CARBON ISOTOPIC MEASUREMENTS FROM FLUID INCLUSIONS IN QUARTZ VEINS OF THE FAYMAR GOLD PROPERTY, DELORO TOWNSHIP, NORTHWESTERN ONTARIO

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ABSTRACT

The Faymar Gold Property, near Timmins Ontario, is cross-cut by two quartz-carbonate veins. Isotopic measurements of carbon species in fluid inclusions in these quartz-carbonate veins, reveal the presence of CO_2 and other light carbon species (eg. CH_4). The inclusion contents were liberated using thermal decrepitation. The results obtained are found to vary quite significantly with various periods and temperatures of heating. The most useful results were obtained from samples heated for 5 minutes at 550°C. The short heating period reduces fractionation and reaction effects. Mass spectrometer measurements of the carbon isotopes reveal that the CO_2 and total carbon in the inclusions are characterized by a $\delta^{13}C$ of -3.0 and -4.7 respectively. A magmatic source for the fluids most easily explains these values. Petrographic observations indicate that secondary inclusions dominate. Thus, the isotopic measurements are of fluids which post-date the deposition of the quartz-carbonate or at least represent a late stage of this process. Since the mineralization in the veins also appears to be secondary to the quartz-carbonate (ie. in fractures), it is possible that the carbon species in the inclusions are distinct of the mineralizing fluids.

ACKNOWLEDGEMENTS;

I would like to thank Dr. H.P. Schwarcz for acting as my supervisor and counsellor in this interesting and challenging study. I am also extremely grateful to Martin Knyf, whose patience, technical expertise, and guidance in the lab enabled me to obtain the isotopic analyses for this study. The samples and some data were supplied by Andy Fyon and are gratefully acknowledged. Also, I owe a very special thank you to Andy Fyon for his invaluable advice and for allowing me to interrupt his busy schedule with my numerous queries. Finally, I would like to thank my girlfriend Lola for her support and assistance during the write-up of this thesis.

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CHAPTER 1

1.1 Introduction

Hydrothermal quartz veins are common hosts to mineralization and economic ore deposits. A determination of the origin of these ore forming fluids would be a useful tool in mineral exploration. Fortunately, a trace of these fluids is preserved in the form of fluid inclusions in the quartz. These inclusions are believed to represent samples of the fluid actually existing at various times in the geologic history of the quartz vein (Roedder, 1979). Many papers have been published dealing with fluid inclusions and the available information indicates that CO_2 is a common constituent of the included fluid.

This thesis is a study of the stable carbon isotopes in fluid inclusions of the Faymar quartz veins. Unfortunately, a detailed study of the structure and components of the fluid inclusions was not possible but would have been very useful in interpreting the data obtained. However, the results do provide some information on the origin of the CO_2 in the inclusions. Probably more important is that, due to the range in sample material and different analytical techniques, it is difficult to obtain an accurate and unambiguous carbon isotopic analysis of any fluid inclusion. This stresses the importance of examining the available published data with great care, especially when details of the analytical technique are not supplied.

1.2 The Problem

The Faymar quartz veins are an example of gold-mineralized discordant quartz veins in Archean rocks of the Canadian Shield. Most recent models for these discordant veins suggest that a CO_2 rich fluid was responsible for their deposition(Fyon, 1980; Fyon and Crocket,1980, 82; Whitehead et al.,1981). Essentially all the gold-mineralization in the Timmins area is emplaced in a quartz-carbonate host-rock. Recent studies by Fyon(Ph.D. thesis, in prep) of the carbonate, show little or no correlation between the grade of gold mineralization and $\delta^{13}C$ of the carbonate. But there is a correlation between the $\delta^{13}C$ and the presence of gold at all i.e., all the carbonatized rocks have virtually the same carbon isotopic signature. Thus, if the CO_2 trapped in the inclusions is associated with the carbonate deposition, then it may be of some value as an exploration tool.

Most of the native gold in the vein quartz of the area occurs along fractures in those veins (Smith, Cloke and Kesler,1984). Thus, the mineralization appears to be secondary or at least a late stage of the quartz-carbonate deposition. The possibility exists that the mineralizing fluid may have had a distinctly different carbon isotopic signature than the fluid involved in the quartz-carbonate deposition. If the $\delta^{13}C$ of the CO_2 in the fluid inclusions is found to be unrelated to the carbonate, it may be possible to link the origin of this CO_2 to the mineralizing fluid i.e., distinct from the fluid responsible for carbonatization.

1.3 Fluid Inclusion Background

1.3.1. Fluid Inclusion Trapping

As a result of the regularities inherent in the process of trapping fluid inclusions, three general classes have been established by Roedder (1979). These are:

a) primary inclusions

b) secondary inclusions

c) pseudo-secondary inclusions

Primary inclusions result from the sealing off of irregularities during crystal growth. These inclusions presumably contain samples of the fluid present during this growth period. They are generally large and isolated or randomly arrayed.

Secondary inclusions form in healed fractures and hence contain later fluids. Because of their location, they are commonly flat and occur in planar arrangements.

Pseudo-secondary inclusions form in crystal fractures during crystal growth. These also occur as planar arrangements in the crystal but do not cross-cut crystal boundaries.

1.3.2. Fluid Inclusion Content

Petrographic studies of fluid inclusions by Roedder

(1979) and others, have revealed the common occurence of two or three phases within a single inclusion. These include a liquid phase, a solid phase and a gaseous phase. The most abundant component in the liquid phase is usually H_2O and sometimes CO_2 (Roedder, 1984). A solid phase is sometimes observed in these inclusions and is usually composed of some combination of the major solutes occuring in the fluid. These include Na, Ca, Mg, Cl, SO_4, HCO_3 (Roedder, 1984). The solids are known as daughter minerals. NaCl is the most common but carbonates, oxides, silicates, sulphates and sulphides are also possible (Roedder, 1984). Finally, a round gaseous bubble is typical in most inclusions. The bubble commonly represents the coexisting vapor phase of the fluid but it may also contain other non-condensible gases.

Of interest to this thesis are the possible carbon compounds in these three phases and their isotopic signatures. A list of possible species containing carbon, as suggested by Roedder (1984), includes CO_2, CO, C_xH_y, H_2CO_3, and HCO_3 . However, many of these species may be non-existent or insignificant in the Faymar inclusions. A study by Smith, Cloke and Kesler (1984) , in an area just north of the Faymar veins has shown that H_2O is the dominant component of the inclusions in most samples, with the balance made up by CO_2 and minor amounts of CH_4, CO and N_2(Table 1) . Thus, in my analysis of the Faymar fluid inclusions, CO_2 is assumed to be the main source of oxidized carbon while CH_4 is treated as the principle source of reduced carbon. Other carbon species are probably also present but their volumes are assumed to be negligible. As a result, their contribution to the carbon isotopic signature is insignificant.

The origin of the expected CH_4 is probably inorganic. It is possible that the CH_4 and CO_2 represent the fractionated end product of the initial CO_2 in the system. Barnes (1979) states that some CO_2 may convert to CH_4 during cooling of the fluids. The reaction can be written as :

$$CO_2 + 2\ H_2O = CH_4 + 2\ O_2$$

If this is the case, a simple mass balance equation using the CH_4 and CO_2 should give the isotopic signature of the total carbon in the fluid.

TABLE 1. Gas chromatographic analyses of fluid inclusion contents given in mole percent. Samples were obtained from quartz veins in the Timmins area. (Data from Smith, Cloke and Kesler, 1984)

Sample number	H_2O	CO_2	CH_4	CO	N_2
			(%)		
MJS-47	92.461	6.982	0.167	0.209	0.181
MJS-1	86.856	12.469	0.267	0.204	0.204
MJS-35	94.116	5.600	0.156	0.064	0.064
MJS-35	93.867	5.589	0.176	0.222	0.146
Au-1	89.241	10.289	0.294	0.032	0.144
Au-1	86.632	12.686	0.380	0.138	0.164
MJS-62	96.686	2.081	0.558	0.041	0.634
MJS-12	98.521	1.316	0.051	0.006	0.106
MJS-12	98.988	0.937	0.037	0.014	0.024
MJS-51	98.546	1.250	0.071	0.065	0.068
MJS-51	97.832	1.835	0.078	0.174	0.081
MJ-23	31.553	31.514	33.437	0.551	2.945

1.4 Geology

1.4.1. Geologic Setting

Geographically, the studied quartz veins are located in the Timmins area of Northern Ontario. The samples were obtained from the Faymar Gold Property located in the Deloro Township, a few kilometers south of Timmins (Fig. 1). They were supplied to the writer by Andy Fyon, who collected them during previous work in the area.

The two quartz veins in the study area are hosted in Archean aged terrain. The discordant veins are essentially parallel and dip at steep angles towards each other, probably intersecting at depth. Both veins are located in shear zones and are hosted in quartz feldspar porphyry ,gabbro, calc-alkaline basalts and pillowed basalts (Fig. 2). There is some evidence of foliation in these rocks.

A total of seven samples from the Faymar system were used in this study. Figure 2 shows the location of each sample site. The actual samples represent loose or eroded fragments of the quartz vein, which were collected along the exposed vein. It is assumed that the fragments originated from the underlying vein and have undergone little or no transportation.

