5.2.0. Carbon and Oxygen Isotope Data From Carbonates.

5.2.1 Carbon Isotopes

Carbon isotope studies have not been used as extensively in ore deposit research as other isotopes, such as H, O and S. This is because carbon bearing-minerals commonly post-date the main stages of mineralization. Nevertheless, investigations of isotope compositions of carbon-bearing species in ore deposits and geothermal systems may still provide valuable information on physiochemical conditions of ore precipitation and on possible carbon sources.

5.2.2. Carbon Isotopic Variation

5.2.2.1 Near-Surface Environments

The $\delta^{13}C$ value of the atmosphere is about -7 $^0/_{00}$, except in highly polluted areas (Hoefs, 1980). The dissolved carbonate in the oceans occurs mostly as HCO_3-, and has $\delta^{13}C$ values near 0 $^0/_{00}$ which suggests isotopic equilibrium with atmospheric CO_2. Modern marine carbonates have $d^{13}C$ values in the range -1 to +2 $^0/_{00}$, with an average of +1 $^0/_{00}$. This suggests that limestones are in isotopic equilibrium with the HCO_3- in the oceans. The $\delta^{13}C$ value of marine organic carbon falls between -30 and -10 $^0/_{00}$ with an average of -22 $^0/_{00}$. Fluids derived from the dissolution and decarbonation of limestone may acquire carbonate (CO_2, H_2CO_3, HCO_3-) which becomes incorporated into the fluid phase. The $d^{13}C$ values of aqueous carbonate produced by such processes may depend on: (1) the $d^{13}C$ values of the carbonate mineral; (2) the relative proportions of the aqueous species; (3) the isotopic fraction factors between fluid species and the carbonate mineral and (4) the degree of decomposition of the carbonate. Under equilibrium conditions, the relative proportions of the aqueous species depends upon both the temperature and the pH of the fluid, whereas the isotopic fractionation factors depend solely on temperature.

5.2.2.2 Carbon Isotopic Composition of the Mantle and Crust

The $\delta^{13}C$ values of diamonds in kimberlites show a very wide range of values between, -35 to +5 $^0/_{00}$, clustering within a range -5 ± 2 $^0/_{00}$, with regional variations (Hoefs, 1980; Deins and Gold, 1973). Whether or not these values represent the $\delta^{13}C$ of mantle

carbon is debatable because the mechanisms and ages of diamond formation are not thoroughly understood. This apparent heterogeneity of mantle carbon may represent (1) the original heterogeneity of the primordial earth or (2) the effects of mantle-crust interaction. The former may hold true because meteorites exhibit a very wide range $\delta^{13}C$ values, from -30 to > +50 $^0/_{00}$ (Hoefs, 1980). Acquired heterogeneity may also be possible if crustal organic material has been recycled back into the mantle by subduction processes. The majority of carbonate associated with carbonatites and kimberlites have $\delta^{13}C$ values in the range of -4.0 to -7.0 $^0/_{00}$ similar to that of diamonds (Baertschi and Silverman, 1951). It is commonly assumed that the CO_2 derived from the mantle should have a $\delta^{13}C$ value around -5 $^0/_{00}$ (Ohmoto and Rye, 1979). Carbon in granitic, mafic and ultramafic rocks shows a much wider range in $\delta^{13}C$ values than average carbonatites (Sheppard and Dawson, 1973). The $\delta^{13}C$ values are commonly between +2 and -10 $^0/_{00}$ for carbonate minerals and -15 to -30 $^0/_{00}$ for reduced carbon (Hoefs, 1980). This spread of data is probably due to a secondary ground water origin or re-equilibration at low temperatures (O'Neil *et al.*, 1969; Hoefs, 1980).

5.2.3. Carbon Isotopic Variations in Archaean Terrains

Hydrothermally precipitated carbonate minerals in veins and wall rocks of Archaean auriferous lode systems are a conspicuous component of the gangue assemblage. This indicates that CO_2 bearing hydrothermal fluids are intimately associated with the gold mineralization. Numerous fluid inclusion studies have documented the presence of oxidized C species associated with gold mineralization processes, where CO_2 is generally 5-20 mol. % (Smith *et al.*, 1984; Ho *et al.* 1985; Ho, 1987; Robert and Kelly, 1987).

From the carbon isotope composition of these minerals, possible sources of the hydrothermal fluids can be inferred or rejected for Archaean mesothermal gold deposits. Recent studies of Archaean gold lode deposits (Donnelly *et al.* 1977;, Fyon *et al.*, 1982, 1983; Golding and Wilson 1983; Golding *et al.*, 1987; Spooner *et al.*, 1985; Kerrich, 1987; Kerrich and Fyfe, 1981; Smith, 1986) have all contributed to the understanding of carbonate precipitation mechanisms and have helped to developed theories on the source of the carbon. Even so, there are various contrasting and controversial views and there are many aspects which remain enigmatic, especially with regard to the origin of the carbon. This is because most fluid inclusion data and stable isotope studies cannot unequivocally discriminate between the two end member genetic hypotheses for the origin of carbon;(1)Juvenile, derived directly from the mantle (Fyon *et al.*, 1984; Colvine *et al.*, 1984; 1988) or from granitic, porphyritic (Burrows *et al.*, 1986; Burrows and

Spooner, 1987; Cameron and Hattori, 1987; Spooner *et al.*, 1987; 1985) or lamprophyric (Rock *et al.*, 1987; 1988 a,b) intrusions.(2)Via decarbonation or dissolution of pre-existing carbonates and/or dehydration of silicates during deep level granulite metamorphism (Groves *et al.*, 1985; Kerrich, 1983; Kerrich and Fyfe, 1979; Golding *et al.*, 1987).

The Archaean granodiorite-hosted molybdenite deposit at Mink Lake, Canada, has been identified as a magmatic deposit where the CO_2-H_2O fluids responsible for mineralization were derived from the cooling intrusion (Burrows and Spooner, 1987). Other Archaean deposits have indistinguishable carbon isotope ratios to the Mink Lake intrusion, implying that they too are magmatic.

The $\delta^{13}C$ of magmatic CO_2 is estimated to range from -3 to -7 $^0/_{00}$ (Hoefs, 1980) and thus approximates to that of the deduced Archaean mesothermal fluids. The variations observed within and between deposits may be explained by isotopic shift induced by minor amounts of methane (< 10 mole %) present in the fluid. A contribution of carbon from the oxidation or hydrolysis of low ^{13}C-bearing hydrocarbons in interflow sediments may produce more severe ^{13}C depletions (Fyon *et al.*, 1982, 1984).

Archaean sea water has been proposed as a source of hydrothermal carbon (Fyon and Crocket, 1982; Kerrich and Fyfe, 1981), however the following points argue against this source. The $\delta^{13}C$ of dissolved Archaean sea water is estimated to have been approximately 0 $^0/_{00}$ (Schidlowski *et al.*, 1975). Thus sea water recharging into the oceanic crust would be stripped of dissolved CO_2 by buffering reactions with calcium-aluminosilicates, such as clay or zeolites (Thompson, 1971) to produce dispersed calcite. The product of such a sea water recharge process would result in vesicle-filling calcite with an $\delta^{13}C$ value of 0 to -3 $^0/_{00}$, depending on the temperature and water/rock ratios. The derivation of hydrothermal carbon by prograde decarbonation reactions of this material would result in CO_2 gas which would be enriched in ^{13}C by +3 to +5 $^0/_{00}$, relative to the starting material (Sheppard and Schwarcz, 1970). Thus CO_2 gas generated by the carbonatization of disseminated calcite, formed during the low temperature sea water alteration of basalts, would have a $\delta^{13}C$ value of 0 to +4 $^0/_{00}$, a value which is inconsistent with the deduced $\delta^{13}C$ of gold related hydrothermal fluids. Major gold deposits have $\delta^{13}C$ values too negative (Hollinger-McIntyre, -3.1 ± 1.3 $^0/_{00}$; Golden Mile -3.4 ± 0.4 $^0/_{00}$) to have been derived from CO_2 liberated during metamorphic decarbonation of this carbonate. Dispersed regional calcite unrelated to mineralization in the Timmins area (Schidlowski *et al.*, 1975) and the Yilgarn Block (Golding *et al.*,

1987) have average $\delta^{13}C$ values of -1.7 $^0/_{00}$ and -1.4 $^0/_{00}$ respectively, values which are consistent with regional sea water alteration.

