morton, 1969; McGetchin and Silver, 1970).



## FIELD WORK

Kimberlite occurrences are rare throughout the world, but they are remarkably uniform in their characteristics. They are a fine ground-mass of serpentine, carbonates, olivine, pyroxene, garnet, and accessories with xenocrysts of olivine altered to some degree (Williams, Turner and Gilbert, 1954). The matrix of the kimberlites of the Navajo Reservation have typically euhedral to subhedral altered olivine xenocrysts and abundant lithic fragments in a ground mass of predominately very fine grained serpentine, with minor very fine grained carbonate and opaques. The kimberlite localities of interest to this study in the Four Corners area of the Navajo Indian Reservation are Garnet Ridge, Buell Park, and Green Knobs. Garnet Ridge, in the extreme northeast corner of Arizona, is on the north-south structural trend of the Comb Ridge monocline. This structure seems to be associated with extremely deep faulting and possible crustal weakness (McGetchin and Silver, 1972). On the same trend are several similar diatremes to the north, Mule Ear and Moses Rock pipes. Buell Park and Green Knobs are kimberlite pipes located on the Defiance uplift to the north of Gallup, New Mexico.

The kimberlites of this area intrude into the Cutler formation, reddish sandstones of Permian age. These kimberlites, and related intrusives, have been dated (Naeser, 1971) at about 31 million years, using fission track annealing data from accessory minerals in xenoliths. The presence of xenoliths of Mancos shale indicates an age younger

than late Cretaceous (Malde and Thaden, 1963).

The kimberlites in this area show relatively sharp contacts with the rock into which they intrude. There is no evidence of thermal metamorphism or alteration of the sandstone wall rock, but there is minor bleaching of included shale fragments. The temperature of intrusion of kimberlite diatremes in this area have been estimated from fission track annealing temperatures of apatite and sphene to be between 300° and 500° C (Naeser and Stuart-Alexander, 1969). This low temperature would account for the lack of alteration of the wall rock, but with such low temperatures, the mechanism of intrusion is highly speculative. However, according to Dawson (1972) this low temperature intrusion is only characteristic of "diatreme-facies kimberlite," brecciated and fragmental material resulting from rapid expansion of solubilized gases such as carbon dioxide, with a more typical magmatic intrusion at greater depths. This mechanism for explosive volcanism has been investigated by Bennet (1971), who concluded that the velocities associated with such intrusive mechanisms may be on the order of the speed of sound with accompanying extremely high gas pressures. Such pressures and speeds would provide a mechanism not only for intrusion, but also for intense brecciation and rounding of included rock fragments, as are found in kimberlites in this area. This rapid release of pressure in the intrusive material would also be accompanied by adiabatic cooling, and the final result would be an intrusion at low temperatures, with numerous xenoliths. In all of the diatremes in the area, the strata surrounding the intrusions show little sign of deformation as a result of intrusion; instead, fragmentation of country

rock supplies the abundant xenoliths found in the intrusive body. This lack of chemical and thermal metamorphism, and abundant evidence of mechanical fracture of the kimberlite breccia, may indicate that the process for intrusion was one more nearly related to boring than to other, more quiescent, forms of intrusion.

All of the occurrences of kimberlite in this study show inclusion of the wall rock into the kimberlite as xenoliths. Garnet Ridge xenoliths represent the different rock types through which the kimberlitic material passed during intrusion. The rock types vary from igneous and high grade metamorphic rocks representing the lower crust and upper mantle to sedimentary types representing stratigraphically higher sequences that were incorporated into the intrusive body and settled downward. The number of inclusions of a given rock type is generally inversely proportional to the distance through which it was transported due to dilution by intervening rock types. That is, the sedimentary types that are stratigraphically very close to the present level of excavation are extremely numerous, and the inclusions representing the mantle are extremely rare. In fact, no inclusions that can be unequivocally identified as deep mantle products were collected in this particular study, although dunite nodules representing the upper mantle (as defined by Jackson and Wright, 1970) were collected from Green Knobs, New Mexico. There also seems to be a morphological relationship between the type of inclusion and the extent of upward transport. The rocks that are from the immediate stratigraphic units are large, blocky, and angular, showing no signs of mechanical abrasion. The rocks that are interpreted as being of mantle origin are generally

less than five centimeters in diameter and show high degrees of rounding and in some cases extreme polishing (Watson and Morton, 1969), indications of transport.

The balance of samples used in this study are from basaltic localities. The characteristics of these nodules may be related to Jackson's rough zonation of the upper mantle and the sampling of these regions by the host basalt, similar to the deep sampling of kimberlites. Previous work has been done on some of these localities, and it is for this reason, partly, that these particular sites were considered. The Hawaiian sample from the 1801 flow of Hualalai has been considered by Roedder (1965), White (1966), and Gramlich and Naughton (1972). This sample, a magnesian olivine dunite nodule, showing an abundance of gaseous and fluid filled inclusions, was received from D.W. Peterson at the U.S.G.S. Volcano Observatory in Hawaii.

Lherzolithic samples from several volcanic areas in Arizona and New Mexico were used: Peridot Cove in the southern part of Arizona, Vulcan's Throne in northern Arizona, and Kilbourne's Hole in southern New Mexico. All of these nodules are predominately forsteritic olivine, with lesser amounts of predominately clinopyroxene and minor orthopyroxene, spinel and opaques. They are all fresh and unaltered and show very sharp contacts with the surrounding basalt where the basalt is still in contact with the nodule. Indeed, some of the nodules show flat surfaces in contact with the basalt, possibly a mechanical fracture surface. Microscopic analysis indicates some gradation across the contact, but it appears to be mechanical rather than chemical alteration. Surrounding many of these nodules that are still in the

including basalt is a region of extreme vesiculation, which may be due to primary gas escaping from the nodule into the basalt; the basalt shows very little vesiculation away from the contact. This indicates that the xenolith's place of origin was extremely gas-rich in comparison with the host basalt and that the nodules were included and transported to lower pressure regions too fast for the gas to distribute or mix away from the nodule border. Such rapid transport also precludes the chance for alteration of the nodule by the liquid. The out-gassing of the nodule may also protect the nodule from alteration while in contact with the liquid basalt since gas escaping from the nodule acts as a barrier which the contaminating melt cannot cross.

## PETROGRAPHIC ANALYSIS

The nodules from basalts that were used in this study are of two general types: lherzolites, consisting predominately of olivine and lesser amounts of orthopyroxenes and clinopyroxenes with accessory amounts of spinel and opaques; and dunites, composed predominately of olivine. Within a sample locality the samples are surprisingly uniform in appearance and mineralogy. This is illustrated best by the suite from Peridot Cove, Arizona (see Appendix, Petrographic Descriptions).

Also, from locality to locality, where the included nodules are lherzolites, there is a surprising similarity. Many of the samples show a preferred morphological orientation of the larger olivine grains as well as kink banding and undulatory extinction. The smaller, rather equant, grains of olivine do not share these characteristics, possibly indicating that there has been recrystallization of the larger grains to the smaller. Many lherzolite samples also exhibit rather common examples of triple junction points between olivine grains, also indicating the process of recrystallization. There are occasional gas inclusions in the larger olivines that appear to be primary, indicating that the recrystallization may not have taken place at a stage much later than that of initial crystallization. The presence of recrystallization and of strain features in the individual mineral grains and slight foliation may indicate mantle fabric (Kushiro, 1972).

Xenoliths from kimberlites, on the other hand, show a wide variety

of rock types. The two samples used in this study, dunites from the Green Knobs pipe in New Mexico are very similar. They are both partially altered olivine nodules, with some optically discernable carbonate in the serpentine.

During the petrographic analysis of these samples, particular attention was given to the presence or absence of gaseous inclusions, and the nature of their occurrence. Roedder (1965) did considerable optical and physical analysis of inclusions in similar rocks. According to Roedder, the contents of these inclusions are samples of the volatile phase of the magmatic or metamorphic system at the time the mantle rocks were crystallized. The inclusions generally take the form of spherical bubbles, solitary if primary, and in planes or trains if secondary. Primary inclusions are formed simultaneously with crystallization by the inclusion of a fluid droplet or a gas bubble adhering to the growth surface into the crystal. Secondary inclusions are formed when there is a fracture in the crystal which then heals, trapping any volatile components of the system (Roedder, 1962). By the shape of the secondary bubbles, the extent of healing can be ascertained, the more nearly spherical the inclusion, the more complete the healing process. In the extensive petrographic study of dunites from Hawaii and other localities, Roedder deduced from freezing point and vaporization point data that the most common gaseous and fluid components are  $H_2O$  and  $CO_2$  (Roedder, 1972). The only sample in this study that showed abundant inclusions was the Hualalai 1801 dunite nodule, composing no more than one per cent of the rock by volume. Of the gaseous and fluid inclusions, the vast majority of the inclusions

were secondary. In some instances, two immiscible liquid phases could be distinguished, as well as a bubble of vapor. The vapor bubble often showed distinct Brownian motion which can be influenced by monitoring the amount of infrared in the illuminating light with filters.

The primary inclusions, although uncommon, indicate that CO<sub>2</sub> and water were components of the system at the time of crystallization of the minerals. The presence of fluid CO<sub>2</sub> inclusions indicates that the gas was above its critical pressure, existing as an immiscible liquid and possibly a component of the silicate system. This small amount of volatile component could affect the melting characteristics of the silicate to a great degree.

The remainder of the samples show only occasional gaseous inclusions, accounting for much less than one per cent of the rock. In Peridot Cove and Kilbourne Hole lherzolites, the inclusions are generally in the olivine and appear to be of primary origin. Gaseous inclusions were not detected in the Green Knobs samples at all because the alteration of the olivine to serpentine eliminated any that may have existed. Most of the inclusions are on the order of several microns in diameter and in all but the Hawaiian dunite were uncommon.

Several samples not directly related to the primary goal of this study were used as stock material to develop the different procedures relating to the identification and extraction of volatiles. Several samples of vein quartz were investigated in the same way as the ultramafic nodules, showing the same general relationships of primary and secondary inclusions in the development of the quartz.