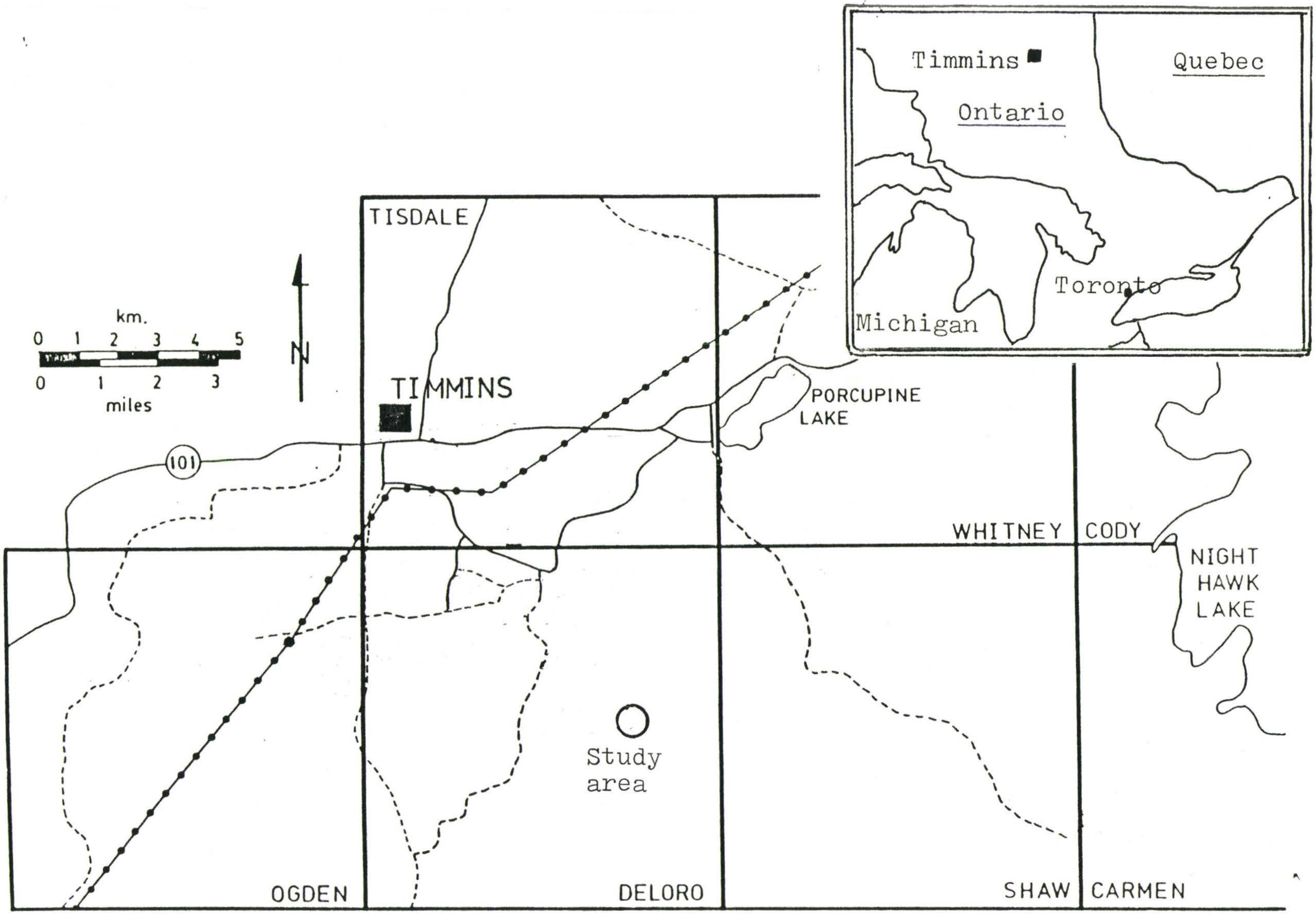


FIG. 1 Location map of the Faymar Gold Property, near Timmins, Ont.

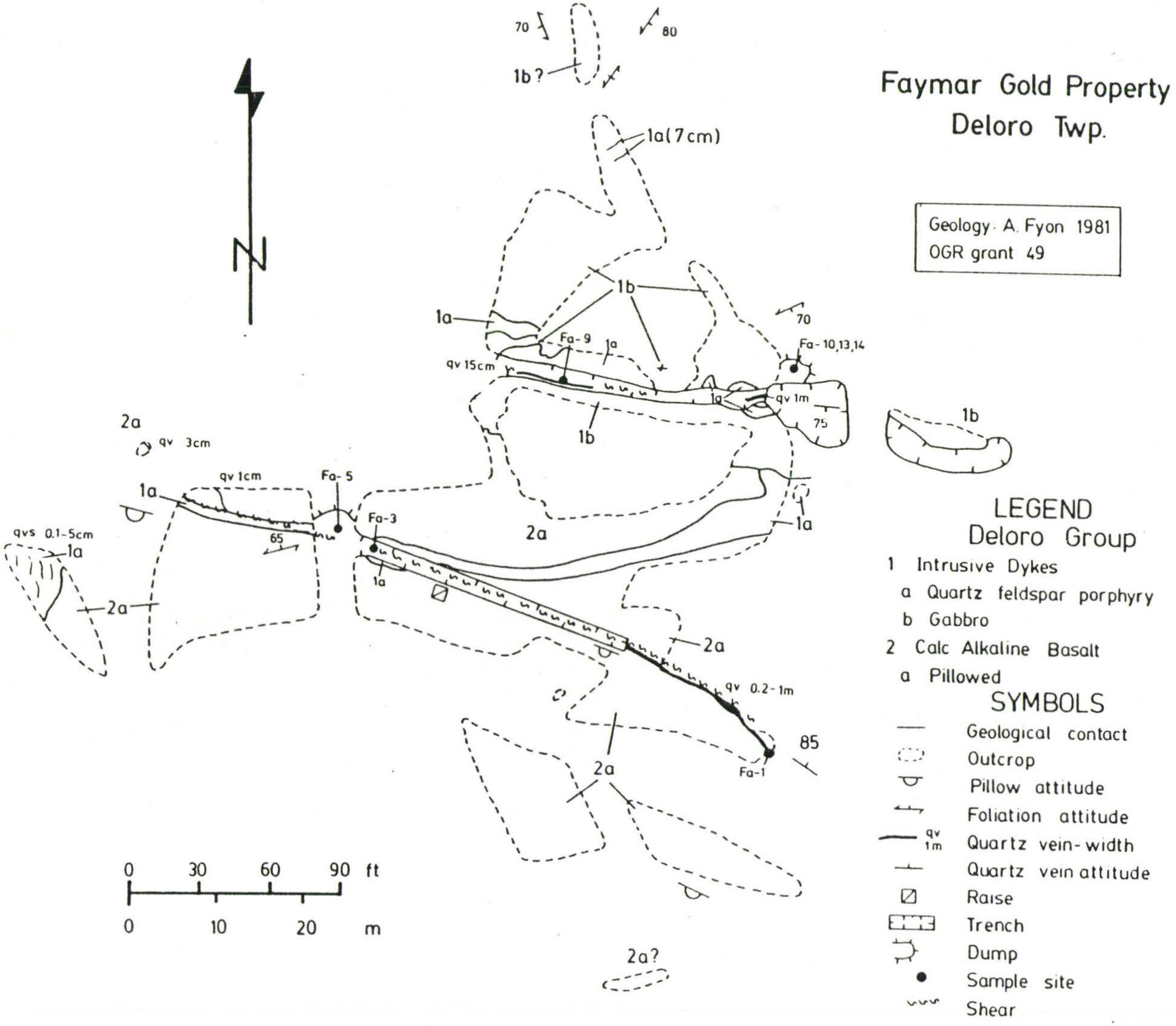


FIG. 2. Simplified geologic map of the Faymar gold property. Sample sites are located along exposed surface of the two quartz veins.

1.4.2 Hand Sample Description

The mineralogy of the samples is quite simple. In hand specimens, they consist of quartz with minor occurrences of carbonates, sulphides and wallrock material. The quartz itself is not clear, indicating the presence of numerous flaws and micro-fractures. Tiny voids could be recognized in sample fragments using a binocular microscope.

The carbonate in the samples is a mixture of calcite and rare dolomite. Samples Fa-14, Fa-13 and Fa-10 contain some easy to recognize carbonate crystals. The remaining samples lacked any large, visible carbonate crystals. However, it is assumed that carbonate pockets are distributed throughout the samples. Indeed, an acid test revealed the presence of carbonate material in all the samples.

A third major component of the hand samples is wallrock material. Wallrock fragments were attached to all the samples. However, an attempt was made to reduce wallrock contamination in the samples to be analysed.

Finally, a minor occurence of sulphide mineralization (e.g. chalcopyrite, pyrite, ..) was observed in many of the samples. It was impossible to avoid contamination of the prepared sample because of the disseminated character of this sulphide material.

CHAPTER 2

2.1 Isotopic Background

2.1.1 Isotopic Notation

Values obtained from the mass spectrometer analyses are actually reported as δ values. The δ value is the isotopic composition reported as a ‰ deviation relative to a standard. The δ value is defined as follows:

$$\delta_x = \frac{R_x - R_{std}}{R_{std}} (10^3)$$

In this study, carbon isotopes are the ones of interest. Thus, R_x is the $^{13}C/^{12}C$ ratio for the sample and R_{std} is the $^{13}C/^{12}C$ ratio of the Chicago PDB standard i.e., $^{13}C/^{12}C = 0.0112372$ (Craig, 1957). The δ value initially obtained was relative to the GCS standard used in the laboratory and subsequently related to the PDB standard.