In the Canadian and Western Australian greenstone belts there are zones of intense carbonatization superimposed upon the early dispersed calcite. These are commonly centred on quartz carbonate veins or on shear zones (Burrows and Spooner, 1986; Wood *et al.*, 1986). These zones of carbonatization are regionally distributed and are related to late zones of deformation and gold mineralization (Fyon and Crocket, 1982). In the Timmins greenstone the $\delta^{13}C$ values of replacement dolomite-ankerite and magnesite range from -5 to 0 $^0/_{00}$, with a mode of -3.5 $^0/_{00}$, while Western Australia carbonates have a mean $\delta^{13}C$ value of -5.1 $^0/_{00}$ (Golding *et al.* 1987).

Groves *et al.* (1988), also recognized two Archaean carbon-in-carbonate reservoirs which predate the regional metamorphism and gold mineralization in the Norseman-Wiluna greenstone belt of Western Australia. These reservoirs are the sea floor alteration and fault-controlled regional alteration and have been shown to have completely different carbon isotope compositions. The depleted $\delta^{13}C$ values for the fault-controlled regional alteration ($\delta^{13}C$ = -4.8 $^0/_{00}$) implies a juvenile source of carbon flux from the mantle. Groves *et al.* (1988), proposed that the existence of these two carbon-in-carbonate reservoirs, and variations in values between individual deposits, negated some of the fundamental assumptions used to support magmatic fluid models. They propose that the fault-controlled carbonate reservoir is likely to have provided the CO_2 for metamorphic fluids involved in gold mineralization, because it occurs at lower stratigraphic levels and is concentrated along crustal structures which subsequently controlled the distribution of gold deposits. The fault-controlled alteration involved CO_2 of mantle or magmatic origin, channelled by transcrustal fault systems (McNaughton *et al.*, 1990). Thus it would be difficult to distinguish between models which invoke the reworking of this mantle derived carbonate into metamorphic fluids, from those which involve the direct involvement of mantle fluids. Golding *et al.* (1987), Perring *et al.* (1987), Kerrich (1986) and Kerrich *et al.* (1987) emphasize the "pronounced provinciality" of carbon isotope data and suggest that this favours the generation of CO_2 by metamorphic (greenstone belt - scale), rather than by magmatic (mantle - scale) processes. However, the carbon isotope data on mantle-derived carbon illustrates that the $\delta^{13}C$ values for mantle-derived CO_2 themselves are not uniform. The "provinciality" is typical of carbonate carbon isotope data (Deines and Gold, 1973). Furthermore, it is difficult to assess the degree to which the "provinciality" in the Archaean data reflects differences in isotopic composition at the

source, isotopic fractionation between oxidized and reduced carbon species during fluid evolution from source up to and at deposition, or isotopic fractionation during progressive fluid/rock interaction at the depositional site.

In a stable isotope study of carbonate minerals of the Barberton and Murchison greenstone belts, Smith (1986) concluded that two sources of carbon could be identified. The first of these is possibly due sea water alteration, while the second, with a $\delta^{13}C$ value of $\pm$ -7 $^0/_{00}$ is derived from a mantle origin. He noted that the most of the carbonates from the mineralized Antimony Line could not have been derived from Archaean sea water and were most likely to have been derived from a primary source.

A combination of various sources could produce the desired $\delta^{13}C$ for the observed hydrothermal fluids. However, the uniformity of the $\delta^{13}C$ over broad areas, regardless of stratigraphic position, rock type or gold tenor, even on a world-wide scale, argues against such a model. Small systematic variations within carbonates may arise due to the interaction of hydrothermal fluids, but may also occur as a result of immiscible separation of CO_2 + CH_4, as well as Rayleigh fractionation effects.

Several studies of the fluids involved in metamorphism and vein formation within metamorphic terrains have reported CO_2 contents of the fluids, thus suggesting a complex source for the CO_2 (Kerrich *et al.*, 1987; Frost and Frost, 1987). However, granulite fluids are widely documented to be CO_2 rich with very low H_2O contents, and are not mixed H_2O-CO_2, as observed in gold related deposits (Touret, 1981). The transformation of lower crustal rocks to granulites during Archaean cratonization as the most important process driving the ore-fluid system (as proposed by Colvine *et al.*, 1988) is based on two lines of evidence. First that lithophile element enrichment is a characteristic of the deposit (Kerrich, 1986; Davies *et al.*, 1982) and is considered to be directly complimentary to the depletion of these elements in granulites and second, that the calculated $\delta^{13}C$ values can be equated with a juvenile source. However, Kerrich (1989), discounts this model as its fails to account for several important features, including the characteristic LIL-systematics of K-silicate alteration.

5.2.4. Isotopic Composition of the Murchison Schist Belt Carbonates

^{18}O and ^{13}C were determined for ferroan-dolomite from the altered, mineralized Discovery Shaft and Malati Store intrusions and the sheared auriferous pyritic schist at Discovery Shaft. Carbonated schists which occur regionally, but are unrelated to any mineralization, were also analysed to test the hypothesis that a sea water alteration carbonate component exists in the Murchison Schist belt (Smith, 1986). Quartz-carbonate veins from various abandoned quartz-lode deposits along the southern flank of the Murchison schist belt were also analysed to see whether the fluids responsible for alteration and mineralization in the granitoid intrusives were also related to spatially associated quartz-lode deposits. Samples of stibnite-calcite mineralization from the Antimony Line were analysed to obtain the isotopic composition of the fluids involved in the mineralization of this structure.

5.2.5. Methods

CO_2 was liberated from the carbonates with 100% phosphoric acid at 25 °C. The reaction is as follows:

$$3CaCO_3 + 2H_3(PO_4) = 3CO_2 + 3H_2O + Ca_3(PO_4)_2$$

The samples were allowed to stand overnight to allow complete liberation of the CO_2. The gas was analysed on a dual inlet mass spectrometer for ^{13}C and ^{18}O. Duplicate samples were run for most of the samples and a precision of 0.1 $^{0}/_{00}$ was obtained for the carbon isotopic determinations and 0.2 $^{0}/_{00}$ for the oxygen values. The dual sample inlet allows the sample under investigation to be compared against a laboratory standard. A reference carbonate sample (ALME 18, USGS) was run periodically to check for malfunctions of the mass spectrometer and for any problems with sample preparation, especially those associated with $\delta^{18}O$ determinations. Apparent differences in $\delta^{18}O$ of a sample can arise as a result of;

(1) The temperature of the acid reaction,

(2) The carbonate to acid ratio and

(3) the grain size of the carbonate.

Consequently an attempt was made to use similar physical conditions during sample and standard preparation so that internal variations could be eliminated.

The carbon isotopes are presented as $\delta^{13}C$ per mil relative to a standard where:-

$$\delta^{13}C\ {}^{0}/_{00} = \frac{(^{13}C/^{12}C)i - (^{13}C/^{12}C)std \times 1000}{(^{13}C/^{12}C)std}$$

where i represents the ratio of the sample.

The carbon isotope standard is the Chicago PDB sample, where $^{13}C/^{12}C = 0.0112372$, (Craig, 1957).

The oxygen isotope data is presented as $\delta^{18}O$ per mil relative to a standard, where

$$\delta^{18}O\ {}^{0}/_{00} = \frac{(^{18}O/^{16}O)i - (^{18}O/^{16}O)std \times 1000}{(^{18}O/^{16}O)std}$$

where i represents the ratio of the sample.

The standard used here is Standard Mean Ocean Water (SMOW) (Craig, 1961).

5.2.6. Results

5.2.6.1 Carbon Isotopes

The results obtained for the granitoid bodies and the surrounding, regionally carbonated schist are depleted in ^{13}C, relative to PDB, and show a wide range of the $\delta^{13}C$ data from -2.89 ${}^{0}/_{00}$ to -10.42 ${}^{0}/_{00}$. The albitized intrusions were found to have a restricted range in $\delta^{13}C$ values. The $\delta^{13}C$ isotopic composition of the carbonates from the Discovery Shaft and Malati Store intrusions, as well as the pyritic schist at Discovery Shaft Mine, are presented in Table 5.2.1. The isotope composition of the regionally carbonated schists, the quartz-lode deposits and the Antimony Line samples are presented in Table 5.2.2. The various statistical parameters are presented in Table 5.2.3.