## ANALYTICAL PROCEDURES

### Sample Preparation

Since a major objective of this study was to investigate the presence of carbon in very low concentrations, the problem of contamination was of utmost importance. The greatest care was taken to prevent possible contact even of the primary field specimen with any unduly organic contamination. Further, a cleaning procedure was developed to minimize the possibility of adding carbon to the samples.

Since the samples were rather friable, the rock was reduced to millimeter size grains and interior portions were selected. Outer portions of the nodules were removed with limited physical contact since they were more likely to be contaminated. This reduction was followed by a primary rinse with water to remove any obvious surface dirt or other contaminants.

Following the rinse, the sample was soaked overnight in four normal hydrochloric acid. This soaking assured removal of any secondary carbonate that might have been deposited within the permeable samples by ground water or surface processes. After another thorough rinsing with water, the sample was then subjected to an oxidation procedure to remove any organic contamination on the surfaces of the grains. The oxidizing solution consisted of one part of a saturated solution of sulfuric acid and potassium dichromate and three parts distilled water, which was left in contact with the sample overnight. The solution assured removal of any surface carbon since silicates

react slowly in sulfuric acid to form a gel. Following this rather vigorous treatment, the samples were rinsed to neutrality with distilled water to remove the oxidizing solution. After the final rinse, the samples were heated at 100°C to dryness overnight.

Throughout this cleaning procedure, the samples were maintained in their respective containers, so that the containers would receive the same treatment as the samples. As well as assuring a clean container, this method prevents any contamination of the sample from its container. Following cleaning procedures, any remaining large fragments were disaggregated. The simply disaggregated sample was used for total carbon fusion and vacuum crushing or as the stock sample, finely pulverized, for non-volatile carbon fusion and carbon extraction. This pulverization was conducted in a high alumina porcelain Spex milling vial, which had undergone a similar cleaning procedure to that for the samples. Similar material was analyzed by Fuex (1970) for carbon contamination to samples and was found to be very low.

The above cleaning procedure avoids contamination from contact with the obvious sources of carbon, but one additional source might also cause contamination of the samples, especially of finely crushed samples. The adsorption of gases on the surface of the finely divided material could contribute CO<sub>2</sub> from the atmosphere. This phenomenon was observed when samples of extremely inclusion-rich rock were crushed, since the released gases were adsorbed onto the extremely active surface of the powder. Heating of the sample overnight in the same manner as the initial drying removed both the adsorbed water and

excess gases adsorbed onto the surface. However, there will still be adsorption of atmospheric gases; such adsorption of atmospheric carbon dioxide may adversely affect the determination of subsequent amounts and isotopic distributions in the sample.

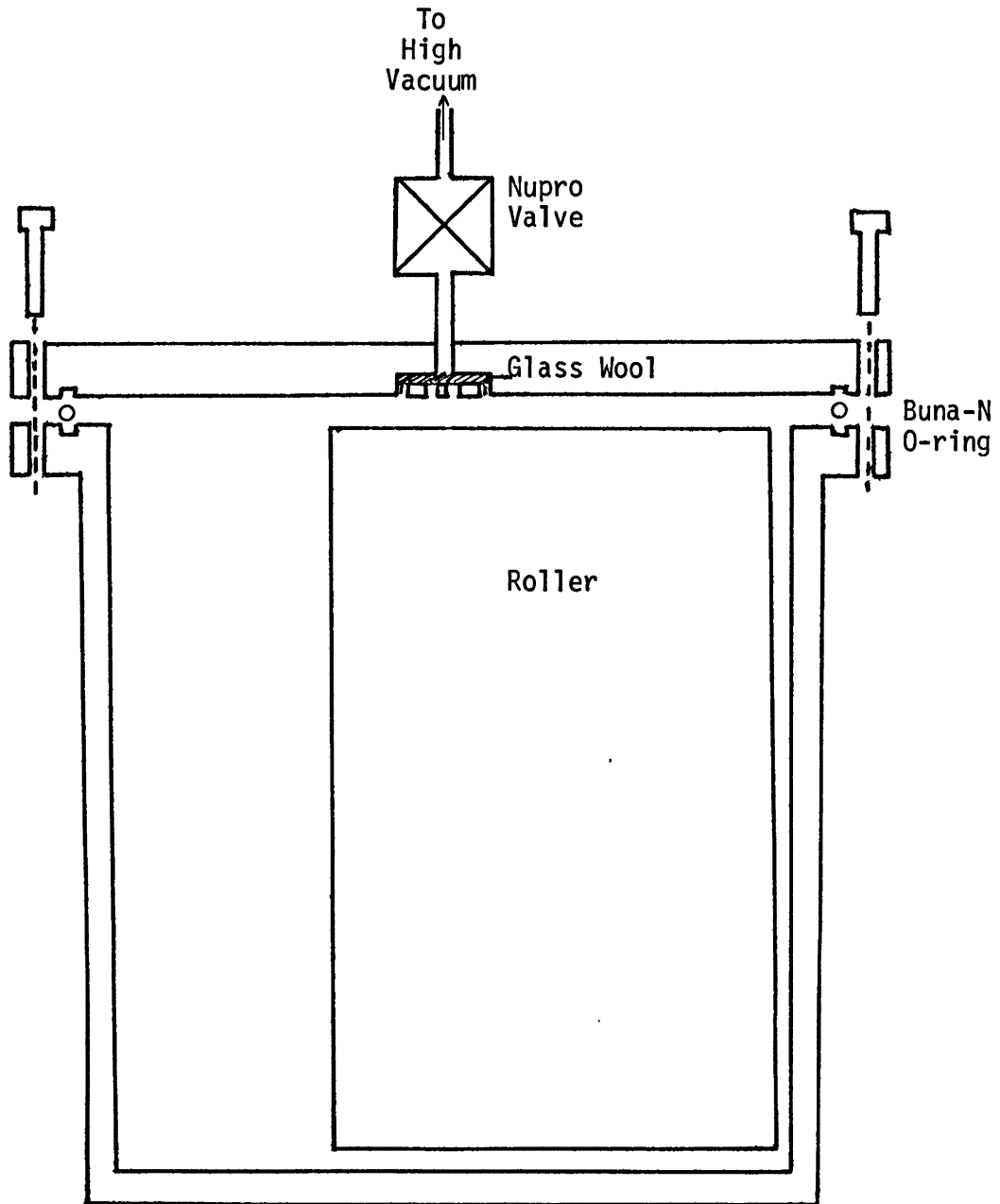
### Volatile Carbon Extraction

The extraction of volatile forms of carbon, that is, carbon as one of its gases, requires only physical processing. The process used in this study was one of crushing under vacuum (Goguel, 1963), and analyzing the released gases by gas chromatography. The instrument used was a Perkin-Elmer 990 gas chromatograph with thermal conductivity detectors. The sensitivity of the detectors and the resolution of the columns allowed analysis of samples of gas less than one micro-mole in size.

The actual crushing device used for the release of the volatile phases of carbon (Fig.1 ) is a vacuum rolling mill. The container was constructed of stainless steel and flanged to accept a Buna-N "O" ring. The sample was crushed by means of a cylinder of stainless steel whose diameter is slightly greater than the radius of the crusher body. In this way, there was a gentle crushing instead of an impact type of crushing action. This should prevent the production of carbon dioxide from high energy impact as observed by Goguel (1963) in ball mill experiments on calcite.

The construction and valving of the vacuum crusher is such that the assembled crusher with sample can be removed from the high vacuum line after evacuation and rolled on a separate piece of equipment.

# VACUUM CRUSHER



All Construction  
Stainless Steel

Fig. 1

Although this procedure has inherent disadvantages, such as increased possibility of an atmospheric leak through a valve or seal, there seems to be no alternative to this technique for processing large samples. A large amount of sample is necessary to recover enough included gas to analyze isotopically; much smaller samples are required to analyze for the included gas species only.

The procedure was standardized to a crushing time of six hours. During a crushing period of this length, most of the sample was reduced to a grain size less than 105 microns. The finer the sample is crushed, the greater the number of inclusions is broken, releasing more of the included volatiles. The more volatiles released, the more representative the sample will be of the residual carbon.

After crushing the sample, part of the released gas adsorbs onto the increased surface area of the sample. To facilitate the removal of the sample gas from the crusher in preparation for analysis, the crusher may be heated. This heating is very effective at driving off the gases, but temperatures that are effective in degassing the adsorbed gases also cause degassing of organic gases from the Buna-N "O" ring. For this reasons, the gas is extracted from the vessel at room temperature. By repeating the extraction of the sample a number of times, with a waiting period for the adsorbed gas to degas from the crushed material, the sample gas only is collected.