Hence, the δ value is simply the relative difference in isotope ratios between a sample and a standard, expressed in parts per thousand or ‰. A sample with a $\delta^{13}C$ value of -10.0 ‰ is depleted in ^{13}C by 10 ‰ or 1 % relative to the standard. The absolute isotopic ratios are unnecessary.

2.1.2 Fractionation

The isotopic fractionation factor between two substances A and B is given as:

$$\alpha_{A-B} = \frac{R_A}{R_B}$$

An example of isotope exchange which applies in this study can be written as:

$$^{13}CH_4 + {}^{12}CO_2 = {}^{12}CH_4 + {}^{13}CO_2$$

This can be re-written in the form of a fractionation factor between the CO_2 and CH_4 :

$$\alpha = \frac{(^{13}C/^{12}C)\ CO_2}{(^{13}C/^{12}C)\ CH_4}$$

These fractionation factors have been calculated by Bottinga (1969) for a number of systems involving calcite, cabon dioxide, graphite and methane. The carbon dioxide/methane and carbon dioxide/calcite systems are important in this study and displayed as Figure 3 and Figure 4 respectively. These curves display the fractionation factors that can be expected at isotopic equilibrium for various temperatures. It can immediately be noted that the fractionation factor decreases with increasing temperature.

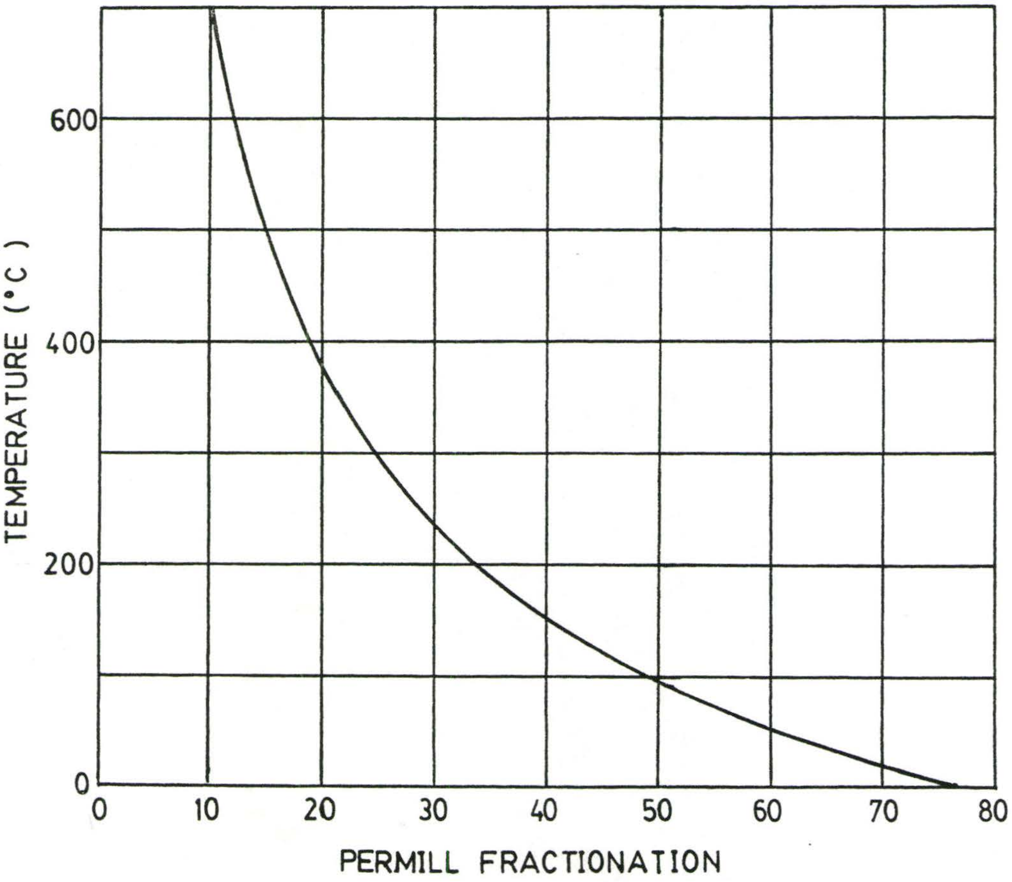


FIG. 3. Fractionation values for CO_2(g)-CH_4(g) (after Bottinga, 1969)

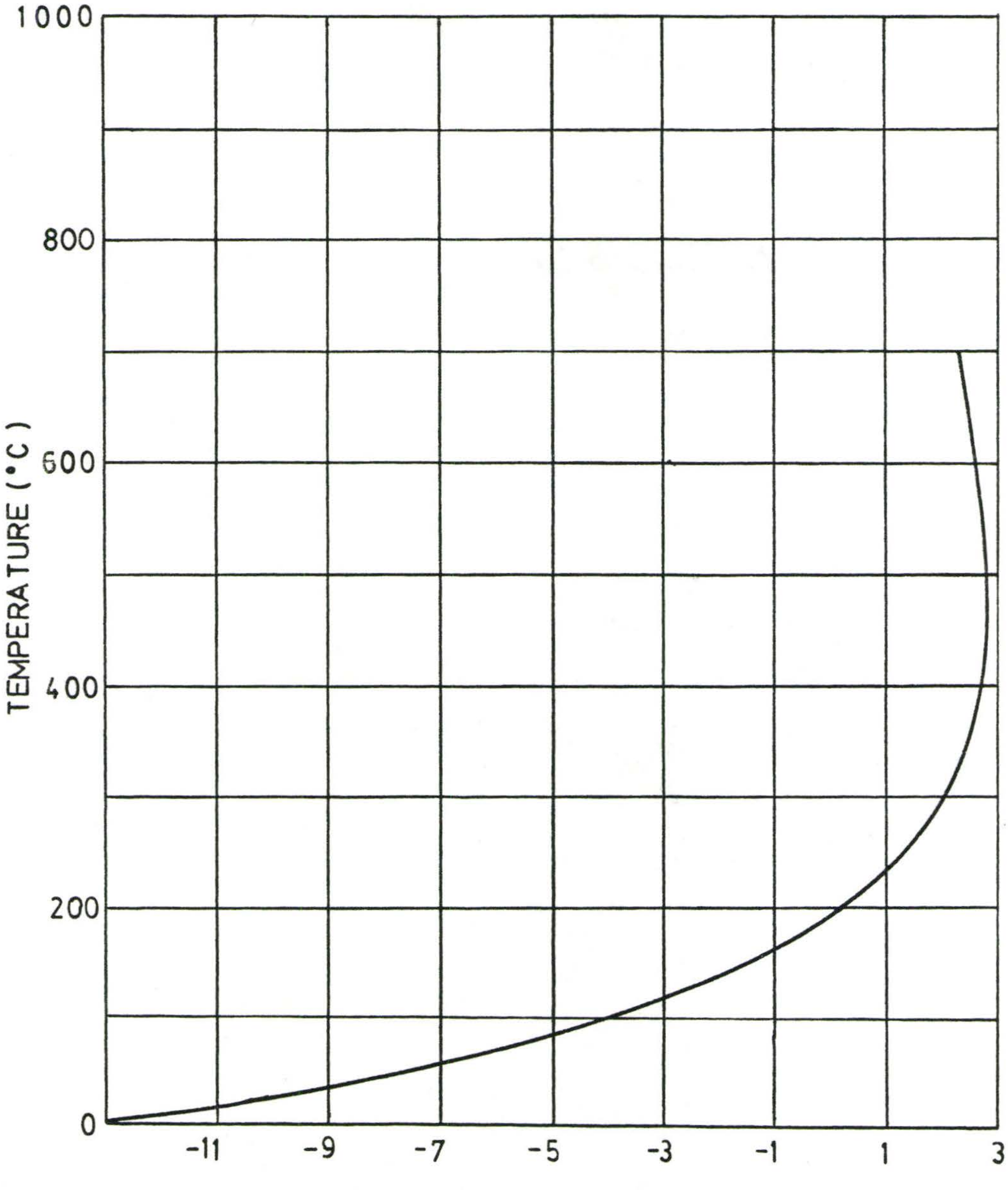


FIG. 4. Fractionation values for CO_2(g)-Calcite (after Bottinga, 1969)

2.2 Analytical Technique

2.2.1 Sample Preparation

In fluid inclusion studies, there are two possible extraction methods; crushing in a vacuum and thermal decrepitation. The latter method was chosen for this study. The first step in preparing the samples for thermal decrepitation was to establish an "appropriate" grain size which would most efficiently release the inclusion contents. A grain size in the 0.250 to -0.750 ɸ range was recommended by Andy Fyon (oral commun.,1984) and subsequently used in this study. This size reduces damage to the inclusions and is easy to load in the tubes.

The crushing process involved reducing the size of the samples using a hammer, followed by repeated passes of the sample material through the crusher. Sieving of the crushed material after each pass was required to obtain a sufficient amount of sample in the selected grain size range. The sieved portion was then bottled, tagged and ready for washing.