Malati Store Intrusion (MSI)			Discovery Shaft Intrusion (DSI)		
Sample	$\delta^{13}C$	$\delta^{18}O$	Sample	$\delta^{13}C$	$\delta^{18}O$
MUL.14	-4.45*	9.87	DIS.12	-3.43*	9.45
MUL.2	-7.78	11.55	KE.34	-4.19*	9.80
MUL.3	-8.09	12.92	DIS.2	-7.72	10.40
MUL.4	-9.03	11.06	DIS.3	-6.16	10.80
MUL.5	-8..4	11.24	DIS.4	-6.56	9.53
MUL.6	-8.04	12.87	DIS.5	-5.70	9.79
MUL.7	-7.04	12.07	DIS.6	-6.77	9.43
MUL.8	-7.95	13.04	DIS.7	-6.55	9.51
MUL.9	-8.11	11.25	DIS.8	-7.47	10.78
MUL.10	-9.45	12.25	DIS.9	-6.69	9.86
MM1.96	-7.01	11.75	DIS.10	-6.33	9.39
MM1.100	-7.58	12.43	DIS.13	-6.24	9.58
MM1.100	-7.35	12.31	DIS.15	-5.39	9.34
MAL.2	-7.78	11.56	KE21.1	-7.37	9.18
MAL.4	-8.15	12.91	KE21.2	-7.55	9.28
MAL.6	-10.42	13.38	KE21.3	-6.21	9.60
MAL.7	-8.80	12.95	KE21.5	-5.99	10.61
MAL.8	-7.94	11.25	KE21.6	-4.85	10.18
MAL.9	-7.20	11.98	KE34.4	-6.92	9.88
MAL.10	-8.30	12.65	KE34.5	-6.41	10.37
MAL.11	-8.08	12.98	KE34.6	-6.29	9.38
MAL.12	-8.45	11.69	PIT.4	-6.06	10.36
MAL.13	-8.15	12.10	11.11	-5.20	9.86
MAL.14	-8.42	11.63	11.10	-6.90	9.24
MAL.15	-7.80	12.69	11.19	-7.10	10.22
MM5.6	-6.90	11.99	11.21	-5.48	9.63
MM5.7	-7.5	11.45	11.20	-6.18	9.73
Average	-8.07	12.15	Average	-6.40	9.98

* - Samples rejected at a 95% confidence limit

Discovery Pyritic Schist (DPS)		
Sample	$\delta^{13}C$	$\delta^{18}O$
ORE.3.1	-6.56	9.85
ORE.9.1	-7.12	10.21
ORE.11.2	-7.46	9.56
ORE.11.3	-5.70	9.88
Average	-6.79	9.88

Table 5.2.1. $\delta^{13}C$ AND $\delta^{18}O$ VALUES FOR CARBONATE FROM THE DISCOVERY SHAFT INTRUSION, MALATI STORE INTRUSION AND THE DISCOVERY SHAFT PYRITIC SCHISTS

Regionally Carbonated Schists (RCS)		
Sample	$\delta^{13}C$	$\delta^{18}O$
GEM.1	-5.65*	10.34
GEM.3	-4.39*	11.43
GEM.5	-6.12*	11.34
SUT.9	-5.98*	10.66
MIN.6	-6.25*	11.52
FGT.7	-5.45*	12.51
DFR.1	-7.49*	10.56
LEY.2	-3.52	9.46
LEY.3	-3.60	9.56
LEY.4	-3.48	9.46
LEY.8	-3.10	10.17
SUT.4	-2.89	9.86
SUT.5	-3.41	10.49
SUT.7	-4.24	11.20
BVB.3	-3.43	9.32
BVB.4	-3.15	9.69
BER.6	-3.29	10.11
BER.7	-3.05	9.74
ANY.5	-4.70	10.34
ANY.8	-3.00	10.21
MAR.5	-3.70	9.89
MAR.3	-3.64	10.80
LET.1	-3.20	10.01
LET.2	-3.33	9.56
LET.3	-3.20	9.86
LFC.3	-4.12	10.91
LFC.5	-4.26	9.34
Average	-3.52	10.00

Regional Gold-Quartz Lode Deposits (QCV)		
Sample	$\delta^{13}C$	$\delta^{18}O$
BJM.3	-3.45*	9.32
BJM.5	-2.76*	10.23
BJM.7	-3.05*	9.82
LFC.6	-4.13*	9.91
LFC.8	-5.16	9.77
SOT.4	-5.49	10.23
SOT.6	-6.53	9.23
LEY.6	-6.60	10.26
LRY.9	-5.85	10.23
LRY.10	-7.98	12.06
DUC.4	-6.92	12.25
DUC.6	-6.09	10.26
MIN.7	-6.23	11.26
MIN.8	-7.23	11.89
SUT.1	-5.99	12.30
SUT.2	-6.58	11.34
SUT.3	-7.25	10.34
Average	-6.45	10.88
Antimony Line Mineralization		
Sample	$\delta^{13}C$	$\delta^{18}O$
ANT.2	-6.25	10.34
ANT.3	-5.98	11.51
MON.3	-7.06	11.81
MON.4	-6.45	11.21
Average	-6.44	11.22

* - Samples rejected at a 95% confidence limit

Table 5.2.2. $\delta^{18}O$ AND $\delta^{13}C$ VALUES FOR CARBONATE FROM REGIONALLY CARBONATED SCHISTS, REGIONAL GOLD-LODE DEPOSITS AND THE ANTIMONY LINE

Statistics	DSI	MSI	RCS	RCV	DPS
Samples	25	26	20	14	4
Average	-6.40	-8.06	-3.51	-6.28	-6.81
Median	-6.33	-8.04	-3.42	-6.38	-6.84
Mode	-6.29	-8.45	-3.21	-6.53	-
Std. Deviation	0.74	0.77	0.48	0.96	-
Minimum	-7.72	-10.42	-4.70	-7.98	-
Maximum	-4.85	-6.90	-2.89	-4.13	-
Range	2.87	3.52	1.81	3.85	-

DSI = Discovery Shaft intrusion
MSI = Malati Store intrusion
RCS = Regional carbonated schists
RCV = Regional gold-lode deposits
DPS = Discovery Shaft pyritic schist

Table 5.2.3. STATISTICS OF $\delta^{13}C$ VALUES FROM CARBONATE RELATIVE TO PDB

The carbon isotopic ratios of the Malati Store intrusion show the greatest depletion in ^{13}C, the average being -8.06 ± 0.77 $^{0}/_{00}$ (n = 26, mode = -8.45 $^{0}/_{00}$). One value has been excluded, at a 99% confidence limit, as not being representative of the population. In comparison, the Discovery Shaft intrusion carbonates are less depleted in ^{13}C than the Malati Store intrusion, with an average value of -6.40 ± 0.74 $^{0}/_{00}$ (n = 25, mode = -6.29 $^{0}/_{00}$). Two values have been excluded at a 95% confidence limit as not being representative.

The $\delta^{13}C$ values obtained for the albitized intrusives show a marked difference to those obtained from the regionally carbonated schists. The average carbon isotope value for the regionally carbonated schists is -3.5 ± 0.48 $^{0}/_{00}$ (n = 26, mode = -3.21 $^{0}/_{00}$). This value is obtained by excluding seven values which showed anomalous ^{13}C-depleted values (Table 5.2.2). These samples were obtained in reasonably close proximity to the intrusions and are considered to represent carbonate contamination from the intrusive body and are thus not representative of the carbonated schist population. This indicates that fluids originating from the intrusions permeated the country schists, resulting in the precipitation of hybrid carbonate isotope values. Thus the intrusions are not in carbon isotopic equilibrium with the surrounding country rock. This suggests that there are at least two sources of carbon within the Murchison Schist belt.

The pyritic schist at Discovery Shaft has an average $\delta^{13}C$ value of -6.8 ± 0.87 $^0/_{00}$ (n=4, mode = -7.76 $^0/_{00}$). This average value is statistically similar at a 95% confidence limit to the $\delta^{13}C$ of the Discovery intrusion. This indicates that the fluids related to carbonatization in the Discovery intrusion were also responsible for carbonatization of the mineralized pyritic schist which occurs in close proximity to the intrusion. The mineralized schist is however not in isotopic equilibrium with the surrounding schists of the Discovery pit. Quartz-carbonate veins associated with gold mineralization along the southern flank of the schist belt have an average $\delta^{13}C$ value of -6.28 ± 0.96 $^0/_{00}$ (n = 14, mode = -6.53 $^0/_{00}$). Four values were excluded at a 99% confidence limit as not being representative of the quartz-vein carbonate population (Table 5.2.2). These four samples have statistically similar carbon and oxygen isotope compositions as the carbonated schists and possibly represent quartz-carbonate veins derived from the country rocks. This is a common problem associated with sampling abandoned mines in obtaining representative material of the mineralized zone. The average $\delta^{13}C$ isotopic ratios for the quartz-carbonate veins associated with gold mineralization are statistically similar at a 95% confidence limit to those of the carbonates within the Discovery Shaft intrusion. This indicates that the fluids responsible for the alteration and mineralization within the granitoids had similar $\delta^{13}C$ isotopic composition to the fluids responsible for spatially related quartz-lode deposits, indicating a similar fluid source.