Another source of possible error that was investigated was the metal of the crusher as a source of methane and hydrogen. To check this source, numerous blank runs were conducted: on the empty crusher, a sample that had been previously crushed, and on soft glass. It was

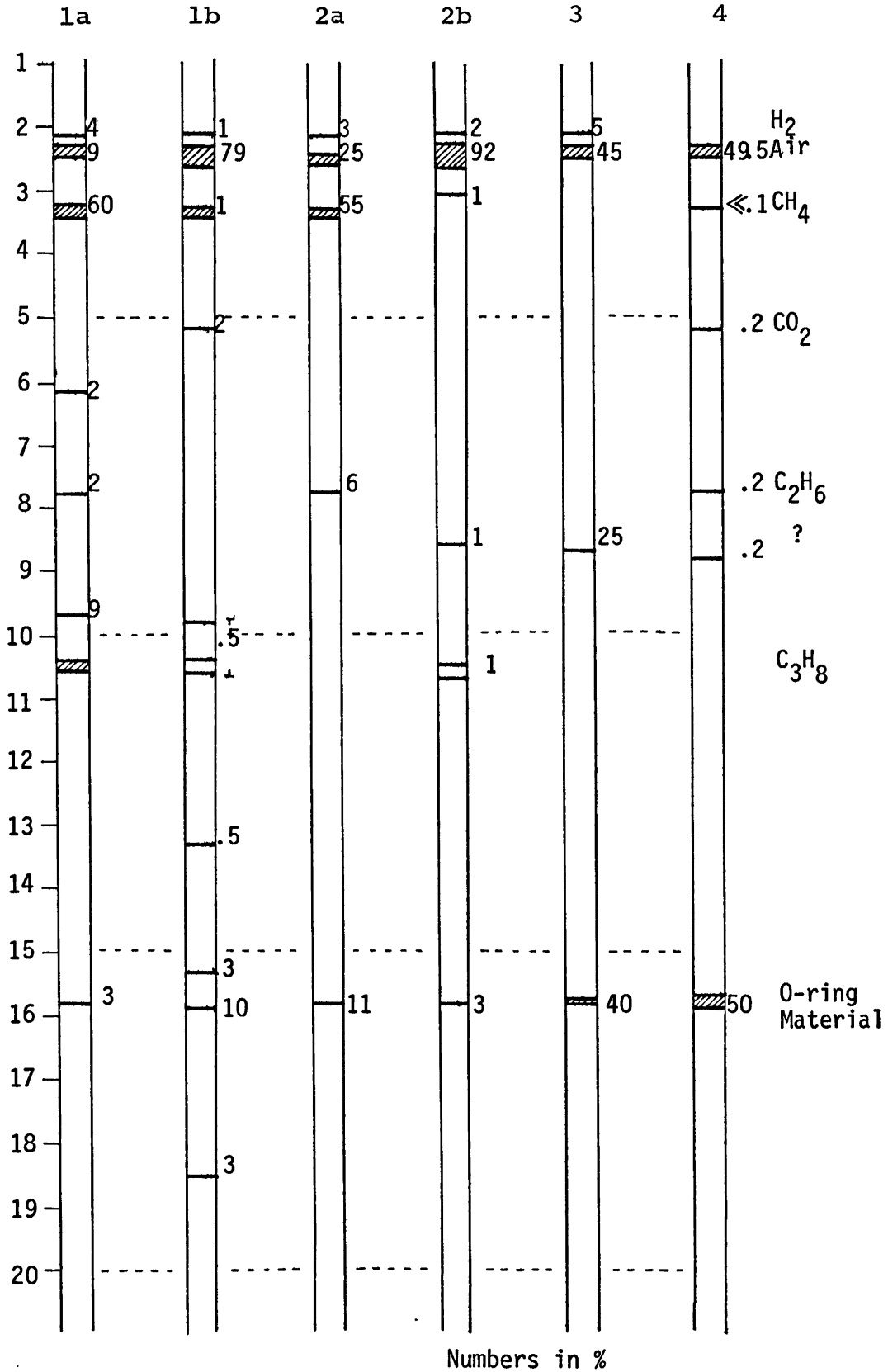
determined that the metal could contribute gas if there was metal to metal contact, as in the empty crusher, but when the soft glass (presumably gasless) was crushed, the gases observed in the empty crusher were absent. From Figure 2, depicting the comparison of the chromatograms of the blank runs, it can be seen that hydrogen may be contributed by the metal but that methane is not, since it was not detected in the glass blank.

The extraction line used for removing the sample gas from the crusher was also used for measurement of the amount of gas and for injection of the gas into the gas chromatograph (Fig. 3). The apparatus consisted of an automatic Toepler pump that removed the gas from the crusher, then either compressed the gas into a calibrated volume for pressure-volume measurement or into the sample loop for injection in the chromatograph. The measurement of the pressure was accomplished on a manometer which was the valveless intake of the Toepler pump. The volume of the loop was precisely determined by filling it with mercury and calculating the volume from the weight and density of the mercury. Simultaneous with compression of the gas into the volume, the mercury of the Toepler pump also rose into the lengthened intake arm, thus acting as a manometer. By knowing the pressure of the gas in a known volume (5.56 ml.; 2.95  $\mu$  mol gas/cm. of pressure) at a known temperature, the amount of gas can be calculated.

After the pressure was measured, the gas was then injected into the gas chromatograph for analysis. The volume used for pressure-volume measurement was also the sample injection loop. This loop was

# CRUSHER BLANKS

## Background Determination



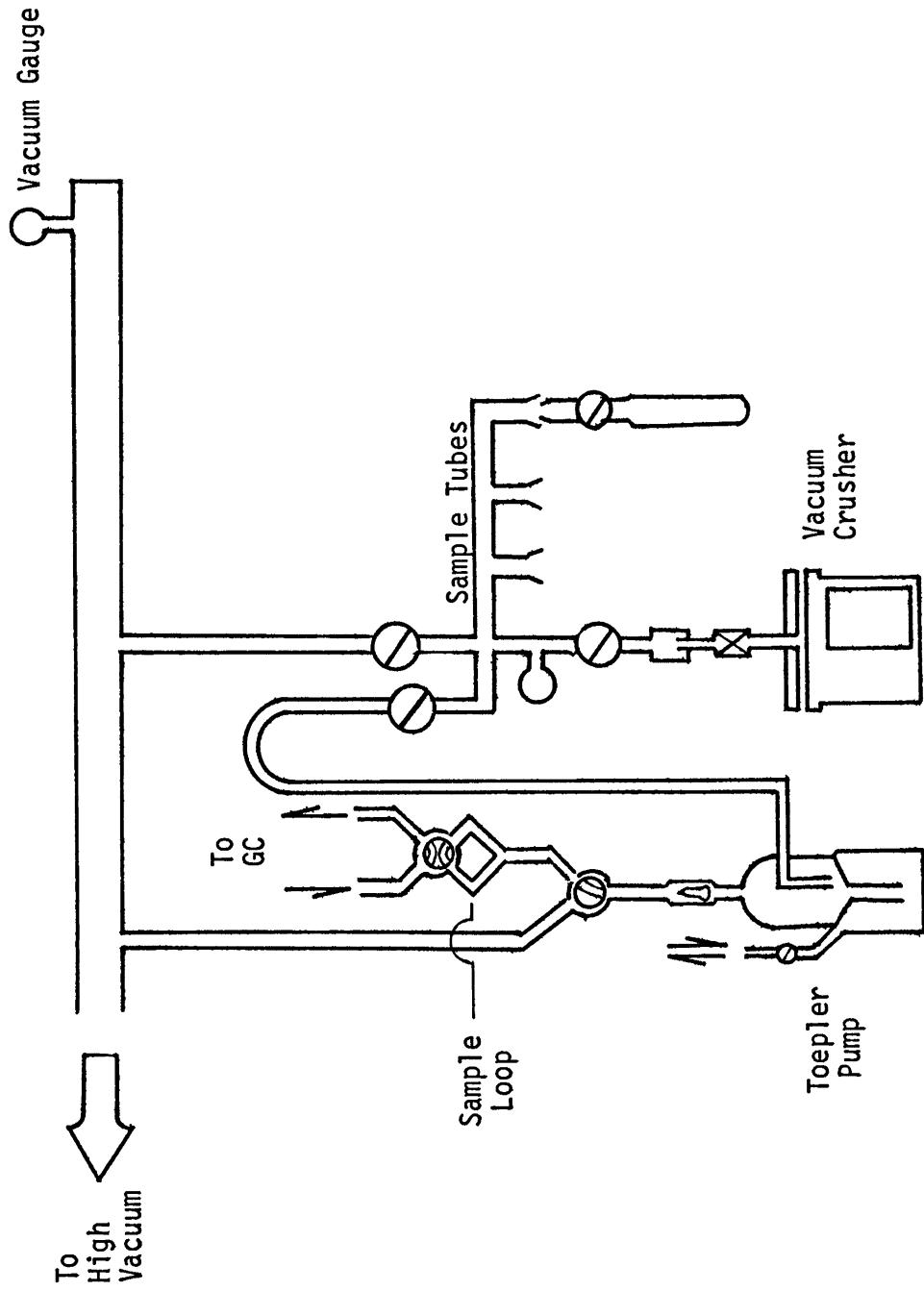
Numbers in %

Fig. 2

Fig. 2 explanation - Specifications on individual blank runs:

- 1) Crusher rolled empty
  - a) extracted without heating
  - b) followed by extraction with heating (about 80° c)
  
- 2) Crusher re-rolled empty, but not reopened before re-rolling
  - a) extracted without heating
  - b) followed by extraction with heating (about 80° c)
  
- 3) Crusher loaded with 78 grams of soft glass, extracted without heating
  
- 4) O-ring material heated to about 80° c





VOLATILE EXTRACTION SYSTEM

Fig. 3

separated from the carrier gas stream of the gas chromatograph by a four-way valve. By turning the four-way valve, the carrier gas was diverted through the loop, injecting the sample into the gas chromatograph as a compact slug of gas. In other words, no noticeable peak broadened or overlapped due to streaming out of the sample prior to arrival at the gas chromatograph inlet.

The columns on the chromatograph were eleven foot, three-sixteenths inch diameter copper coils packed with 80-100 mesh Porapak-Q packing material (Waters Associates). Helium was used as the carrier gas. The packing medium was a porous polymer bead that acted as both a liquid phase and a solid support phase. It was specifically effective in separating stable gases and low atomic weight organic compounds. The atmospheric gases are nitrogen, oxygen, carbon monoxide, argon, and carbon dioxide; the organic compounds are the alkanes and alkenes from one carbon to about five carbons. Although the Porapak-Q is efficient at resolving the organic gases and carbon dioxide, it is rather ineffective at resolving the stable gases. Oxygen is resolved as a distinct shoulder on the nitrogen peak and can be used for calculations satisfactorily, but argon and carbon monoxide are both totally unresolved and buried under the nitrogen peak. The failure to resolve argon and carbon monoxide from nitrogen is the major disadvantage of using this polymer packing material, but the resolution of the organic gases and carbon dioxide was considered of prime importance in this study.