Washing of the samples involved reacting the sieved fraction with acid. Aqua-regia, which is a 3:1 mixture of HCl and HNO_3 respectively, was used . This solvent removes both the carbonate and sulphide material from the crushed sample. This washing process was repeated several times. Before replacing the acid, the samples were rinsed with water. For the final rinse, distilled water was used. The samples were dried at a temperature of 70°C for a period of two days and sealed in clean sample bottles.

Individual samples could now be prepared. Initially, 7 grams of sample material was used in each tube since the amount of gas to be released was unknown. However, because of the limited amount of sample material, the sample size was reduced to 4 or 5 grams. The glass tubes containing the sample material were connected to a vacuum line and pumped out for several hours. The tubes were sealed with the sample material under vacuum. At this stage, the samples were ready to be heated.

2.2.2 Decrepitation of Inclusions

Thermal decrepitation was used in this study. This method of gas extraction exhibits some severe difficulties. Of main concern here is that thermal decrepitation favours reactions in the gas phase or between solids and gases(Hoefs, 1974). Studies by Piperov and Penchev(1973) and Cuney et al. (1976), indicate that at about a temperature of 400°C, compounds in the fluid phase begin to react with one another. Also, at this temperature, only a small number of the inclusions do decrepitate (Cuney et al., 1976).

In an attempt to reduce these effects, the temperature and duration of heating were carefully chosen. Since high temperatures are expected to maximize the yield and reduce fractionation, the approach was to use a maximum temperature with the available equipment. Pyrex and quartz glass tubing were used in the decrepitation process and these can withstand temperatures of up to 550°C and 950°C respectively. As a result, these were the temperatures selected for the decrepitation of the inclusions. The duration of heating was used mainly as a control of the degree of fractionation. Long heating periods allow a greater isotopic exchange between the carbon bearing compounds.

The analytical methods used in this study were chosen to examine two possibilities:

a)The CO_2 in the system has undergone little or no fractionation. Thus, its isotopic signature is representative of the main fluid generation.

b) The original carbon in the system has undergone reaction and fractionation to produce a mixture of CO_2 and CH_4 of differing isotopic composition. Thus, the original isotopic signature of the carbon can be determined by oxidizing the CH_4 and then obtaining a total carbon value.

The first possibility was examined by decrepitating the inclusions and analysing the CO_2 liberated. For the second possibility, CuO was added to each sample. The CuO served as an oxidizing agent, oxidizing any reduced carbon (i.e. CH_4) and providing a total carbon value (Hoefs,1979). Thus, for each analytical technique, samples were prepared with and without CuO.

Thermal decrepitation is a process which relies on high temperatures to increase the fluid pressure in inclusions. This subsequently fractures the host rock, releasing the inclusion contents (Kreulen, 1980). In this study, both temperature and period of heating were varied in an attempt to maximize decrepitation and control reactions between the released phases.

Three different methods were used. In each case, the sealed glass tubes were heated for the prescribed time in a muffle furnace which had been pre-heated to the prescribed temperature.

Method 1 - 3 hours at 550°C

This combination was expected to ensure maximum decrepitation and allow the system to attain isotopic equilibrium.

Method 2 - Time study at 950 °C

The purpose of this analytical technique was two-fold:
a) Narrow the fractionation range using the high temperature.
b) Observe any trend in the δ value with extended heating.

Method 3 - 5 minutes at 550 °C

This method represents an attempt to reduce reaction between the liberated gases and restrict any fractionation effect. Isotopic equilibrium was not expected.

The possibility that short heating periods would preferentially decrepitate weaker inclusions and only liberate certain isotopic populations was not examined. It is assumed that the short heating period of 5 minutes raises the temperature of the sample material sufficiently to decrepitate most of the inclusions.

2.2.3 Isolation of CO_2 Gas

After heating of the tubes, they were cooled in air and stored for periods of up to one week. The tubes were attached to the mass spectrometer apparatus through a tube cracker, which was used to release the gases in the tubes. Once in the line, the gas was passed over various cold traps (Fig. 5) (i.e. dry ice and alcohol, liquid nitrogen), to separate out the H_2O and CO_2. Non-condensible gas was pumped away (e.g. CH_4, N_2, etc...).

No attempt was made to measure the $\delta^{13}C$ of the released CH_4 directly. This could have been done by trapping it on a molecular sieve, cooled with liquid N_2 and reacting it with CuO in a sealed tube. However, because of a lack of time and of problems inherent with this method, it was not used in this study.

2.2.4 Isotopic Analysis

The purified CO_2 which was retained in the N_2 trap, was analysed for $\delta^{13}C$ on a VG 602D mass spectrometer. Corrections were made for contributions of ^{17}O. The results are quoted with respect to the PDB standard. The precision of replicate analysis is within 0.1 ‰. Accuracy is checked periodically by analysis of a standard graphite, NBS-21.

The size of all the CO_2 samples was sufficient to obtain normal precision of isotope analysis. However, the cold finger on the mass spectrometer had to be used for most samples because of the small volume of CO_2 gas.

2.2.5 $\delta^{13}C$ of Carbonate Minerals

$\delta^{13}C$ values for the carbonate minerals (ferroan dolomite and calcite) hosted in the quartz vein, are reported in Table 5. A number of these analyses were supplied to the writer by Andy Fyon(Ph.D. thesis, in prep.). These analyses involve reacting the carbonate mineral with phosphoric acid and analysing the liberated CO_2.

2.2.6 Volume Measurements

A limited number of volume measurements were made using a manometer and McCleod gauge(Fig. 6). The purpose of measuring the volumes was to determine the mole fraction of CO_2 and CH_4 in the inclusions. This data can in turn be used in mass balance equations. Unfortunately, the McCleod gauge was not calibrated such that the volumes of CH_4 could only be reported in terms of mercury displacement (Table 6). The volume measurements were made from samples heated for 5 minutes at 550°C.

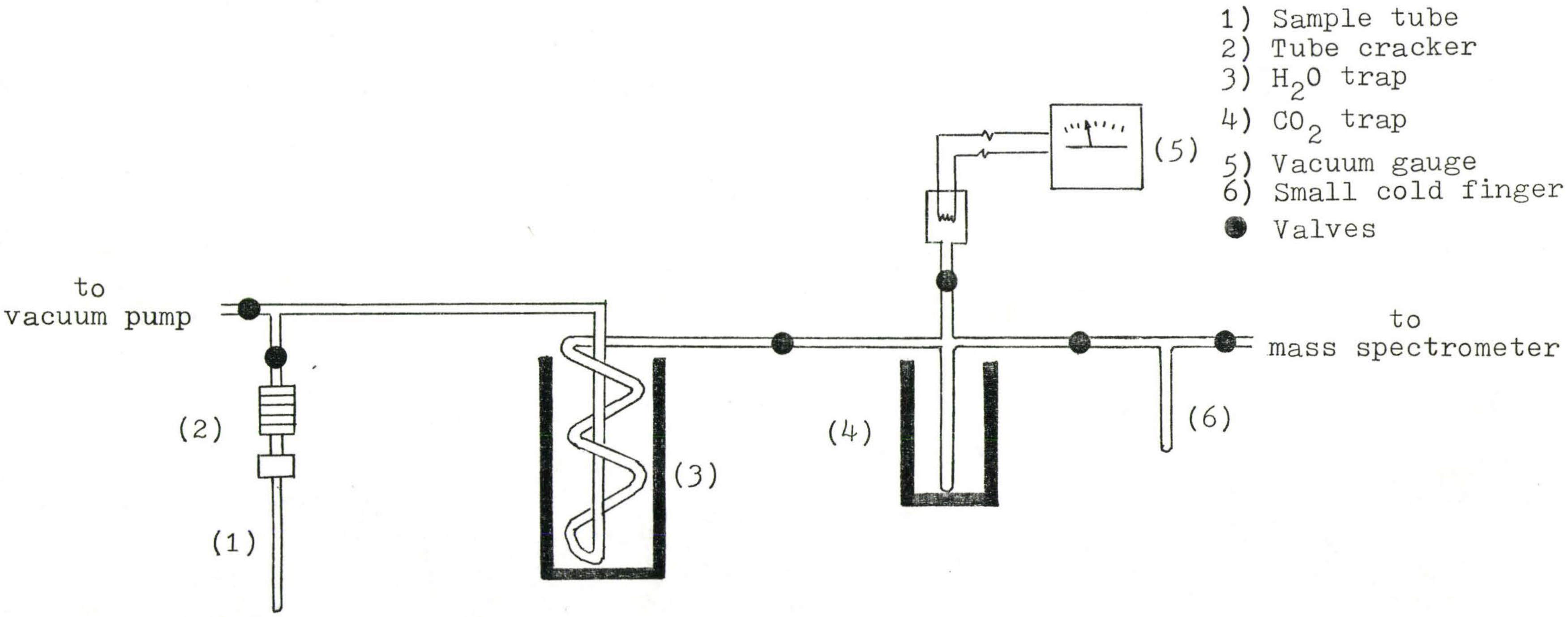


FIG. 5. Apparatus used to isolate CO_2 for mass spectrometer analysis. Small CO_2 samples are retained in the smaller cold finger.