The $\delta^{13}C$ content of the carbonate from the mineralized zones of the Antimony Line samples average at -6.44 $^0/_{00}$. This result is statistically indistinguishable, at a 95% confidence limit, to the results of the Discovery Shaft samples.

The $\delta^{13}C$ isotopic composition of the carbonates in the albitized intrusions and the Antimony line are distinctly different from the regional carbonate alteration, which suggests that the latter has not been involved in the mineralizing event and represents another carbon source.

5.2.6.2 Oxygen Isotopes

The $\delta^{18}O$ values for this study have a narrow range from +9.18 to +13.38 $^{0}/_{00}$ and are presented in Table 5.2.1 and Table. 5.2.2. The statistics of the $\delta^{18}O$ data are presented in Table 5.2.4. The carbonate samples excluded from the populations on the basis of their anomalous $\delta^{13}C$ values have also been excluded from the $\delta^{18}O$ data base. The Malati Store intrusion carbonate contains the heaviest oxygen isotope ratios, with an average value of +12.15 ± 0.67 $^{0}/_{00}$ (n = 26, mode = +11.25). The $\delta^{18}O$ values for the Discovery Shaft intrusion carbonate have an average value of +9.98 ± 0.45 $^{0}/_{00}$ (n = 25, mode = +8.86)

Statistics	DSI	MSI	RCS	RCV
Samples	25	26	20	13
Average	9.98	12.15	9.99	10.88
Median	9.73	12.08	9.88	10.34
Mode	9.86	11.25	9.56	10.26
Geometric Mean	9.80	12.13	9.99	10.83
Std. Deviation	0.45	0.67	0.53	1.02
Minimum	9.18	11.06	9.32	9.23
Maximum	10.78	13.38	11.2	12.30
Range	1.60	2.32	1.88	3.07

DSI = Discovery Shaft intrusion
MSI = Malati Store intrusion
RCS = Regionally carbonated schists
RCV = Regional quartz-lode deposits

Table 5.2.4. STATISTICS OF $\delta^{18}O$ VALUES FROM CARBONATE RELATIVE TO SMOW

The $\delta^{18}O$ values of the carbonates from the regional schists are depleted, relative to the Malati Store intrusion, but have values similar to the Discovery Shaft intrusion, with an average value of +9.99 ± 0.53 $^{0}/_{00}$ (n=20, mode = +9.56). The auriferous pyritic schist at Discovery Shaft has an average $\delta^{18}O$ of +9,87 $^{0}/_{00}$ (n = 4, mode = +9.82), which is statistically similar to the Discovery Shaft intrusion.

The similarity between the regional schists, Discovery Shaft intrusion and the Discovery Shaft pyritic schist is possibly due to late oxygen exchange resulting from assimilation of country rock and possible late fluid circulation set up by the intrusive body.

The regional gold quartz-carbonate veins have an average $\delta^{18}O$ value of +10.88 $^0/_{00}$ (n = 13, mode = +10.26) and a large range of 3.07 $^0/_{00}$ (+9.23 to +12.7 $^0/_{00}$), excluding four values rejected on the basis of their $\delta^{13}C$ values. The large range suggests variable fluid rock ratios during their formation and/or interaction and oxygen exchange with possibly late, low temperature fluids from various sources.

All the intrusions have statistically different $d^{18}O$ values to the quartz-lode deposits (at a 95% significant level). If a similar fluid source is evoked for the mineralization within the granitoids and the quartz-lode deposits, as indicated by the $\delta^{13}C$ isotopes, then processes responsible for the variable $\delta^{18}O$ values must be proposed. The $\delta^{18}O$ variations are likely to be due to differences in the temperature, since the $\delta^{18}O$ fractionation of carbonates is highly temperature dependent, especially at lower temperatures. Oxygen exchange with late fluids and variable fluid rock ratios would also have resulted in variable oxygen exchange.

The plot of the $\delta^{13}C$ versus $\delta^{18}O$ for the hydrothermal carbonate from this study (Figure 5.2.1) show that the intrusions plot in distinct fields, with the Malati Store intrusion carbonates having distinctly heavier oxygen and lighter carbon than the Discovery Shaft intrusion. The regional carbonated schists have distinctly heavier carbon than either of the two intrusions, but have similar oxygen isotope compositions to the Discovery Shaft intrusion. The Antimony Line carbonate has carbon and oxygen isotopic compositions that plot within the zones defined by the Malati Store and Discovery Shaft intrusions. This has important genetic implications for the source of the mineralizing fluids within the Antimony Line, as the data indicates similar fluids were responsible for the mineralization. There is a negative correlation between the carbonate $\delta^{18}O$ and $\delta^{13}C$ within the intrusion and between the combined data of the Discovery Shaft and Malati intrusion. There is a fairly large isotopic variation between the two intrusions studied but only a small variation within individual intrusions. This suggests that varying fluid:rock ratios may be responsible for the intra-intrusion carbonate $\delta^{13}C$ - $\delta^{18}O$ variations, as suggested in previous sections. The Discovery Shaft intrusion has probably been characterised by a lower fluid:rock ratio as suggested by the lower degree of alteration. Further reactions brought about by small amounts of methane would also produce a shift towards heavier carbon (Ohmoto and Rye, 1979: Ohmoto, 1972, 1976), a notion which is supported by fluid inclusion data which suggests that fluid inclusions from beryls in the Discovery and Cobra pits contain small amounts of CH_4 (Dr. Yin Yin Nwe. per. com., 1990).

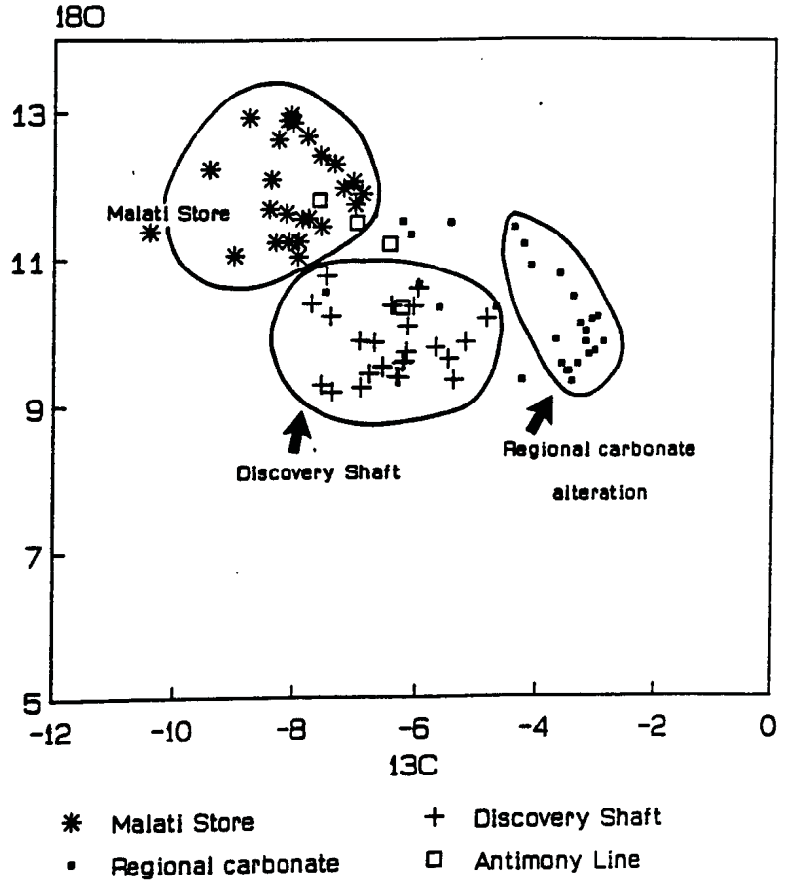

Figure 5.2.1. Plot of $\delta^{13}C$ versus $\delta^{18}O$ values for hydrothermal carbonate from this study.