Gas chromatography is not a positive identification technique, but a relative one. That is, it can indicate the presence of more

than one gas species, but cannot identify the gases as to their species. It is based on the phenomenon that different gases have different solvent-solute relationships to the column packing material. If two gases have very similar adsorption or solution characteristics, a given packing material or liquid phase may not resolve them. Since the process of separation is not specific, the columns must be standardized for different gases. This was done by injecting known gases into the chromatograph and noting the retention time or other retention parameters. In this study, the retention time of the gases at a calibrated flow rate and with temperature programming was used for identification purposes. A standardized temperature and flow rate was used for all measurements. Amounts of the component gases were calculated by the relative areas of the peaks and the injected samples.

### Fusion Extraction

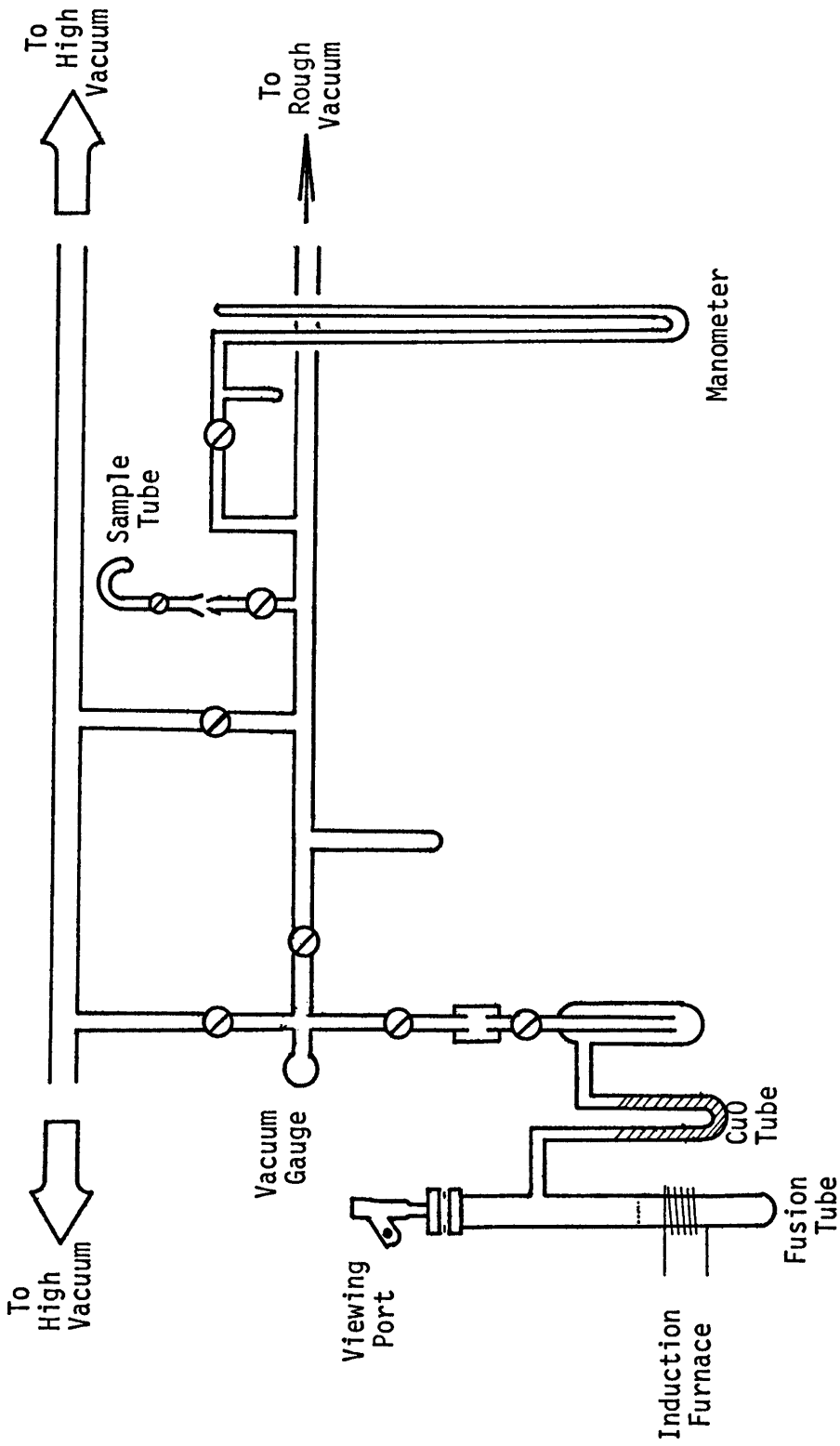
The method for extraction of all forms of carbon is based on fusion of the sample under a low pressure oxygen buffered atmosphere. The intent of this facet of the study was to provide a total carbon value for the rock against which a mass balance of the separate types of carbon could be compared.

The advantage of this type of analysis for total carbon over such methods as combustion is that the fusion extraction of carbon is more complete and, thus, with thorough fusion, should not be surface related. Combustion has been shown to be incomplete in its yield of carbon from igneous rocks (Fuex, 1970). Repetitive combustion of

igneous rocks in the study by Fuex showed that additional amounts of carbon dioxide were produced with successive combustion treatments. On the other hand, sample fusion permits exposure to high temperature oxidizing condition with the resulting carbon gases representative of the total carbon content. At the high temperature of fusion, the gases may be, initially, a mixture of carbon monoxide and carbon dioxide. The contact of the gases with heated copper oxide after the fusion process converts any reduced carbon gas to carbon dioxide. Refusion of a previously fused sample yields no additional gas, an improvement on the combustion method of extraction of carbon from igneous samples.

Fusion also assures sampling of all forms of carbon. By fusing the sample, both non-volatile carbon in the form of graphite, carbonate or other solid form and the included volatile carbon is extracted. Roedder (1965) demonstrated that gaseous and fluid inclusions in olivine were not ruptured throughout the rock at temperatures approaching those of fusion. In this respect the fusion of the samples is a much more thorough sampling method than combustion. More representative sampling occurs when the large fragments of inclusion-rich sample are analyzed for total carbon by combustion.

The extraction line consists essentially of a vacuum-tight quartz envelope in which the sample is fused (Fig.4 ). The sample is held in a molybdenum crucible and suspended in the fusion region by a wire of the same material. Prior to loading the sample, the molybdenum crucible is heated under vacuum and with oxygen to clean the crucible of any organic contamination. After the sample is loaded and the



FUSION APPARATUS

Fig. 4

crucible assembly is suspended in the furnace, the assembly is heated to degas atmospheric gases and water at several hundred degrees Centigrade. The heating source for both the pretreatment and the fusion is an induction furnace. The fusion of the sample is accomplished by raising the power of the induction furnace slowly to maximum and then maintained at fusion temperature for twenty minutes. During this operation, a copper oxide section is heated to supply a low oxygen pressure and to afford a catalytic surface for oxidation of reduced carbon gases. The gases evolved from the sample and converted to carbon dioxide are trapped cryogenically and purified. The sample is then transferred to a manometer for measurement and thence to a sample tube for introduction to the mass spectrometer, the manometer having been calibrated for pressure of sample versus the absolute amount of gas.

With this method of extraction and handling of the gas sample there is the possibility of production of non-carbon gases, some of which have similar transfer characteristics to carbon dioxide. This would result not only in a fallacious amount of carbon from the sample, but also in contamination of the mass spectrometric values for the carbon isotopes, since some of these gases can have the same atomic weight as carbon dioxide. The most probable non-carbon gases that might cause contamination are sulfur and nitrogen oxides. These could be produced from sulphides in the case of sulfur and from included gases in the case of nitrogen. There have been some natural nitrides reported, but these are exceedingly rare. The similarity of cryogenic properties of carbon dioxide with these gases makes it

extremely difficult to separate the gases from one another. In this study, the occurrence of sources for contaminating gas is considered to be low and their contaminating factor very low.

For a given sample, two separate fusion extractions were conducted, the first consisting of fusing the whole rock. That is, the sample was extracted after only simple disaggregation of the rock to individual grains, and no further crushing. This is referred to as total fusion. This samples all of the forms of carbon, both volatile and non-volatile, and gives a value for the summation of the forms of carbon. The second fusion was done after the sample had been pulverized for an extended time in a high alumina Spex miller/mixer vial. This reduced the sample to a very fine grained size and ruptured the majority of the inclusions of gas or fluid. After drying overnight, this sample was then ready for extraction of the residual carbon components. This was referred to as the residual carbon value, both the carbonate and the non-carbonate forms being included.

#### Other Extraction Methods

Extraction of the carbonate carbon from the other types of non-volatile carbon was done by acid evolution, the treatment of the sample with acid to react with the carbonate and release carbon dioxide. The acid used was 100% phosphoric acid (anhydrous). Acid evolution was conducted on the finely powdered material prepared for the non-volatile fusion. The phosphoric acid is not so reactive that it is likely to attach any non-carbonate forms of carbon to any

appreciable extent. The evolved carbon dioxide can be transferred and measured in the same manner as the gas produced in the fusion portion of the analysis.

In addition to the above methods of extraction, the included gas sample, obtained by crushing, can be combusted to carbon dioxide, thus allowing the analysis of isotopic content of the carbon in the gas and fluid inclusions; this is referred to as the volatile carbon fraction. In developing the technique, gases extracted from milky variety vein quartz were combusted and analyzed. These samples proved to be by far the most gas rich samples encountered in the course of this study. To combust the gas sample, the gas was introduced into the standard combustion line and circulated over the hot copper oxide portion of the system to oxidize the carbon volatiles to carbon dioxide. The carbon dioxide was then measured and collected in the standard manner for introduction to the mass spectrometer.