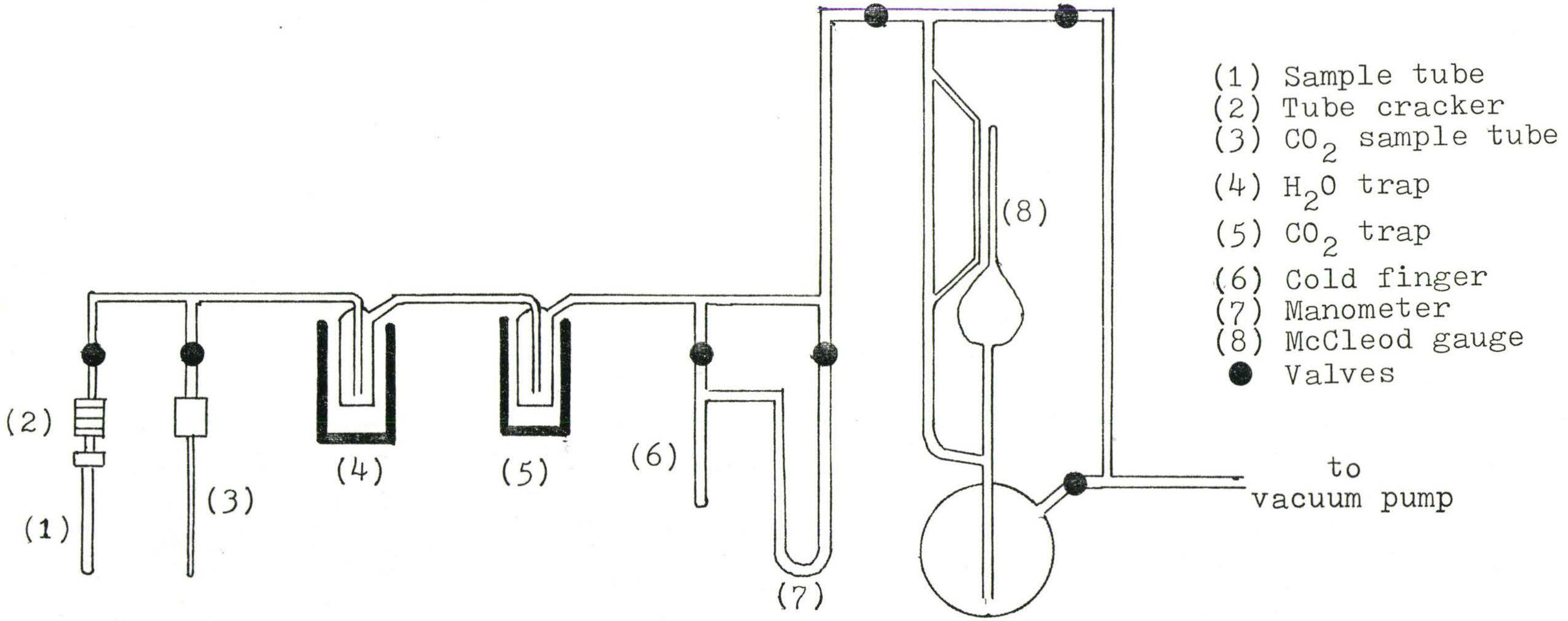


FIG. 6. Apparatus used to make volume measurements. The manometer was used to measure CO_2 volumes and the McCleod gauge was used for CH_4 volumes.

CHAPTER 3

3.1 Results

3.1.1 Petrographic Study

Five minerals, quartz, carbonate, chlorite, mica and sulphide have been identified in thin sections of the samples. The quartz is the dominant mineral and the sulphide is located in breccia zones within the quartz. This is in accordance with the findings of Smith, Cloke and Kesler (1984).

A thin-section examination of the fluid inclusions reveals that most of the inclusions are arranged as bubble trains which cross-cut the minerals and grain boundaries (Fig. 7). According to Roedders' criterion (see previous discussion), this is evidence that most of the inclusions are secondary. Some larger inclusions, with no preferred position or orientation, were also observed (Fig. 8) . These may represent primary inclusions. A gas bubble was recognized in most of the inclusions.

FIG. 7. Photographs display the common occurence of bubble trains, visible in thin sections. These represent secondary fluid inclusions.

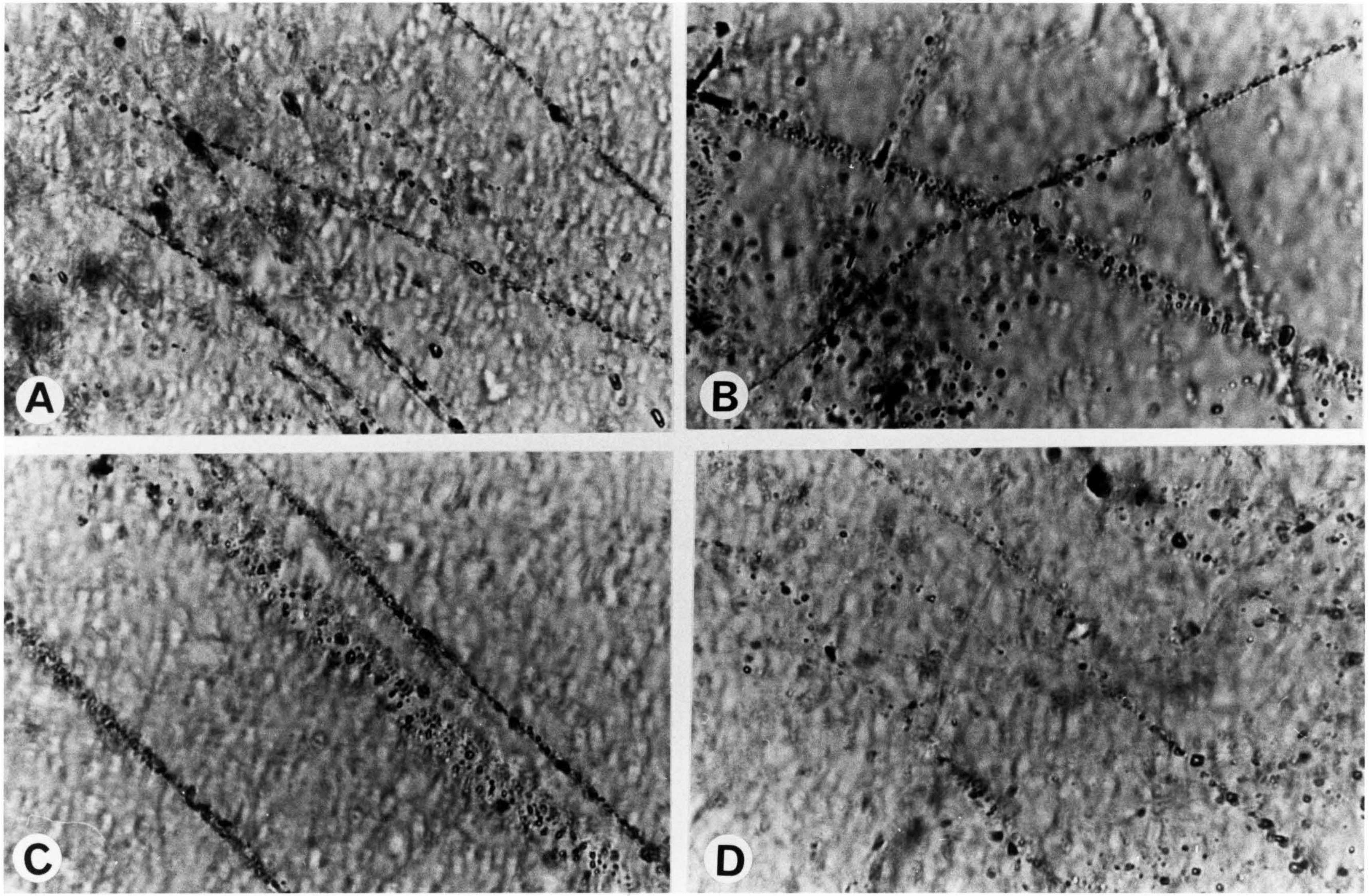
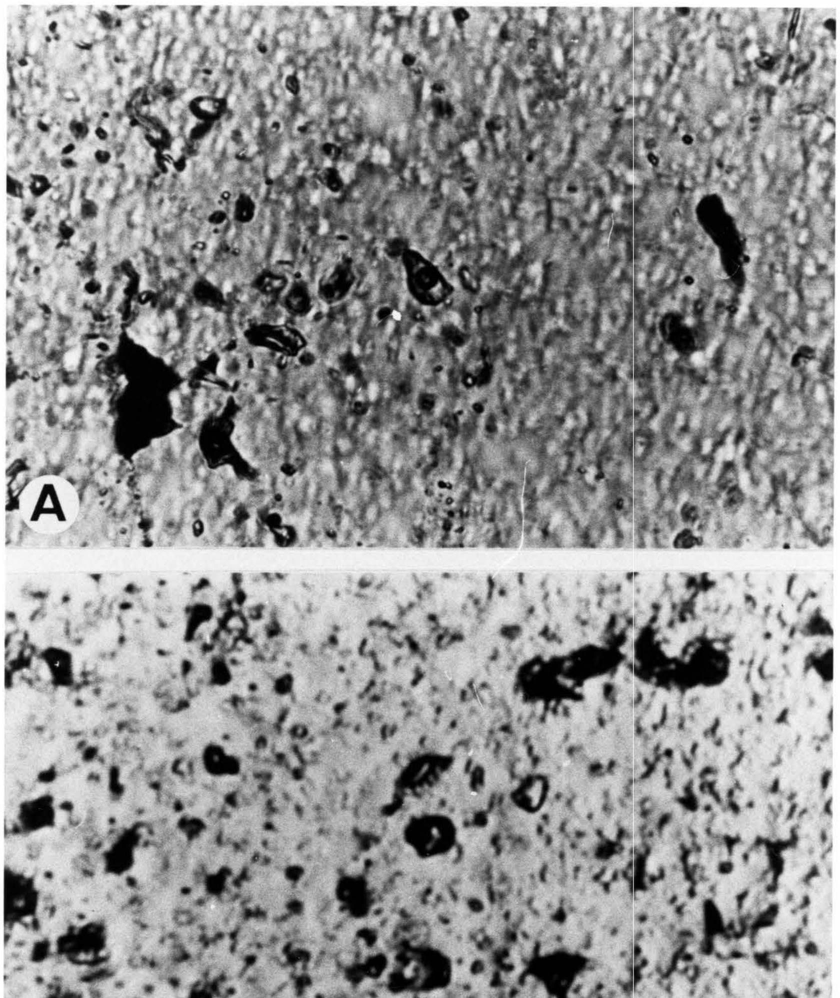

A
B
C
D

FIG. 8. Photographs of large fluid inclusions with no preferred orientation. These are believed to represent primary fluid inclusions. A gaseous bubble is visible in many of the inclusions.