Temperature variations may also produce the observed isotopic variations. The carbonate-water fractionation curves for $\delta^{18}O$ are positively sloped and, hence, late (lower temperature) carbonate will be enriched in ^{18}O relative to the fluid. Using the calcite-water fractionation curves of O'Neil *et al.*, (1969), calcite is enriched in ^{18}O by $+5.5\,^{0}/_{00}$ at 300 °C and $+9.8\,^{0}/_{00}$ at 200 °C. The fluid inclusion microthermometric data indicate homogenization temperature variations of 50 - 100 °C within the intrusions, which could explain the observed $\delta^{18}O$ variation. Phase separation can also produce $\delta^{18}O$ variations due to the fractionation effects between CO_2 and H_2O. In the case of a finite carbon reservoir, the residual CO_2 and late formed carbonate would be enriched in ^{18}O (Ohmoto and Rye, 1979). This would produce a positive increase in the $\delta^{18}O$ value of the carbonate. Using the extrapolated experimental data of Thode *et al.* (1965) for dissolved carbonate - CO_2(gas) fractionation at temperatures above 130 °C, the CO_2(gas) is enriched in ^{13}C. Hence, in a finite reservoir with phase separation, the precipitated carbonate would be depleted in ^{13}C. At low temperatures ie. below 300 °C, the ^{13}C-CO_2 - carbonate fractionation becomes significant. At 300 °C, the fractionation factor is insignificant ($<1\,^{0}/_{00}$). A temperature decrease from 300 °C to 200 °C would result in a

$1\,^{0}/_{00}$ decrease in the $\delta^{13}C$ value of the precipitated carbonate. The fluid inclusion and equilibrium isotope fractionation temperatures indicate that alteration in the Malati intrusion occurs at a lower temperature than the Discovery Shaft intrusion (200 - 250°C, compared to 300 to 350 °C). The difference in $\delta^{13}C$ values between the two intrusions is $1.66\,^{0}/_{00}$. Hence, the observed differences in the $\delta^{13}C$ and $\delta^{18}O$ values within and between the two intrusions can be largely accounted for by the lower temperature of alteration within the Malati Store intrusion. The carbonate with in the Discovery Shaft intrusion has a similar oxygen isotope composition to the of the regional schist. It is possible that interaction with the country rock carbonates during granodiorite emplacement would have resulted in oxygen exchange. The limited samples from the Antimony line for this study, together with data of Smith (1986), also show slightly negative correlations for the carbonate rocks. Thus with time and/or variable fluid:rock ratios, the carbonates appear to evolve to higher oxygen and lower carbon isotope ratios. The exact mechanism for this process is speculative but the $\delta^{18}O$ variation is most likely to occur as a result of cooling, or possibly to late fluid interaction.

There is a positive correlation between the $\delta^{13}C$ and $\delta^{18}O$ for carbonates from gold-related alteration from the Western Australian deposits. This has been attributed to source heterogeneity, temperature - controlled oxygen isotope evolution and phase separation (Groves *et al.*, 1988).

Figure 5.2.2. is a $\delta^{13}C$ versus $\delta^{18}O$ plot of the fields defined by the albitized intrusions and the regional carbonate alteration, as well as the values from the carbonate associated with auriferous quartz-lode deposits along the southern flank of the schist belt. The isotopic composition of the quartz-carbonate veins are distinctly similar to the carbonate from the albitized intrusions. Generally, the auriferous veins are dissimilar to the regional carbonate alteration, thus excluding this later carbonate from ore forming processes. This infers that similar fluids were responsible for gold mineralization within the albitized intrusions and structurally controlled quartz-lode deposits. The few samples plotting within the regional carbonate field are likely to be due to sampling problems in abandoned mines.

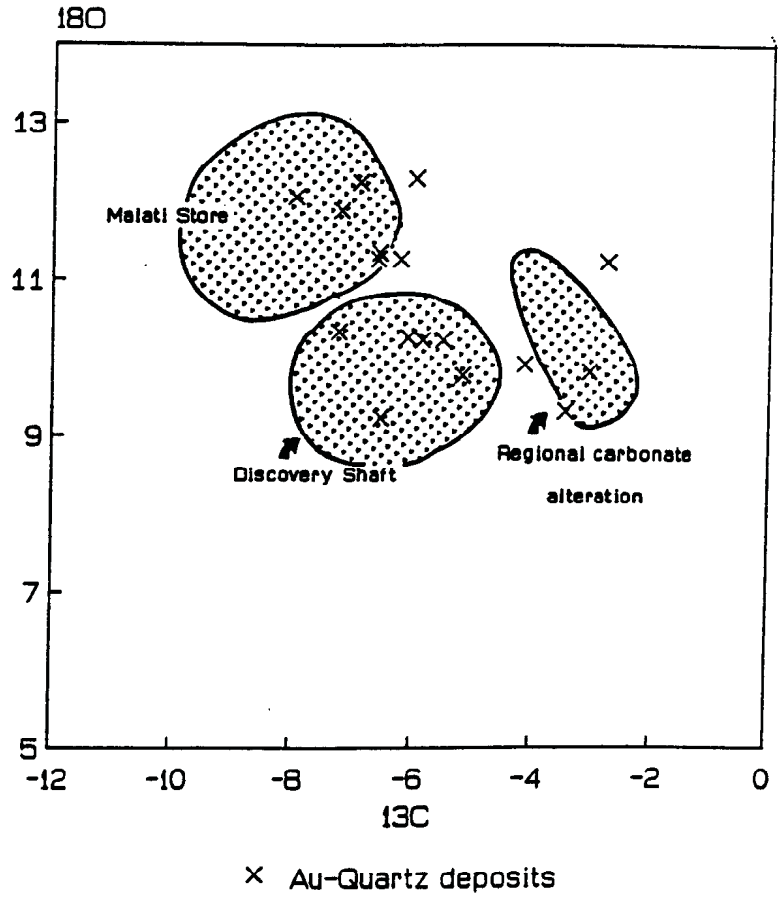

Figure 5.2.2. Plot of $\delta^{13}C$ versus $\delta^{18}O$ showing the distribution of the carbonate from the albitized intrusions and the regional carbonate alteration, compared to the carbonate from the regional gold quartz-lode deposits (X).

Figure 5.2.3 is a graphical representation of the data from this study compared to $\delta^{13}C$ data from a variety of Archaean gold deposits. Although gross similarities to other Archaean gold deposits are present, generally the carbon isotopic compositions from the Murchison area are more negative than most other Archaean deposits.

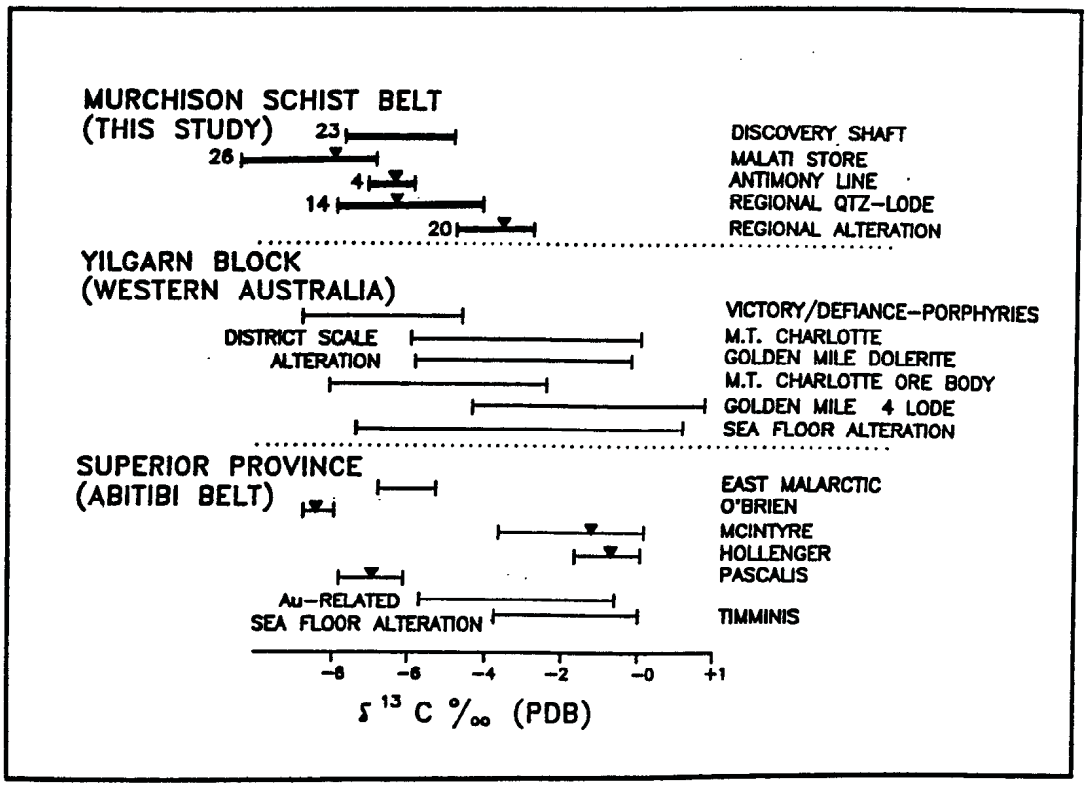

Figure 5.2.3. Carbon isotope values from carbonate from this study compared to $\delta^{13}C$ values from hydrothermal carbonate from other Archaean terrains.
(Adapted from Colvine *et al.*, 1988)

5.2.7 Conclusions

Two distinct, isotopically different fluids appear to have been responsible for the carbonation which occurs in the Murchison schist belt. This indicates that there are at least two carbon sources in Archaean terrains. The carbon associated with gold mineralization is isotopically light (-7 ± 1.0) compared to the carbon associated with the intense regional carbonate alteration (-3 ± 1.0 $^{0}/_{00}$).