### Isotopic Ratio Determinations

After the gases are in the form of carbon dioxide, they can be introduced into the ratio mass spectrometer for isotopic analysis. The mass spectrometer used was a Nier-McKinney type with a six-inch radius, 60° sector analyzer tube. This type of mass spectrometer has three separate ion beam collectors, which collect the three molecular weights of carbon dioxide. That is, molecular weights 44, 45, 46 are collected and the currents from the 44 and 46 mass beams compared to that of the 45 mass ion beam. This combination was used because the contributions of the two carbon isotopes is such that carbon 12



is mainly in the mass 44 and 46 beams and carbon 13 is in the 45 mass ion beam. This value for the sample is then compared with the like values for a standard gas to permit expression of the value of the sample in terms of the standard. That is

$$\delta^{13}\text{C}_{\text{sample}} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \times 1000$$

where  $(^{13}\text{C}/^{12}\text{C})$  are the ratios of isotopes of carbon in the respective gases and the final value is in parts per thousand (per mil, ‰).

The standard gas used in this study is a limestone supplied by the National Bureau of Standards, NBS #20 Solenhofen limestone. The standard gas is prepared by treating the limestone by the acid evolution extraction technique.

After analysis of the sample carbon dioxide against the standard gas, the value is corrected to be in terms of the widely used reference standard, the Peedee belemnite (PDB) carbonate. This correction of one standard to another reference standard is :

$$\delta^{13}\text{C}_{(x-A)} = \delta^{13}\text{C}_{(x-B)} + \delta^{13}\text{C}_{(B-A)} + \delta^{13}\text{C}_{(x-B)} \delta^{13}\text{C}_{(x-A)} \times 10^{-3}$$

where  $\delta^{13}\text{C}_{(x-A)}$ ,  $\delta^{13}\text{C}_{(x-B)}$  are values of the sample with respect to a working standard B and a reference standard A and  $\delta^{13}\text{C}_{(B-A)}$  is the value of B with respect to A (Wedepohl, 1969). In this way, the values of a sample compared against one working standard may be compared to those of another standard by the mutual conversion to a single reference, in this case PDB. This simplifies the comparison of data in that there is no need to convert to a number of standards when comparing data from different sources. Although there seems to be a very small

inaccuracy inherent to the commonly used conversion from standard to PDB, the error is very small and well within the experimental error.

The mass spectrometer used for this study was constructed in the Rice University Geology Department not only for carbon, but also for oxygen and hydrogen isotope analyses. Although the mass spectrometer is capable of a high order of precision, the precision of the sample preparation techniques are in no way comparable. This aspect of the study, the aspect of the analysis of the techniques of sample preparation themselves, is an important facet of the project.

Variations in the isotopic values of extracted carbon is most noticeable in the fusion technique. It was noted that what may seem to be identical samples and sample preparations are different in isotopic values of the extracted gas: minor differences in preparation can have perceptible effects on the final preparation of the sample gas. Therefore, once a routine for sample preparation is established, it should be adhered to without exception. Not only must the preparation routine itself be reproducible, but also all aspects of the supporting systems should be consistent from run to run. The single most variable aspect of the fusion preparation line is the induction furnace. There appears to have been transient differences in power output to the crucible from analysis to analysis. This aspect of the reproducibility of the fusion technique was only partially investigated. The amount of carbon in the sample itself may also affect the final precision of the extraction. The lower the concentration of carbon in the sample, the more efficient the extraction technique must be to extract out a representative sample of the carbon. High temperature extraction

techniques were used to increase the efficiency of the carbon extraction as compared to results from combustion techniques. Since isotopic fraction generally decreases with increasing temperature, then the higher temperature used for extraction should decrease any fractionation, so that even if extraction is not absolutely complete, the carbon extracted will be isotopically representative.

## RESULTS AND CONCLUSIONS

### Volatiles

In the samples used for this study, the most common gases released from inclusions were methane and hydrogen. This combination recurred in all samples except the inclusion-rich dunite from Hawaii. This extremely inclusion-rich sample had a preponderance of carbon dioxide as well as methane, hydrogen, and possibly a trace of ethane. The total yield of gas from this inclusion-rich sample was also the largest of any of the ultramafic samples. The Hawaiian dunite yielded 0.30 micromols of gas per gram of sample, opposed to approximately 0.03 micromols of gas per gram of sample for the most gas-rich of the lherzolites. The identification of carbon dioxide in the Hawaiian dunite agrees with the findings of Roedder (1965) for similar samples analyzed by heating and cooling stage microscope techniques.

In the volatile extraction of the Hawaiian dunite, the gas from the crushed sample was analyzed in two separate steps. The first aliquot was removed from the crusher while the crusher was at room temperature. This part of the sample proved to contain only a trace of carbon dioxide. The second portion of gas was produced after heating the crusher assembly to approximately 70° C for several hours. This portion of the gas extracted from the dunite was 95% carbon dioxide. This gas was adsorbed onto the crushed material and was degassed at slightly elevated temperature. This gas was not analyzed isotopically; the initial low yield of gas required analysis of the second portion

in the same manner for composition, and after the gas chromatographic analysis there was insufficient gas for isotopic analysis.

The remainder of the analyzed lherzolites contained gas amounts much lower than the Hawaiian dunite and well below the minimum amount of gas required for mass spectrometric analysis. Thus, the isotopic ratios of the gases could only be roughly estimated by mixing techniques, comparing the carbon isotope ratio of a known sample with the same sample spiked with the unknown.

Roedder (1965) roughly determined the pressure in the inclusions containing liquid carbon dioxide in Hawaiian dunite, and determined the pressure to be between 2500 and 5000 bars at the time of filling. At this high pressure, the amount of gas in the small number of inclusions, and at grain boundaries, could presumably have a discernable effect on the total carbon ratios. This effect is seen by comparing the isotopic ratios of the samples fused without volatiles with the ratios of samples fused for total carbon. Roughly speaking, the volatile carbon is therefore somewhat lighter than the residual carbon. This association can be seen most clearly in Figure 5, on samples H-1, KH-1, PC-2, and PC-4.

Sample PC-6 shows just the opposite relationship. In this sample, the volatile carbon seems to mix with the non-volatile carbon to cause the total carbon to be heavier than the residual carbon alone, but this single value may be random due to poor extraction or contamination.

Residual carbon, the carbon that is not removed by crushing, may assume the form of carbonate, or possibly very small grains of carbon compounds trapped in the structure of the minerals, as identifiable

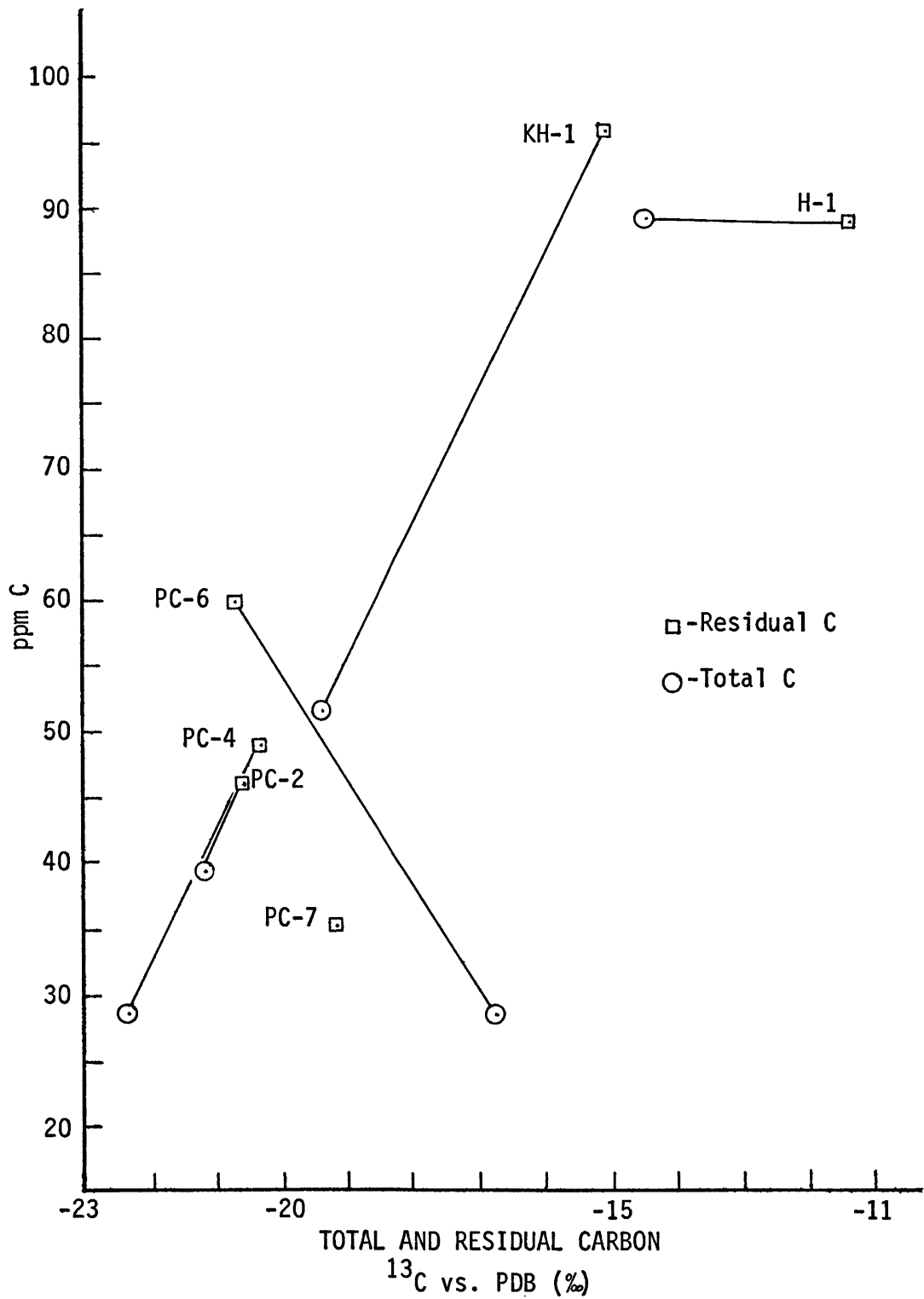


Fig. 5

VACUUM CRUSHING

Sample	Wt., gms.	Gas Species - in moles x 10 <sup>-6</sup>							ppm C	Notes
		H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	CO <sub>2</sub>	Total		
KH-1	94.00	.3	1.0					1.26		
KH-1	82.46	1.0	2.6					3.6		
KH-1	121.0	.1	.5					.53		
PC-2	79.4	.01	.1					.07		
H-1	100.0	.5	1.5	.1			28.3	30.3	3.5	
PF-1	29.28	5.1	105.2	.2	.1		80.5	191.1	60	H <sub>2</sub> O abundant*
PF-1	58.32	.1	33.4	2.6			70.8	107.8	21	H <sub>2</sub> O abundant
PF-2	40.05	1.2	2.0	.1	.2		30.2	33.7	10	H <sub>2</sub> O abundant
PF-3	71.19	5.2	1.7		1.4	4.8	64.5	77.6	15	H <sub>2</sub> O abundant
P1. F-1	57.75	3.1	1.3				123.6	128.0	21	H <sub>2</sub> O abundant
Blank, soft glass	77.2	trace						1		

\*By this method of extraction, any water released is condensed in Toepler pump.

carbon minerals, or as volatiles remaining after pulverization. However, in this study, no carbon minerals were identified in thin section. The presence of these forms of carbon is demonstrated strictly by the extraction methods, which leads to the conclusion that the residual carbon occurs as minute disseminated particles in the crystal grains at boundaries, and not as modal components.