A
B
C

3.1.2 Isotopic Data

The $\delta^{13}C$ values for the CO_2 and total carbon from the various analytical techniques are presented in Tables 2, 3 and 4.

The $\delta^{13}C$ values for the total carbon represent the combined isotopic signatures of the CO_2 and reduced carbon in the inclusions. These total carbon values are consistently lighter than the $\delta^{13}C$ values of the CO_2. Also, the volume of gas retained in the liquid nitrogen-cooled trap was observed to be greater from samples containing the oxidizing agent. These two observations confirm the presence of a light, reduced carbon (probably CH_4) in the inclusions. However, some non-condensible gases remained even with the addition of CuO. This indicates that minor amounts of other non-carbon compounds also exist in the inclusions, as predicted by Smith, Cloke and Kesler (1984) (Table 1).

The limited volume data are displayed in Table 6. Absolute measurements were made for the CO_2 but only relative volume measurements were obtained for the non-condensible portion of the gases. Thus, these values are of little or no use in mass balance equations but they are useful in the discussion of the data from Method 3 (see later discussion).

TABLE 2. Results from Method 1:
(3 hours at 550°C)

Sample number	$\delta^{13}C$ in ‰	
	$CO2$	Total carbon
Fa-13	4.9	-14.9
Fa-13	1.0	-11.4
Fa-14	-2.2	-11.0
Fa-14	0.3	-11.0

TABLE 3. Results from Method 2:
(time study at 950°C)

Sample number	Heating period (Hours)	$\delta^{13}C$ in ‰	
		CO2	Total carbon
Fa-13	1	-4.8	-7.5
Fa-13	2	-7.6	-11.7
Fa-13	3	-7.9	-8.2
Fa-13	5	-9.1	-8.4
Fa-13	7	-7.7	-8.0
Fa-14	1	-6.7	-7.3
Fa-14	2	-14.3	-34.7
Fa-14	3	-12.5	-13.0
Fa-14	6	-12.9	-11.7

TABLE 4. Results from Method 3:
(5 minutes at 550°C)

Sample number	$\delta^{13}C$ in ‰	
	CO2	Total carbon
Fa-14	-2.2	-13.4
Fa-14	-2.3	-13.1
Fa-14	-2.8	-10.7
Fa-14	-4.8	-15.5
Fa-14	-1.9	-
Fa-13	-5.3	-21.8
Fa-13	-4.9	-24.2
Fa-13	-5.3	-19.8
Fa-10	-1.8	-11.2
Fa-10	-1.8	-12.6
Fa-10	-2.3	-
Fa-9	-2.3	-2.8
Fa-9	-1.9	-3.2
Fa-5	-2.3	-7.0
Fa-5	-2.7	-5.1
Fa-5	-4.4	-
Fa-3	-5.4	-6.5
Fa-3	-2.2	-6.6
Fa-3	-2.1	-
Fa-1	-2.2	-3.3
Fa-1	-2.2	-3.3

TABLE 5. $\delta^{13}C$ analyses of carbonate hosted in quartz vein.

Sample number	$\delta^{13}C$
Fa-14	-3.9
Fa-14	-2.4
Fa-14*	-3.2
Fa-13	-3.3
Fa-13	-3.5
Fa-13*	-3.4
Fa-10*	-3.3
Fa-5*	-3.3
Fa-3*	-3.4
Fa-1*	-3.7

* from Fyon (Ph.D. thesis, in prep)

TABLE 6. Volume data obtained using apparatus shown in Fig. 6. Note that the CH_4 volumes are not given as absolute values.

Sample number	Volume of CO2 $\frac{\mu\text{moles}}{\text{gram sample}}$	Volume of CH4 $\frac{\text{displacement(cm)}}{\text{gram sample}}$
Fa-14	1.20	-
Fa-14	1.30	1.09
Fa-13	0.99	-
Fa-10	1.54	1.27
Fa-5	2.48	-
Fa-5	2.52	2.15
Fa-3	3.07	-

3.2 Discussion of Results

3.2.1 Method 1 : 3 Hours at 550°C

The $\delta^{13}C$ values from this method (Table 2) illustrate the large fractionation between reduced carbon and CO_2 at this temperature. This was predicted by Bottinga(1969).

The isotopic signature of the CO_2 ranges from -2.2 ‰ to 4.9 ‰, with a mean of 1.0 ‰. The $\delta^{13}C$ for the total carbon ranges from -11.0 ‰ to -14.9 ‰, with a mean of -12.1 ‰. The interesting observation here is that the mean values differ by 13.1 ‰. This exactly matches the fractionation factor between CO_2 and CH_4 (at 550°C) predicted from Figure 3.

These results are difficult to explain. The light total carbon values may indicate that the $\delta^{13}C$ values are dominated by the isotopic signature of the CH_4. However, this implies a very high CH_4/CO_2 ratio in the inclusions, a feature which is not expected from an examination of the data in Table 1.

The heavy values for the CO_2 are also unusual. They are distinct from all other CO_2 values obtained in this study. It is probably safe to postulate that these heavy values are the result of isotopic exchange between the CO_2 and CH_4 through the reaction:

$$^{12}CO_2 + {}^{13}CH_4 = {}^{13}CO_2 + {}^{12}CH_4$$

The fact that isotope exchange probably occured with extended heating suggest that the CH_4 and CO_2 in the Fa-13 and Fa-14 samples are not in isotopic equilibrium in the inclusions. This, in turn, implies that the CO_2 and CH_4 probably occupied separate inclusions in the samples. This would explain the isotopic exchange which occurs upon decrepitation. Thus, it is likely that separate inclusions of methane and CO_2 exist in the samples and that little mixing of the two has occured prior to decrepitation(Fig. 9).

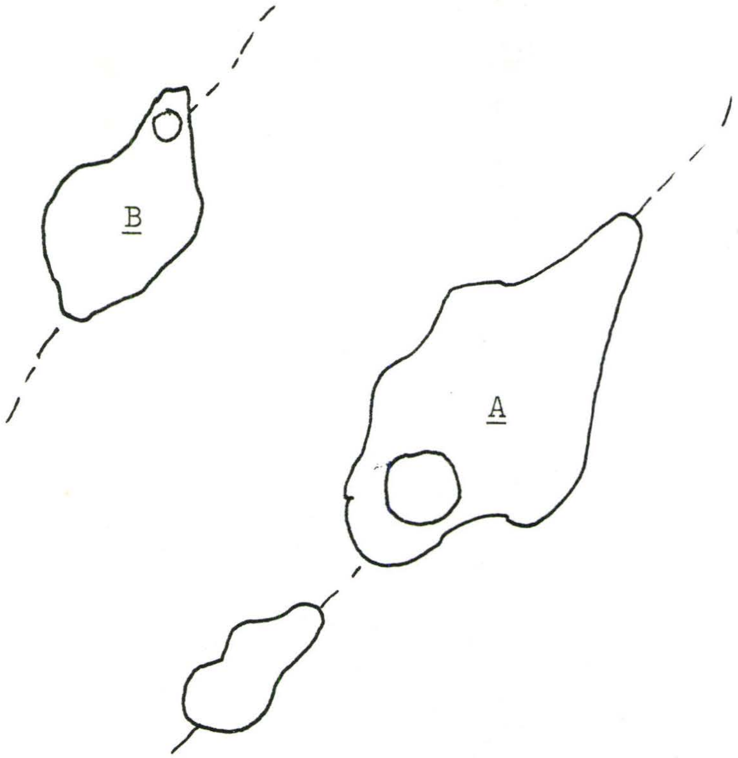


FIG. 9 Schematic representation of fluid inclusions in samples Fa-14 and Fa-13. Inclusion A is CO_2-rich with minor CH_4. Inclusion B has CH_4 as a dominant species. These separate inclusions probably represent multiple fluid generations.

3.2.2 Method 2 : Time Study at 950°C

As predicted by Bottinga(1969) and by Kreulen(1980), the $\delta^{13}C$ values obtained at 950°C display smaller fractionation effects in comparison to the values obtained at 550°C. This implies that isotope exchange was much more complete at this elevated temperature.