The distinctly negative values of the carbon associated with mineralization within the intrusions is interpreted to represent a primary magmatic source, although metamorphic derivation from a juvenile source for the CO_2 cannot be entirely discounted. The carbon isotopic content of the fluid associated with mineralization within the albitized intrusions

and regional quartz-lode deposits is identical to that of the fluids associated with the carbonation and mineralization along the Antimony Line (± -7 $^{0}/_{00}$, Smith, 1986; this study). This similarity can be interpreted to suggest that the mineralizing fluids are genetically related.

The carbon isotope data of Smith (1986), for the regional schists, is also similar to the values obtained in this study (-3 $^{0}/_{00}$). This carbon is interpreted to represent regional Archaean sea water alteration as proposed by Smith (1986). The heavy carbon isotopic composition of this carbonate precludes it from being involved in any ore forming processes in the Murchison Schist belt.

The narrow range of data of the carbonate from this study is strong evidence against metamorphic mixing processes which would be expected to give irregular ranges. The small range of $\delta^{13}C$ and $\delta^{18}O$ values observed within and between the intrusions appears to be due to temperature-controlled isotope evolution, phase separation and late oxygen exchange. The mineralizing fluids were thus derived external to the schist belt. The similarity between the fluids within the granodiorite cupola zones and those of the structurally controlled mineralization throughout the schist belt, suggests that the granodiorite intrusions are intimately related to auriferous fluid generation.

5.3. Oxygen Isotopes of Silicate Minerals.

5.3.1 Introduction

The origin of ore-forming fluids (e.g. magmatic, meteoric, etc.) may be deduced from the analysis of H and O isotopes ratios of the ore forming fluids. Direct and indirect methods can be used to estimate the H and O isotopic composition of these fluids. The direct method involves the determination of the δD and $\delta^{18}O$ of inclusion fluids extracted by decrepitation from host minerals. The indirect method is based on measurement of the $\delta^{18}O$ or δD of hydrothermal minerals (ie. $\delta^{18}O$ from quartz or calcite, and δD for muscovite). The δ value of the mineral is used, together with an estimated temperature of mineralization and the isotopic fractionation factor between the mineral and H_2O, to calculate the δ value of the ore-forming fluid (Taylor, 1979). Uncertainty about the $\delta^{18}O$ fluid values estimated from the indirect method arises largely from uncertainties about the temperature of deposition and the equations for the isotopic fractionation factors. Another source of error in the calculated δ values of fluids is the ambiguity of the effect of fluid chemistry on mineral-water fractionation factors. The results of experimental studies by Truesdell (1974) suggest that a large salinity effect may affect the fractionation factor between minerals and solutions by as much as 3 $^{0}/_{00}$ at temperatures of 600 °C.

The $\delta^{18}O$ content of quartz and carbonate have been used in this study to estimate the $\delta^{18}O$ content of the fluids responsible for the alteration of the granitoids. The temperature of precipitation is estimated from fluid inclusion microthermometry data and from the temperature obtained from the sulphur isotope fractionation between molybdenite and pyrite in the Discovery Shaft intrusion. Using quartz-feldspar and quartz-carbonate $\delta^{18}O$ fractionation, a temperature of gangue mineral precipitation can be theoretically calculated.

5.3.2. Fluid Sources

Sea water, meteoric water and juvenile water may be considered as isotopic references because they have unique isotopic compositions at their source. The term "juvenile" and "magmatic" have been used synonymously by many researchers, but they are not exactly the same. Juvenile water is derived from the mantle and has never existed as surface water. Magmatic water is simply water which co-existed, and is in equilibrium with, magmas. Some granitoid magmas appear to have been formed by partial melting of crustal rocks which contained water (in hydrous minerals) which had previously existed

as surface water. Thus the isotopic compositions of some magmatic waters may be quite different to those of juvenile water. The later is defined as water in isotopic equilibrium with normal mafic magmas ($\delta^{18}O = +6 \pm 0.5\ ^0/_{00}$). Metamorphic waters may vary with the isotope composition of the source rock and the temperature of equilibrium, dehydration, or decarbonation (Taylor, 1979; Ohmoto, 1986).

Taylor and Mclennan (1985), divided granitic rocks into three groups on the basis of their $\delta^{18}O$ composition:-

(1) normal - $\delta^{18}O$ granitic rocks with $\delta^{18}O$ values between +6 and +10 $^0/_{00}$,

(2) high - $\delta^{18}O$ granitic rocks with $\delta^{18}O$ values $> +10\ ^0/_{00}$,

(3) low - $\delta^{18}O$ granitic rocks with $\delta^{18}O$ values $< +6\ ^0/_{00}$.

5.3.3. Archaean Oxygen Isotopes

Oxygen isotope data from vein quartz in Archaean gold-lode deposits have been documented in Canada (Fyon *et al.*, 1982; Colvine *et al.*, 1988; Fyfe and Kerrich, 1982) and Western Australia (Golding, 1982; Golding and Wilson, 1983; Golding *et al.* 1987). In all Archaean gold-lode deposits, the $\delta^{18}O$ value of vein quartz falls consistently in the range of +10 to +16 $^0/_{00}$ (Colvine *et al.*, 1988) and for the most part is independent of the host rock lithology. This suggests that in the majority of cases, high fluid:rock ratios had been established throughout the mineralized zones.

Utilizing experimentally derived mineral-water and mineral pair fractionation equations it appears that the quartz precipitation temperature in Archaean mesothermal mineralization occurred at about 250°C to 375°C, from a fluid $\delta^{18}O$ in equilibrium with the vein quartz calculated to be +5 to $+10\ ^0/_{00}$ (Colvine *et al.*, 1984; McNaughton *et al.*, 1990). The $d^{18}O$ values lie within overlapping fields of magmatic and metamorphic fluids (Colvine *et al.*, 1988). Thus oxygen (and hydrogen) isotopic data cannot unequivocally discriminate between the two genetic end members. Nesbit *et al.* (1986) suggest that low salinity CO_2-rich fluids can be generated by deep meteoric circulation. However the oxygen and hydrogen isotopic data for Archaean gold deposits, are generally not consistent with either a meteoric or marine fluid origin, unless the fluid has undergone extensive oxygen and hydrogen isotopic exchange with the host rocks, in order to become isotopically indistinguishable from either metamorphic or magmatic water (Taylor, 1979). The Lawlers and Lancefield deposits of the Yilgarn Block have low $d^{18}O$ values for this region ($+4\ ^0/_{00}$), which may be interpreted as being due to mixing of an isotopically

lighter fluid (high-latitude meteoric water or sea water) with an igneous/ metamorphic fluid (McNaughton *et al.*, 1990). The same authors note that the consistent $\delta^{18}O$ values for the Yilgarn ore fluids could be due to isotopic equilibrium between ascending ore fluids and the conduit host rocks. In general, Archaean gold-related quartz-carbonate pairs are not in oxygen isotope equilibrium, probably because of the susceptibility of carbonates to later oxygen exchange (Kerrich, 1986).

5.3.4. Samples from this Study

Samples of hydrothermal vein quartz from the stockwork at the Malati Store and Discovery Shaft intrusions were analysed for $\delta^{18}O$ ratios. Whole rock samples from the unaltered Willie intrusion were also analysed. Samples of pure albite from the albitized intrusions were analysed to determine whether an equilibrium fractionation assemblage existed between the albite and quartz and, therefore, whether a temperature of mineral precipitation could be determined. A single $\delta^{18}O$ analysis was undertaken on a quartz sample from the mineralized quartz-gold lode at the Blue Jacket Mine.

5.3.5. Methods of Study

The $\delta^{18}O$ values are expressed using the standard δ-notation in "per mil" units, relative to SMOW (Standard Mean Ocean Water). The oxygen extraction of silicates was performed by the author at the Department of Geochemistry, University of Cape Town, using the technique described by Borthwick and Harmon (1982). Samples of material were crushed and cleaned to remove foreign material and then hand-picked under a binocular microscope to maintain a high degree of sample purity. Between 10 and 20 mg of sample were loaded into nickel reaction vessels which are over-pressured by analytically pure nitrogen to prevent atmospheric contamination. Once loaded, the vessels were evacuated and the samples are allowed to de-gas at 200°C, to approximately 10-5 mbar, for a minimum period of 3 hours. Reaction vessels are then charged with about seven to ten times the stoichiometrically required amount of ClF_3, isolated and heated to between 550 °C and 650 °C, depending on the type of sample. Reaction times varied between 5 and 12 hours. The extracted oxygen is converted to CO_2 by passing it over a hot platinized carbon rod. Manometric yields were accepted if they fell within 2% of the calculated yield for the sample, providing between 50 and 200 µmol of CO_2. Residual gases were passed over heated KBr crystals and frozen into a waste trap. The CO_2 sample was collected by freezing within a liquid nitrogen trap.