### Residuals

The residual carbon can be separated into carbonate and non-carbonate carbon by acid extraction of the carbonate fraction. The residual carbon, other than carbonate carbon, is made up of microscopically undetectible forms of carbon possibly as volatiles at imperfections and not as bonded constituents of the structure. From the deduced range of the volatile carbon ( -21% vs. PDB), the values of the residual carbon was concluded to be heavier than about -21%, and from the carbonate values, the noncarbonate residual carbon is more negative than the -6.78% value for carbonates. Thus the different values for the different forms can very roughly be computed, although the calculations done more carefully would be meaningless. The number of determinations and the accuracy of the extraction techniques allow only the general trend of the values to be determined. With improved extraction methods and more determinations the specific types of carbon can be defined by their carbon isotopic ratio more exactly.

All of the samples extracted from carbonate showed its presence in varying amounts. Even the peridotite nodules from Peridot Cove that showed no alteration of the constituent minerals indicated the presence



of small amounts of carbonate, albeit quite low, 8 ppm., in the lowest value. The nodules of altered dunite from Green Knobs, New Mexico, showed the greatest amounts of carbonate, 127 and 344 ppm., for GK-1 and GK-2, respectively.

The volatile carbon, gases included in the grains of the nodules, are isotopically lighter than the total sample carbon. In other words, the values for the residual carbon are consistently heavier than the values for the total carbon. The values indicated for the volatiles are generally more negative than -21‰ (Fig.5).

Isotopically, the carbonate values are very similar to the carbonate carbon isotope values found by Fuex (1970) and others (Wedepohl, 1969). The average for the carbonate  $^{13}\text{C}/^{12}\text{C}$  versus PDB is -6.78‰. The total fusion values of the Green Knobs samples show influence of the carbonate carbon values. In other words, the samples with the more positive values in the carbonate carbon show more positive values in the fusion carbon values also. This carbonate influence is illustrated very markedly by the two Green Knobs samples: GK-1 has a total fusion value of -13.05‰ and a carbonate value of -4.99‰ and GK-2 has a total fusion value of -7.32 ‰ and a carbonate value of -6.19‰. Each of these two samples reflect the high concentration of carbonate contributing to the total carbon and their respective carbon isotope values. This carbonate may be primary carbonate, since it is neither identified in thin section analysis nor removed by the rather stringent cleaning process, designed to remove non-primary carbonate deposits associated with surficial processes. The carbonate isotopic value seems to substantiate conclusions drawn by Fuex regarding car-

bonate in similar rocks. Alternately, the carbonate in these two samples may be due to alteration of the olivine or from the kimberlite matrix introduced as contamination, as suggested by O'Neil, Hedge, and Jackson (1969).

### Phases of Carbon in the Mantle

The physical state of the carbon in the mantle can be separated into two basic forms: volatile and residual. The volatile forms are either gases or supercritical gases included in the rocks, in inclusions or at structural defects (Green, 1972), or as a mobile phase in the environment of the rocks. The residual forms of carbon are elemental carbon, diamond and graphite, or carbon compounds such as carbonates or carbides. Residual forms of carbon appear as disseminated particles of carbon or carbon compounds in grains or at grain boundaries, or perhaps as carbon atoms disseminated in the structural defects of the mineral crystals.

This study yielded few conclusive results as to the exact mineralogical form of the non-volatile carbon. A considerably more complete picture can be drawn concerning the volatile forms of carbon in the mantle. The exact degree to which these gases represent mantle gases depends upon the depth which the nodules under study represent. Gas mixtures similar in constituents to those extracted from the dunite and lherzolite nodules of this study were found in natural diamonds by Melton, Salotti, and Giardini (1972). Diamonds are generally considered to represent a high pressure and high temperature phase of carbon, perhaps originating at depths of not less than 200 km. (Kennedy

and Nordlie, 1968). If depths of this order are represented by the samples of this study, then the volatiles extracted from the nodules represent the volatiles present at the time of crystallization of the nodules. In the case of primary inclusions, inclusion of the gas occurred with crystallization of the mineral; in the case of secondary inclusions, the volatiles trapped represent the environment at some time after crystallization, during an episode of fracturing and recrystallization of the rock. Unfortunately, the primary and secondary inclusions cannot be distinguished by the method of extraction used in this study, but it can probably be safely assumed that the inclusions of fluid and high pressure gases took place in an environment at depth. The presence of the inclusions in most of the samples in this study indicate that they all may have formed under similar volatile environments, even though the petrological environments of formation may have been somewhat different. In cases of extreme volatile enrichment, as in the cases of kimberlite intrusions, the high concentrations of volatiles in the intruding liquid may be due to differentiation and low gas solubility in the melts.

### General Conclusions

From the data collected during this study, there exists carbon in mantle-derived materials which occurs in several different forms: volatile carbon and residual carbon (non-carbonate and carbonate). These separate forms can be identified isotopically; carbonate residual generally about -6.8‰, non-carbonate residual carbon between -15‰ and -21‰, and the volatile carbon less than -21‰ versus PDB. Since no

sample yielded enough volatile carbon for a direct isotopic analysis, the value of less than -21‰ was deduced from the difference between the values of the total carbon and the residual carbon (value after removal of volatiles).

The presence of different identifiable forms of carbon in the mantle implies that there may be equilibrium between these forms. This might be used to rigorously correlate a given mantle-derived xenolith and its specific measured carbon types and ratios with a specific set of mantle conditions at which it equilibrated.

TOTAL CARBON FUSION

Sample No.	Wt. gm.	Mols*X 10 <sup>-6</sup>	Ppm.	Ratio % vs. PDB
KH-1	7.4467	32	51.8	-19.4
KH-1	6.8872	26	45.4	n.d.
KH-1	7.4549	22	35.6	
H-1	7.7746	57.5	89.1	-14.4
BP-1	8.0803	32.5	48.5	-14.6
PC-2	7.9612	22	33.2	-21.2
PC-2	6.8688	26	45.6	
PC-3	8.1961	10	14.8	n.d.
PC-4	7.9539	17.5	26.5	-22.3
PC-4	8.8854	22.5	30.2	
PC-6	7.5162	17.5	28	-16.7
PC-7	8.5092	9	12.7	n.d.
GK-1	9.4982	40	50.7	-13.1
GK-2	6.9346	600	1000	- 7.3

Recovery Test - Reactor graphite added to sample

PC-2	4.4549	104	281	-23.7
				Dil.= + 5.5
				83% yield

Recovery Test - NBS-21 added to sample

PC-2	4.2536	97.5	276	-25.0
				Dil.= - 6.9
				79% yield

\*Carbon collected as CO<sub>2</sub> gas

RESIDUAL CARBON FUSION

Sample No.	Wt. gm.	Mols*X 10 <sup>-6</sup>	Ppm.	Ratio ‰ vs.PDB
KH-1	6.2054	49.5	95.9	-15.0
H-1	8.2798	115	167	-22.9 ?
H-1	5.3211	39	88	-11.3
PC-2	5.7612	22	46	-20.6
PC-4	5.5739	21	49	-20.3
PC-4	6.-478	60	72	-18.3
PC-6	6.5485	32.5	60	-20.3
PC-7	6.9719	20.5	35.4	-19.2

\*Carbon collected as CO<sub>2</sub> gas

?This sample was not dried well prior to fusion; the values are due in part to adsorbed gas from the inclusions.

CARBONATE EXTRACTION

Sample No.	Wt. gm.	Mols*X 10 <sup>-6</sup>	Ppm.	Ratio % vs. PDB
KH-1	5.0278	41.5	99.7	-5.9
PC-3	4.3263	17.5	48.8	-8.0
PC-4	4.7855	3	8	n.d.
PC-6	3.9649	11.5	55.0	-8.8
PC-7	6.0246	17	34	n.d.
V-3	4.8665	13	32	n.d.
GK-1	4.1136	43.5	127	-5.0
GK-2	4.9809	66	344	-6.2

\*Carbon collected as CO<sub>2</sub> gas

## APPENDIX

### Petrographic Descriptions

H-1 Xenolith from the Hualalai flow of 1801. The sample is dunite enclosed in basalt which is slightly vesicular. The border between the olivine and the basalt is very abrupt and well defined, with no obvious reaction between the nodule and the enclosing basalt.

The olivine is quite uniform in grain size, the average grain size being about 0.5 mm. in diameter and comprises about 99% of the rock, with diopside as the remainder. The grain boundaries between the olivine grains show numerous grain contacts that appear to have been modified by recrystallization. Larger grains of the olivine show undulant extinction and a rough preferred morphological orientation.