With prolonged heating (i.e., greater than 3 hours), the $\delta^{13}C$ values obtained with and without the oxidizing agent become essentially the same. Two possible explanations for this result are:

a) All the reduced carbon in the tubes is being oxidized regardless of whether or not CuO is present. This oxidation is probably the result of the elevated temperature and extended heating period. A possible oxidizing agent is H_2O. The reaction can be written as follows;

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

b) Isotopic exchange at this elevated temperature is extensive. As a result, the fractionation factor between CO_2 and CH_4 is small and the $\delta^{13}C$ of the CO_2 and total carbon are very similar.

The $\delta^{13}C$ values obtained from this method are also difficult to interpret in terms of a possible origin for the carbon. The isotopic values of the CO_2 liberated after one hour of heating are probably the most significant from this method, since they have undergone the least exchange. For Fa-13 and Fa-14, these values fall in the range of -4.8 ‰ to -6.7 ‰ (Table 3). These values are typical of a magmatic source for the CO_2 (see later discussion).

The $\delta^{13}C$ for the total carbon are considerably heavier than the corresponding values from the 5 minute study at 550°C (Table 4). This total carbon value should be the same for all run conditions of a given sample since it is an inventory of all the carbon atoms. Possible reasons for a difference include;

a) Partial or slow reaction of CuO with a reduced, solid C (possibly graphite). The problem here is that graphite was not observed in any of the samples.

b) Incomplete decrepitation of inclusions in shorter runs. This is unlikely since complete decrepitation of the inclusions could be expected within a very short time period at this elevated temperature.

It is obvious from the above discussion, that no simple explanation exists for the data obtained from this method.

3.2.3 Method 3 : 5 Minutes at 550 C

The $\delta^{13}C$ values of the CO_2 obtained from this method range from -1.8 ‰ to -5.4 ‰, with a mean of -3.0 ‰. The $\delta^{13}C$ of the total carbon fall into two clusters. The values from Fa-14, Fa-13 and Fa-10 are much lighter than the values from Fa-9, Fa-5, Fa-3 and Fa-1 (see Table 4) . Thus, in this discussion, Fa-14, Fa-13 and Fa-10 will be referred to as Group 1. The remaining samples are classified as Group 2.

An examination of Figure 2 reveals that all the samples in Group 1 were collected from the same site. Thus the light total carbon values for Group 1 are probably a local anomaly (e.g. graphite) or due to a spatial variation in the isotopic composition of the fluid.

The very narrow range in the $\delta^{13}C$ of the CO_2 component leaves little doubt that the grouping of the total carbon values is related to the abundance or isotopic composition of the reduced carbon component (i.e., methane). If the grouping of values was an isotopic fractionation effect, a corresponding grouping of the $\delta^{13}C$ of the CO_2 would also be expected. This was not observed. Thus, there are two likely explanations for the light total carbon values of the Group 1 samples;

a) Differences in abundance of reduced carbon.

b) Difference in the $\delta^{13}C$ values of the reduced carbon.

The limited volume measurements(Table 6) indicate that the volume of the CO_2 component liberated from the Group 1 samples, per unit weight of quartz, is about 1/2 the volume released by the Group 2 samples. This may be a contributing factor to the light total carbon values for the Group 1 samples. A lower percent of CO_2 would tend to shift the total carbon values towards a lighter value, even assuming a constant $\delta^{13}C$ for the reduced component.

A single measurement of the volume of non-condensibles released by Fa-14, Fa-10 and Fa-5 (Table 6), reveals that Fa-14 and Fa-10(from Group 1) also have a lower non-condensible yield than Fa-5(from Group 2). Thus it is possible that the actual ratio of non-condensible gas to CO_2 in the Group 1 samples may be greater than in the Group 2 samples. The implication here is that most of the non-condensible gas in the Group 2 samples is not methane, etc.. but instead, some unknown species (e.g. N_2) which does not contribute to the carbon isotopic signature.

A simple mass balance calculation demonstrates the considerable amount of methane required to explain the light $\delta^{13}C$ of the total carbon obtained from Fa-14. Using a $\delta^{13}C$ of -2.5 ‰ for the CO_2 and -30.0 ‰ (Hulston and

McCabe, 1962) for the CH_4, a mixture of 60% CO_2 and 40% CH_4 would be required to explain the total carbon value of -12.1 ‰ (Table 4). Even if the $\delta^{13}C$ value of the CH_4 is assumed to be as light as -60.0 ‰, mass balance equations indicate that 20% CH_4 would still be required. This is far in excess of the values listed in Table 1 (from Smith, Cloke and Kesler, 1984).

If mass balance calculations are now performed with the Fa-1 data(Table 4), using a mean $\delta^{13}C$ of -2.1 ‰ for the CO_2 and -30.0 ‰ for the CH_4, a mixture of 96% CO_2 and only 4% CH_4 would be required to explain the total carbon value of -3.3 ‰. These percentages are in much closer agreement with the values in Table 1.

Thus the $\delta^{13}C$ values for the total carbon for Fa-14, Fa-13 and Fa-10 are probably the result of a local event which enriched these samples in ^{12}C enriched CH_4. The data from Table 2 also suggests a high abundance of CH_4 in these samples. This may be due to a localized fluid generation rich in CH_4 or the result of graphite contamination at these sample sites.

The total carbon values from Fa-9, Fa-5, Fa-3 and Fa 1 indicate that these samples were not enriched in in CH_4 or other reduced carbon species. Thus the mean total carbon $\delta^{13}C$ of -4.7 ‰ is assumed to be representative of the main fluid phase. This value will be used in the discussion of possible fluid sources.

A comparison of the isotopic signatures of the CO_2 from Table 2 and Table 4 reveals quite a contrast in the values. As discussed previously, the $\delta^{13}C$ values from Table 2 are probably the result of isotopic fractionation. The mean value of -3.0 ‰ from Table 4 probably reflects the original value of the CO_2 in the fluids much more closely. This is a result of the short heating period used in Method 3, which limits isotopic exchange.

3.3 Fluid Source

From the discussion of Method 3, it is assumed that the $\delta^{13}C$ of the CO_2 and total carbon from the main fluid generation, are -3.0 ‰ and -4.7 ‰ respectively. The -3.0 ‰ value represents the mean of the $\delta^{13}C$ of the CO_2 for all samples analysed using Method 3. The total carbon value of -4.7 ‰ represents the mean for Fa-9, Fa-5, Fa-3 and Fa-1. The total carbon values for Fa-14 Fa-13 and Fa-10 were omitted since these samples are believed to be enriched in light carbon, possibly from a second fluid generation.

Carbon bearing fluids may be derived from a single reservoir or from a mixture of two or more reservoirs. An examination of the carbonate $\delta^{13}C$ values (Table 5), reveals very consistent values. This also applies to the $\delta^{13}C$ values of the CO_2. These consistent values suggest a homogeneous source for the carbon and may also be evidence that the carbon was derived from a single reservoir (A. Fyon, oral commun.,1985). If more than one reservoir was involved, the isotopic signature would be expected to fluctuate much more since the input from each reservoir would probably vary at different sites. However, since the sample sites are proximal to one another, this variation expected from a multiple source would be difficult to detect.

Potential carbon reservoirs are displayed in Figure 10 (Fyon, Ph.D. thesis, in prep.) and in Figure 11 (Hoefs, 1980). A multiple reservoir would involve some combination of these. Combinations that could produce $\delta^{13}C$ values in the -4.7 ‰ range include:

a)Magmatic + decarbonatization carbon

b)Organic carbon + decarbonatization carbon

c)Magmatic + organic carbon

Decarbonatization is believed to be a likely source of CO_2 in metamorphic fluids (Kreulen, 1980). It involves the reaction:

$$5\ \text{dol} + 8\ \text{qtz} + H_2O = 1\ \text{tremolite} + 3\ \text{calcite} + 7\ CO_2$$

The absence of tremolite in any of the samples is strong evidence that the CO_2 was not locally derived from a metamorphic fluid. As a result, possibilities (b) and (a) can probably be eliminated as potential sources of carbon.

Evidence for a mixture of magmatic and organic carbon is quite strong. First, the isotopic signature of the CO_2 (-3.0 ‰) falls within the predicted range for a magmatic origin(see Fig. 11). Secondly, the total carbon values for the samples fall into two broad groups(Table 4) suggesting varied ratios of organic and magmatic carbon (as expected from a multiple reservoir system). Thus, possibility (c) could explain the observed $\delta^{13}C$ values of the total carbon and CO_2.

Assuming that the carbon in the fluid originated from a single reservoir, the total carbon value of -4.7 ‰ points directly to a magmatic source (Fig. 10). The CO_2 in the magmatic fluid probably reacted and fractionated to produce CH_4. This would explain the value of -3.0 ‰ for the CO_2 and the presence of CH_4. The isotopic signature of the CH_4 is assumed to be approximately -30 ‰.

The light total carbon values for Fa-14, Fa-13 and Fa-10 appear to be the result of an abundance of CH_4 rich inclusions in the samples. This CH_4 was probably introduced into the quartz by a separate fluid generation since it does not appear to be in isotopic equilibrium with the CO_2. Thus, it is quite probable that the inclusions represent multiple generations of fluid.