The CO_2 was analysed at the Department of Archeometery, University of Cape Town using a VG micromass 602E, double collector mass spectrometer. The results are the average of duplicate samples.

5.3.6. Results

The results of the $\delta^{18}O$ determinations on the hydrothermal quartz and albite from the albitized intrusions are presented in Table 5.3.1. and Table 5.3.2. respectively. The $\delta^{18}O$ values for hydrothermally precipitated quartz from this study exhibit a narrow range, from +11.94 $^0/_{00}$ to +13.82 $^0/_{00}$. The Malati Store intrusion quartz has the highest enrichment in $\delta^{18}O$, with an average value of +13.58 ± 0.15 $^0/_{00}$ (n = 5). The average value for the Discovery intrusion is +12.06 ± 0.16 $^0/_{00}$ (n = 4). A quartz sample from the Blue Jacket mine has a value of +12.34 ± 01.2 $^0/_{00}$, statistically similar to that of the Discovery Shaft intrusion quartz.

Feldspar (albite) from the Discovery Shaft intrusion has $\delta^{18}O$ values of +9.42 ± 0.08 $^0/_{00}$ (n = 4), while feldspars from the Malati Store intrusion have an average value of +10.35 ± 0.14 $^0/_{00}$ (n = 3).

Discovery Shaft Intrusion (DIS)	
Sample	$\delta^{18}O$ $^0/_{00}$
QZT.2	12.14
QZT.3	11.94
QZT.4	12.25
DTW.2	11.91
Average	+12.06
Malati Store Intrusion (MSI)	
Sample	$\delta^{18}O$ $^0/_{00}$
MAL.1	13.43
MAL.3	13.59
MAL.4	13.82
MUL.130	13.46
MUL.156	13.58
Average	+13.58

Table 5.3.1. $\delta^{18}O$ RESULTS FOR HYDROTHERMAL QUARTZ FROM DISCOVERY SHAFT AND MALATI STORE INTRUSIONS

DISCOVERY SHAFT INTRUSION (DSI)	
Sample	**$\delta^{18}O$ $^0/_{00}$**
DISQ.1	9.40
DISQ.2	9.32
DISQ.3	9.45
DISQ.6	9.52
Average	**+9.42**
Malati Store Intrusion (MSI)	
Sample	**$\delta^{18}O$ $^0/_{00}$**
MALSP.1	10.12
MALSP.4	10.33
MALSP.5	10.61
Average	**+10.35**

Table 5.3.2. $\delta^{18}O$ RESULTS FOR FELDSPAR (ALBITE) FROM THE DISCOVERY SHAFT AND MALATI STORE INTRUSIONS

Willie Pluton (whole rock) = +9.45 ± 0.14 $^0/_{00}$
Blue Jacket Mine (mineralized vein quartz) = +12.34 ± 0.21 0/00

Whole rock analyses of the unaltered Willie Pluton have an average $\delta^{18}O$ value of +9.45 ± 0.14 $^0/_{00}$ (n = 2), a value which falls within the range of "average" granitoids as determined by Taylor and Mclennan (1985).

5.3.7. $\delta^{18}O$ Quartz - H_2O Fractionation

The estimated $\delta^{18}O$ value for the hydrothermal fluids involved in the albitization of the intrusions have been calculated for temperatures at 250°C and 300°C. This temperature range is suggested from the estimate of trapping temperatures obtained from the fluid inclusion microthermometry data and the $\delta^{34}S$ molybdenite-pyrite equilibrium fractionation temperature from the Discovery Shaft intrusion. The experimentally determined quartz-water fraction factors (Clayton, *et al.*, 1972) for temperatures of between 200 °C and 500 °C, have been used to calculate the $\delta^{18}O$ of the hydrothermal fluid:

$$10^3 \ln\alpha = 2.51(10^6 . T^{-2}) - 1.46$$

Where $10^3 \ln\alpha \approx {}^*\delta^{18}O \approx \delta^{18}O_{quartz} - \delta^{18}O_{H2O}$

Discovery Shaft intrusion $\delta^{18}O_{quartz}$ = +12.06 +/- 0.16 $^0/_{00}$

Calculated $\delta^{18}O_{fluid}$ (250 °C) = +4.50 to 4.18 $^0/_{00}$

(300 °C) = +6.04 to 5.72 $^0/_{00}$

Malati Store intrusion $\delta^{18}O_{quartz}$ = +13.58 +/- 0.15 $^0/_{00}$

Calculated $\delta^{18}O_{fluid}$ (250 °C) = +6.01 to 5.72 $^0/_{00}$

(300 °C) = +7.75 to 7.26 $^0/_{00}$

The calculated $\delta^{18}O_{fluid}$ for the Discovery Shaft intrusion at T = 300°C is similar to the calculated $\delta^{18}O_{fluid}$ for the Malati Store intrusion at T = 250°C. This may be interpreted to suggest that fluids of similar $\delta^{18}O$ isotopic composition were responsible for the alteration within the two intrusions, except that precipitation of quartz occurred at a lower temperature within the Malati Store intrusion (T = ± 250 °C), thereby producing the observed enrichment in ^{18}O in the quartz of this intrusion. The suggested higher temperature in the Discovery Shaft intrusion is substantiated by the fluid inclusion microthermometry data (See Chapter 6). Thus the calculated mean isotopic $\delta^{18}O$ value for the hydrothermal fluids is estimated to be +6 ± 1 $^0/_{00}$ by this technique.

5.3.8. $\delta^{18}O$ Carbonate - H_2O Fractionation.

The $\delta^{18}O$ values obtained from hydrothermal ferroan-dolomite in the albitized intrusions may be used to calculate the $\delta^{18}O$ of the fluids in equilibrium with carbonate phases. No data is available for ^{18}O fractionation in the ferroan-dolomite-water system. Similarities in the acid fractionation factor and crystal structure suggest that the dolomite-water fractionation may be relevant. The dolomite-water fractionation equation, as defined by Nothop and Clayton (1966), is for temperatures in excess of 300°C. Thus, use has been made of the calcite-water fractionation curve, as experimentally determined by O'Neil *et al.*, (1969), for the temperature range between 0°C - 500°C. The error induced by the difference between ferroan-dolomite and calcite-water fractionation is likely to be less than 1 $^0/_{00}$ at temperatures greater than 200 °C (Ohmoto 1986).

$$10^3 \ln\alpha = 2.78(10^6 . T^{-2}) - 2.89$$

Where $10^3 \ln\alpha \approx {}^*\delta^{18}O \approx \delta^{18}O_{calcite} - \delta^{18}O_{H2O}$

Discovery Shaft intrusion $\delta^{18}O_{carb}$ = $+9.88 \pm 0.45\,^0/_{00}$
Calculated $\delta^{18}O_{fluid}$ (250°C) = **$+3.06 - +2.16\,^0/_{00}$**
(300°C) = **$+4.76 - +3.86\,^0/_{00}$**

Malati Store intrusion $\delta^{18}O_{carb}$ = $+12.12 \pm 0.67\,^0/_{00}$
Calculated $\delta^{18}O_{fluid}$ (250°C) = **$+5.29 - +4.18\,^0/_{00}$**
(300°C) = **$+7.22 - +5.88\,^0/_{00}$**

The calculated $\delta^{18}O$ value for the fluids is lower ($+4 \pm 1\,^0/_{00}$) than that calculated from the quartz-water fractionation. This indicates a possible lack of isotopic equilibrium between quartz, carbonate and the aqueous phase. It is feasible that fluids of low $\delta^{18}O$ values were involved in isotopic exchange with the carbonates, or that the carbonate underwent low temperature re-equilibration. The fact that the carbonates of the regionally carbonated schists have similar $\delta^{18}O$ compositions to the Discovery Shaft intrusion may be significant. The calculated $\delta^{18}O$ of the fluid in equilibrium with the Malati Store carbonate appears to show a similar $\delta^{18}O$ content as that of the quartz-water fractionation. However the $\delta^{18}O$ data for the Malati Store carbonates suggests either a variation in temperature during carbonate precipitation or an interaction with other late fluids resulting in oxygen exchange. These suggestions indicate that the $\delta^{18}O$ content of the carbonate is not the result of equilibrium fractionation with the precipitating fluid phase.