Virtually all of the grains on the sample show gaseous or fluid inclusions. These inclusions are generally of a secondary nature, and average less than about 5 microns. There are numerous areas of the sample where these inclusions still show distinctly the vermicular nature of the healing fracture, not having healed totally to spherical bubbles. The single phase inclusions appear to be gas while the multiple phase inclusions appear to contain both a liquid and a gas. Roedder (1965) indicated that there are both gaseous and fluid carbon dioxide in many of the inclusions of similar samples from the 1801 Hualalai flow. This sample was contributed by D.W. Peterson of the U.S.G.S. Volcano Observatory, Hawaii.



KH-1 Kilbourne's Hole, New Mexico was the source of this very large nodule from the Rice University collection, approximately 15 inches in diameter. The grain size of the nodule is typically about 2.5 mm. in diameter and generally equidimensional. The rock is about three-quarters olivine, one-tenth hypersthene, one-tenth chrome diopside, with remaining spinel and opaques.

The olivine is colorless or only slightly colored and unaltered. Many of the pyroxene grains show reaction zones where they are in contact with olivine. Some of the obvious grains appear to have a somewhat rounded shape. There is also evidence of strain in the olivine such as distortion of extinction and kink banding. The olivine grains contain a very small number of gas inclusions which are one to two microns in diameter. The olivine was determined to be approximately Fo<sub>90</sub> by X-ray diffraction (Deer, Howie and Zussman, 1962).

The pyroxenes show triple junction points with each other as well as with the olivine. Both types of pyroxenes show a tendency to engulf the olivine, with olivine in embayments being optically continuous with the olivine not included in the pyroxene. The hypersthene and diopside do not show the same including character between each other, however.

The spinel is dark brown and at times is included in the olivine and to a lesser extent in the pyroxene. It appears to be the first to have crystallized along with the opaques, followed by resorption of the spinel and crystallization of the olivine. In examples where the spinel is included in the olivine, impressive embayments are formed with spits of spinel projecting into the olivine. At the time the

pyroxene began crystallizing, the olivine began to be resorbed and altered to pyroxene at boundaries; these fine borders are generally optically continuous with the pyroxene. The larger olivine grains often show kink banding, and roughly preferred morphological orientation. The smaller olivine grains show no such orientation or straining, perhaps due to recrystallization.

PC-2, PC-3, PC-4, PC-6, PC-7

All from Peridot Cove, Arizona, these samples are very similar, virtually identical.

The nodules are generally about three quarters olivine, one quarter pyroxene (predominately clinopyroxene), and the remainder dark brown spinel. Some of the olivine shows fluid and gaseous inclusions, probably primary in nature. These samples all show minor straining in the larger olivine grains and perhaps a slight preferred orientation of the olivine. From optical determinations alone, the olivine composition is high in magnesium (optical approximation).

In the nodules that are still included in the basalt, the border between the two is very sharp, with no obvious reaction other than a slight mechanical disaggregation of the nodule. The basalt is very fine grained with a large component of glassy groundmass.

V-3 This sample, from Vulcan's Throne, Arizona, is an altered dunite, the olivine approximately Fo<sub>85</sub> (optical approximation). In thin section the extent of alteration is not as high as it appears in hand specimen. The unaltered olivine shows numerous gas inclusions, mainly secondary. This sample was collected for the Fuex study (1970).

GK-1 From Green Knobs, New Mexico, this sample is an altered dunite from the kimberlite plug. The olivine is moderately altered to serpentine along fractures and grain boundaries. The unaltered olivine is moderately high in magnesium (optical approximation). The serpentine veins also contain some carbonate and opaques. There is only minor pyroxene (orthopyroxene).

The nodule is highly rounded and almost spherical, possibly indicating mechanical abrasion during transport to the present location. This sample was collected for the Fuex (1970) study.

GK-2 Identical to GK-1 above, but collected for the present study, this sample is also from Green Knobs, New Mexico.

BP-1 This sample, from Buell Park, Arizona, is composed of hand-sorted individual olivine grains from ant beds on the flanks of the central kimberlite plug. The grains of olivine are generally about two to three mm. in diameter, probably a function not only of the sorting of xenocrysts in the kimberlite, but also the sorting of the collection by the ants. Although other smaller olivine grains exist, the predominant size at the ant beds is quite uniform. There are various shades of color, but the color is not indicative of any major difference in the olivines, since the olivines are all the same composition ( $Fo_{95}$  by X-ray).

The following samples were ancillary to the main topic of study:

1. Vein quartz from the Packsaddle Formation near Llano, Texas,
2. Vein quartz, "milky" and vein quartz, "clear" from the Packsaddle

Formation near Llano, Texas. The samples were collected near each other, but from two separate veins.

3. Vein quartz, from the Palmetto Formation near Ash Meadows, Nevada.

These samples were used primarily for developing and testing the gas chromatography-vacuum crushing apparatus for extraction of volatiles from the rocks. They are very coarse grained quartz, with abundant fluid and gaseous inclusions.

Soft glass, used as a blank for the vacuum crusher, tested and developed the gas chromatograph-vacuum crusher apparatus.

PC-2 Spiked with either reactor grade graphite or National Bureau of Standards #21 graphite, PC-2 was used as a test of the fusion apparatus recovery.

## Detailed Sample Preparation

All of the samples for this study were treated in an identical manner, with the intent to keep carbon contamination to a minimum while removing any naturally occurring secondary mineralization.

1. The field sample was first reduced to manageable size using an Estwing crack hammer and chisel on a hard iron plate. To keep from contaminating the sample with carbon from the steel of the hammer or chisel, the sample was wrapped in aluminum foil, bright side away. The specific brand of hammer and chisel were chosen because of their extreme hardness, thus preventing the material of the hammer from streaking the sample.

The extremely friable nature of most of the rocks aided the reduction of the hand specimen to smaller fragments. Very little effort was required to completely disaggregate the sample completely.

2. After the initial reduction in size, the samples were washed with water to remove any loose dirt. Fragments that were located at the margins of the nodule were removed to reduce mineralization of the border.

3. The samples were then soaked overnight in a 3 N solution of hydrochloric acid and water to remove any carbonate surficially associated with the grains or in easily accessible locations. The goal was to remove all secondary carbonate and to leave the primary carbonate intact.

4. After removing any carbonates the samples were soaked overnight in a strongly oxidizing acid solution: concentrated sulfuric acid saturated with potassium dichromate, 1:3 with water. Any carbon contamination on the rocks that was accessible to the solution was oxidized and released. After the rocks had been in this solution, there was a gel of the dissolved silicates representing the outer portions of the grains. This alteration indicated that the solution had exposed new material and removed the outer most part of the samples, the part most likely to be contaminated.
5. After the acid treatment, the samples were washed to neutrality, a procedure that required numerous rinses with distilled water.
6. The samples were then dried at 100° C overnight.

The entire cleaning process took place in containers in which the samples were to ultimately be stored, reducing the possibility of contamination from the containers to the level of the sample itself. The containers were covered with a new sheet of aluminum foil, dull side down, and capped with their lids. After capping, the samples were not allowed to touch the aluminum foil in the course of analysis, if at all possible.