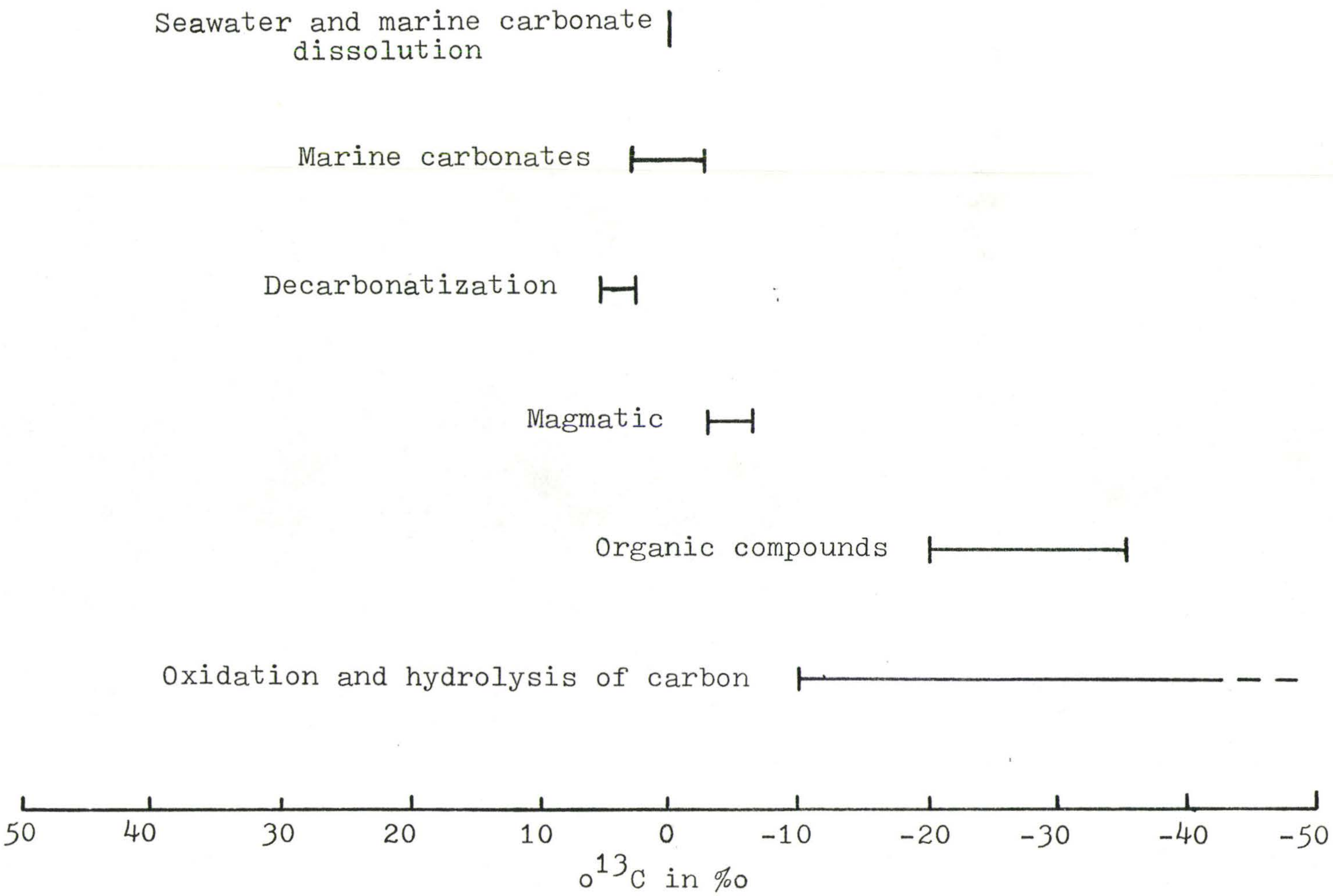


FIG.10. Carbon reservoirs, with their carbon iotopic compositions (from Fyon, Ph.D. thesis, in prep).

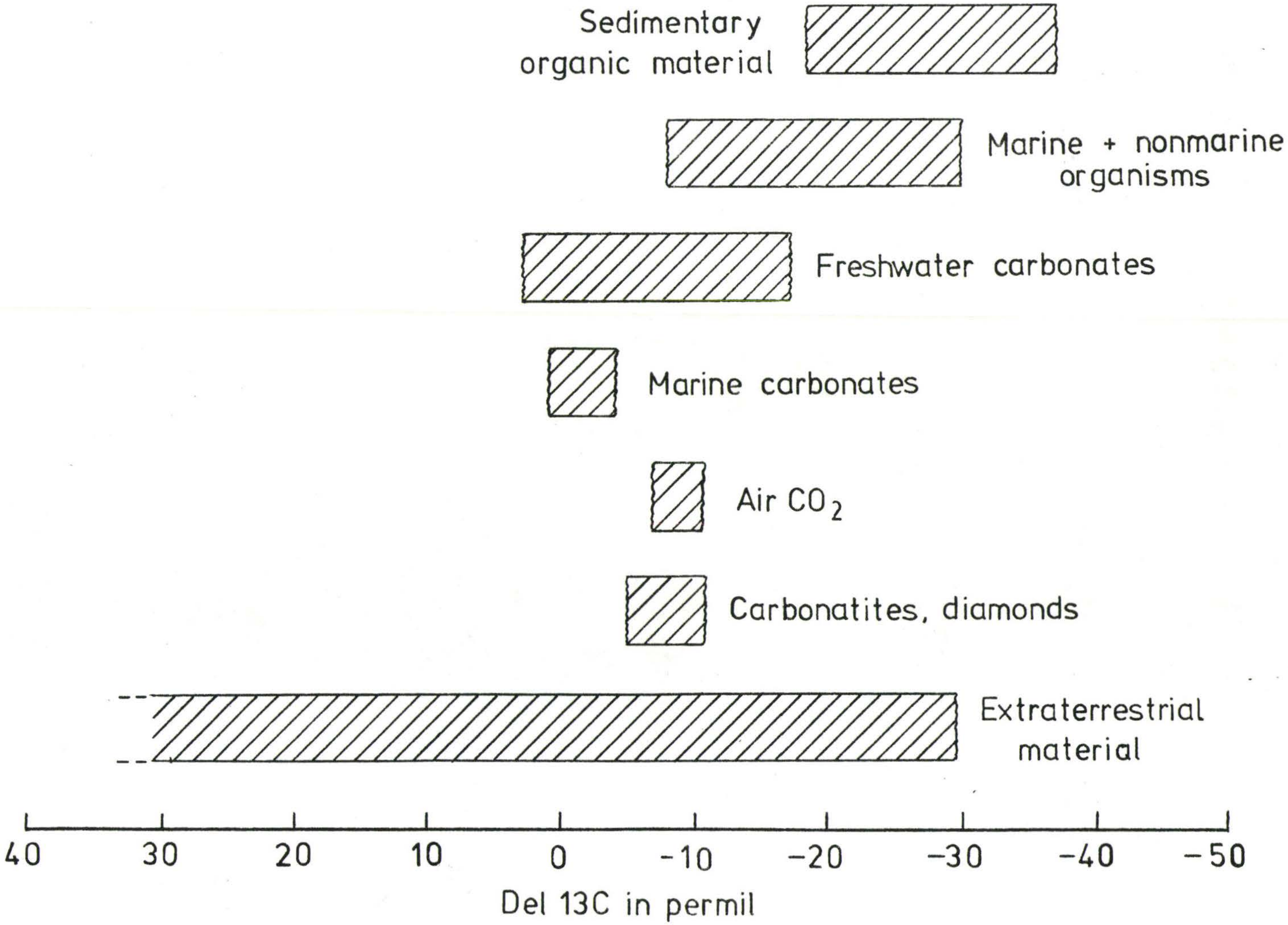


FIG. 11. Carbon isotopic composition of various sources of carbon (from Hoefs, 1980)

CHAPTER 4

4.1 Conclusions

Of the three analytical methods used in this study, Method 3 (5 minutes at 550°C) appears to be the most useful. This combination decrepitates a majority of the inclusions but reduces fractionation and reaction effects to a minimum. The carbon isotopic values obtained from this method are assumed to be representative of the carbon in the inclusions.

The carbon appears to have been derived from a magmatic reservoir. This interpretation is supported by the mean total carbon value of -4.7 ‰, for the samples Fa-9, Fa-5, Fa-3 and Fa-1(Method 3), which falls exactly within the range of $\delta^{13}C$ values for a magmatic source. The light total carbon values for Fa-10, Fa-13 and Fa-14 (Method 3) are believed to represent a secondary, local enrichment in CH_4 or other reduced carbon species. This is also supported by the light total carbon values obtained for Fa-14 and Fa-13 using Method 1 and 2.

Petrographic evidence, combined with Roedders' criterion, indicates that a majority of the fluid inclusions are secondary. As a result, the contents are not samples of the CO_2 rich fluids which deposited the quartz-carbonate vein material. Instead, they represent a later fluid generation. Thus, the carbon isotopic signatures obtained from the "batch" analyses of the inclusions are probably representative of this later fluid generation.

The observation that most of the mineralization in these veins is located in fractures and breccia zones, suggests that the mineral-bearing fluids are also secondary to fluids which deposited the quartz-carbonate host. The interesting possibility here is a correlation between this ore-bearing fluid and the fluid inclusion contents. If this correlation does exist, then it may be possible to identify these ore-bearing fluids using the carbon isotopes associated with the fluid. However, since only one vein system was studied, it is impossible to conclude that ore-bearing fluids have a distinct carbon isotopic signature.

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