# SAMPLE PREPARATION

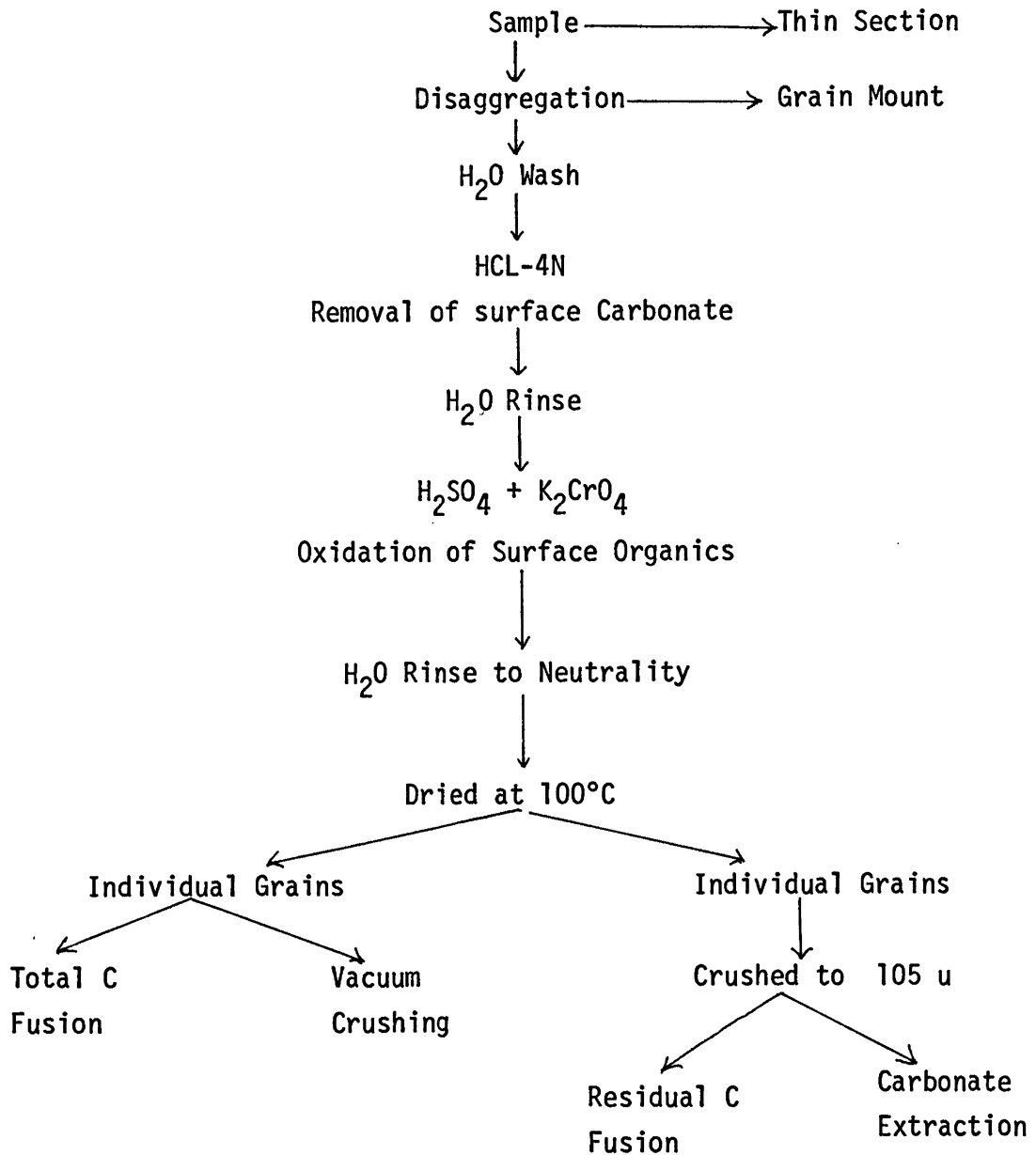


Fig. 6

## Detailed Extraction Procedures

A. The fusion was conducted in a high vacuum line, isolatable from the diffusion pumps. The line consisted of a quartz fusion tube approximately one and three-quarters inches in diameter and six inches in length. This fusion tube was located as a terminal appendage of the line, easily accessible to a high frequency induction furnace. The samples were loaded and unloaded from the top of the fusion tube which was flanged with a Varian Conflat type flange, accepting copper gaskets for the seal. The fusion tube was connected to the cold trap by a "U"-shaped copper oxide filled quartz tube. The copper oxide used was reagent grade wire, in about one-quarter inch lengths.

The crucibles used in the fusion apparatus were three-quarters inch in diameter by one inch in height. They were molybdenum to withstand high temperature for extended periods. However, molybdenum readily forms oxides, which sublime at relatively low temperatures, resulting in decreasing wall thickness of the crucible and accompanied by eventual failure of the wall due to uneven heating.

The crucibles were cleaned from previous samples with concentrated hydrofluoric acid. Then prior to loading with sample, the crucible was placed in the fusion tube and brought to a dull heat in the presence of a small amount of oxygen to remove any carbon contamination. The crucible was then loaded about three-quarters full, to prevent spillage of powdered sample; a hole may be formed in the center of the powdered sample with the spatula to further ensure against loss due to blow out.

The crucible was suspended in the central region of the quartz tube



by molybdenum were, and the system sealed. The system was then evacuated to high vacuum, about  $1 \times 10^{-5}$  torrs. Prior to the fusion of the sample, the crucible and sample were heated gently to degas adsorbed atmospheric gas and water. The degassed portion was then pumped away and the system evacuated again.

To fuse the sample, the working coil of the induction furnace was positioned symmetrically around the crucible for maximum heating efficiency. The furnace was turned on and raised in power very slowly, to prevent any material from being expelled from the crucible. The furnace was raised to maximum power, and allowed to heat the sample to fusion for twenty minutes.

It was found for the samples that were predominately olivine, the maximum temperatures were too low for total fusion. Samples that were partially altered were easily melted to a glass, however.

This inconsistent melting from sample to sample may account for the spread of isotopic data. However, the spread of the amount of carbon should be affected more than the actual carbon ratio because the carbon should not undergo any appreciable fractionation at such high temperatures. The ultimate temperature reached in these experiments was about  $1550^{\circ}\text{C}$ . On the other hand, if the different types of carbon are extracted in different manners, then the lack of total fusion of all samples might have a definite effect on the carbon ratio values.

In an attempt to remedy the inconsistent melting, a sample was mixed with a small amount of flux, sodium fluoride. But upon heating, the flux vigorously dehydrated, and blew part of the sample out and fluxed the inner side of the fusion tube liner. Thus, simple addition

of this flux is not considered to be the most appropriate manner in which to solve this problem. The more appropriate way would be to improve the degree of fusing, either by increasing the power or by improving the coupling between the working coil and crucible by changing the diameter or the number of coils.

In order to check the recovery or the extent of carbon extraction from a sample, recoveries from spiked samples were examined. To a precisely weighed amount of powdered sample, a small known amount of graphite was mixed. PC-2 was chosen because it had been analyzed previously and had a low carbon content. Two different graphites were used; a reactor grade commercial graphite, and the National Bureau of Standard's graphite standard, #21. For both of the graphites and the sample, the carbon isotopic value was known. Therefore, both quantitative recovery and the isotopic fractionation could be checked.

Recovery from the graphite-spiked samples were very close, 83.4% and 79.3% of the maximum carbon (reactor grade and NBS #21, respectively). To calculate the ratio of the samples as determined from a mixture with a known amount of added carbon, the isotopic ratios of the mixture, the added graphite and their respective amounts must be known.

If the extracted gas contains all of the sample carbon (based on previous runs), then the unextracted carbon is due solely to the spike carbon. Thus of the total graphite added, only part of it was recovered. By the equation for a mixture of different gases (Fuex, 1970):

$$R_{\text{spl}} = 1/x_{\text{spl}} (x_{\text{spl}} + x_{\text{dil}})R_{\text{mix}} - x_{\text{dil}}R_{\text{dil}}$$

where:	Test #1	Test #2
$R_{sp1}$ = isotopic ratio of the sample =	-1.0%	-11.0%
$R_{dil}$ = isotopic ratio of the sample =	-28.17%	-27.79%
$R_{mix}$ = isotopic ratio of the sample =	-23.68%	-25.01%
$x_{sp1}$ = amount of sample carbon =	0.0002 gms.	0.0002 gms.
$x_{dil}$ = amount of dilutant carbon =	0.0010 gms.	0.0010 gms.

From these results, either there was possible fractionation of the carbon during extraction, or the amounts of test carbon were so small that error in measuring and in extracting completely outweighs the spiked results. To determine which is the case would be of extreme importance to the reliability of the data.

B. Attached to the volatile extraction system was a demountable vacuum crusher six inches in diameter and about six inches high to extract large volumes of gas necessary for ratio mass spectrographic analysis. To efficiently crush the sample a roller (Fig.1) of hard stainless steel was placed in the crusher with the sample around the roller. By running a standard procedure on a sample and then determining the distribution of grain size, the efficiency of the crusher was evaluated. Upon sieving the sample, about 85% of the sample is less than 105 microns. This reduction of grain size from millimeter size assures the maximum rupture of gas and fluid filled inclusions, but even upon crushing to this grain size, not all of the inclusions are broken.

After reduction to grain size, the increase in clean surface allows adsorption of the released gases. To degas this adsorbed gas, the

sample must be heated under vacuum. It was noted that in some cases, the adsorption had been very efficient and that virtually all of the carbon dioxide was held until heating.

The crusher used in this study uses a Buna-N "O" ring to seal the flanges. It was found that the material used in the "O" ring outgassed organic compounds when heated. These compounds were not specifically identified as to species, but their presence was confined to the high molecular part of the chromatograms. To avoid these high carbon species, the sample gas was analyzed where possible without heating the crusher.

After extraction of the gas from the sample, it must be compressed and measured quantitatively. The sample side of the automatic Toepler pump was equipped with a thermocouple vacuum gauge which indicated when the pump had been reduced to its lowest pressure, in this case, about ten microns of pressure. The intake of the pump had also been modified with a manometer which determined the amount of sample gas ( $PV=nRT$ ). After compressing the sample gas into the sample loop, it could be injected into the gas chromatograph by turning the four-way stopcock to the position so the carrier gas stream swept through the loop and pushed the sample into the chromatograph (Fig. 3).

The chromatograph's detector (a thermal conductivity detector) was set to an appropriate scale for the initial size of the sample. The smallest sample size analyzed in this study was approximately less than  $0.02 \text{ cm}^3$  of gas at STP, or less than one micromol of gas. Since such small samples can be analyzed on this apparatus, the constituents of the sample can be analyzed even when there would not be enough

sample for an isotopic analysis.

The general purpose columns used on the gas chromatograph were copper tubing, eleven feet by three-sixteenths inch, and packed with Porapak-Q, a medium selected for separating light hydrocarbons and some of the stable gases. The disadvantage of this type of packing is that it will not resolve nitrogen, carbon monoxide, argon, or oxygen. A different arrangement of columns and packings, however, might result in a good resolution of both the hydrocarbons, carbon dioxide, and the stable gases; two columns could be used in tandem for this purpose. The first column should contain Porapak-Q to resolve the carbon dioxide, and the second column something like molecular sieve to separate the stable gases. Molecular sieve is quite efficient at resolving nitrogen, argon, and oxygen, as well as some of the light hydrocarbons, but adsorbs and holds carbon dioxide irreversibly. Thus there should be detectors after both the Porapak-Q column and the second column. In this arrangement, the carbon dioxide is detected and measured before it can be adsorbed on the second column.

The gas chromatograph used for this study was a Perkin-Elmer 990, which was programmed at a flow rate of sixty milliliters per minute of helium carrier gas with the columns at ambient room temperature. After injection of the sample, the standard program began with two minutes at room temperature to allow the atmospheric gases to move through the columns while at their lowest temperature. Then a rapid increase in temperature speeded up the elution of carbon dioxide and any hydrocarbons; the increase was 24°C per minute with a maintained maximum temperature of 150°. In this program the atmospheric gases

emerge at about two minutes, methane at about three, and carbon dioxide at about five minutes, with poor resolution of only the atmospheric group of gases.

### Crusher Background

Crusher background must be taken into account when interpreting the chromatograms of the sample gases. From the runs without any material in the crusher ( fig. 2 ), air and a very small amount of hydrogen were recognized as constant background components, as well as small amounts of organic compounds evolved from the "O" ring.

Methane was a component of the gas in the soft glass blank only when there was excessive metal to metal contact. The sample or other material being crushed acts as a lubricant between the two moving metal parts of the crusher. That the methane is produced during the rolling process is demonstrated by the fact that after the first rolling of the empty crusher only a very small amount of methane evolved during heating, but when rolled again during the second empty rolling, there was more methane evolved when extracted cold.

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