5.3.9. $\delta^{18}O$ Feldspar - H_2O Fractionation

The $\delta^{18}O$ of the fluid in equilibrium with the feldspar may be calculated using the feldspar - water fractionation relationship of O'Neil and Taylor (1967). Sodium and potassium feldspars have identical isotopic properties within the limit of analytical uncertainty.

$$10^3 \ln\alpha = 2.91(10^6 . T^{-2}) - 3.41$$

Where $10^3 \ln\alpha \approx {}^*\delta^{18}O \approx \delta^{18}O_{spar} - \delta^{18}O_{H2O}$

Discovery Shaft intrusion $\delta^{18}O_{spar}$ = +9.42 ± 0.08 $^0/_{00}$
Calculated $\delta^{18}O_{fluid}$ (250 °C) = **+5.42 - +5.88 $^0/_{00}$**
(300 °C) = **+6.77 - +6.55 $^0/_{00}$**

Malati Store intrusion $\delta^{18}O_{spar}$ = +10.35 ± 0.14 $^0/_{00}$
Calculated $\delta^{18}O_{fluid}$ (250 °C) = **+6.39 - +6.11 $^0/_{00}$**
(300 °C) = **+7.74 - +7.46 $^0/_{00}$**

The feldspar - H_2O fraction indicates that the feldspars were in equilibrium with a fluid with a $\delta^{18}O$ content of +6 ± 1 $^0/_{00}$, at a temperature of 250°C, in the Malati Store intrusion, and at 250 to 300°C in the Discovery Shaft intrusion, similar to the figure calculated from quartz-water fractionation.

5.3.10. $\delta^{18}O$ Quartz - Carbonate Fractionation

Experimentally determined data indicate that at equilibrium, $\delta^{18}O$ quartz > $\delta^{18}O$ carbonate for temperatures below 800°C (Battener and Bird, 1974). The $\delta^{18}O$ temperature fractionation for the quartz-carbonate mineral pair is an inverse relationship and, at low temperatures, the ^{18}O fractionation into the quartz increases ie. $\delta^{18}O_{qzt} >> \delta^{18}O_{carb}$. A possible equilibrium temperature may be determined using the average $\delta^{18}O$ values of quartz and carbonate from the experimentally determined quartz-calcite fractionation curves of O'Neil *et al.*, (1969)

Discovery Shaft $\delta^{18}O$ quartz = +12.06 $^0/_{00}$
$\delta^{18}O$ carbonate = +9.88 $^0/_{00}$
${}^*\delta^{18}O$ = +2.26 $^0/_{00}$
where $10^3 \ln\alpha \approx {}^*\delta^{18}O \approx \delta^{18}O_{qzt} - \delta^{18}O_{carb}$

The $*\delta^{18}O$ value indicates an equilibrium assemblage where $\delta^{18}O_{qzt} > \delta^{18}O_{carb}$. The calculated temperature using the extreme values is 170 ± 20°C. This temperature is rather low and suggests late, low temperature re-equilibration.

Malati Store intrusion $\delta^{18}O$ quartz = +13.58 $^0/_{00}$

$\delta^{18}O$ carbonate = +12.15 $^0/_{00}$

$*\delta^{18}O$ = +1.43 $^0/_{00}$

where $10^3 \ln\alpha \approx *\delta^{18}O \approx \delta^{18}O_{qzt} - \delta^{18}O_{carb}$

The $\delta^{18}O$ values are indicative of an equilibrium assemblage, ie. $\delta^{18}O_{qzt} > \delta^{18}O_{carb}$. However the calculated temperature is in excess of 380 °C and is thus not consistent with the fluid inclusion or other isotope data. The quartz-carbonate $\delta^{18}O$ fractionation does not, therefore, reflect an equilibrium assemblage.

The $\delta^{18}O$ content of vein quartz from the Blue Jacket mine (+12.34 $^0/_{00}$) and the $\delta^{18}O$ from the carbonate from this vein (-10.86 $^0/_{00}$) produce a temperature of >430 °C. This temperature is also too high to represent a equilibrium fractionation.

Thus the carbonates within the albitized intrusions show evidence for low temperature re-equilibration, or late fluid exchange, and cannot be used to calculate temperatures from the quartz-carbonate fractionation or the isotopic content of the fluid.

5.3.11. $\delta^{18}O$ Quartz - Feldspar Fractionation

Experimental data indicate that $\delta^{18}O_{quartz} > \delta^{18}O_{feldspar}$ for all temperatures. The $\delta^{18}O$ temperature fractionation for quartz-feldspar is an inverse relationship. Thus, at low temperatures, the equilibrium temperature of mineral precipitation may be determined using the fractionation curves of Blattener and Bird (1974);

Discovery Shaft $\delta^{18}O$ quartz = +12.06 $^0/_{00}$

$\delta^{18}O$ spar = +9.41 $^0/_{00}$

$*\delta^{18}O$ = +2.65 $^0/_{00}$

where $10^3 \ln\alpha \approx *\delta^{18}O \approx \delta^{18}O_{qzt} - \delta^{18}O_{spar}$

The $*\delta^{18}O$ value indicates an equilibrium assemblage where, in fact, $\delta^{18}O_{qzt} > d^{18}O_{spar.}$ The calculated temperature using the quartz-alkali feldspar fractionation curve is 310 °C to 375 °C (calculated using the extreme values) This compares favourably with other temperature determinations for the Discovery Shaft intrusion.

Malati Store $\delta^{18}O$ quartz = +13.58 $^0/_{00}$

$\delta^{18}O$ spar = +10.35 $^0/_{00}$

$*\delta^{18}O$ = +3.23 $^0/_{00}$

where $10^3 \ln\alpha = *\delta^{18}O = \delta^{18}O_{qzt} - \delta^{18}O_{spar}$

The $\delta^{18}O_{qzt}$-spar value also indicates an equilibrium assemblage where $\delta^{18}O_{qzt} > \delta^{18}O_{spar.}$ The calculated temperature, using the quartz-alkali feldspar fractionation curve, is 290°C to 240 °C.

The $\delta^{18}O$ quartz-feldspar fractionation again suggests that the quartz-feldspar $\delta^{18}O$ content represents an equilibrium assemblage. Furthermore the alteration at the Malati Store intrusion clearly occurred at a lower temperature (240 °C to 290 °C) than that of the Discovery Shaft intrusion (310 °C to 375 °C) as suggested previously.

5.3.12. Conclusions

The $\delta^{18}O$ isotope ratios of the silicate minerals suggest that the fluids involved in the alteration and mineralization of the granodiorite intrusions had a $\delta^{18}O$ content of +6 ± 1 $^0/_{00}$. The mineral fractionation factors suggest that the Discovery Shaft intrusion alteration temperature (300 - 350 °C) was slightly higher than that of the Malati Store intrusion (250 - 300 °C). The differences in temperature are confirmed by fluid inclusion microthermometry data (see later). The similarity of the calculated $\delta^{18}O$ value for the fluid between the various albitized intrusions suggests that a large, isotopically homogeneous, fluid source affected the area.

The quartz-carbonate $\delta^{18}O$ fraction in the intrusions is not considered to represent an equilibrium fractionation assemblage due, to the variability of the $\delta^{18}O$ content of the carbonate. Thus the $\delta^{18}O$ values from the carbonate cannot be used reliably to estimate temperatures of precipitation, or to calculate the $\delta^{18}O$ of the fluid from which the carbonate precipitated. The lack of equilibrium fractionation is due either to the susceptibility of carbonate minerals to late, low temperature re-equilibration, or to oxygen exchange with later fluids of possible connate origin.

The equilibrium quartz-feldspar fractionation militates against pervasive low temperature spilitic alteration for the elevated Na_2O contents of the albitized intrusions. The elevated Na_2O (± 8%) for trondhjemites of the Canadian Shield has reverse quartz-feldspar fractionation (ie. $\delta^{18}O$ feldspar> $\delta^{18}O$ quartz), which indicates a low temperature fluid interaction (Kerrich 1986). This is not a feature of the Murchison albitites.

Figure 5.3.1. shows the calculated $\delta^{18}O_{fluid}$ versus the temperature range for various deposits types (adapted from Colvine *et al.*, 1984). The position "F" is the calculated $\delta^{18}O_{fluid}$ and the precipitation temperature for the mineralized albitized intrusions from this study. The results of this study compare favourably with the results obtained for other Archaean quartz-lode deposits, emphasising the isotopic and temperature similarities between the Archaean mesothermal fluids responsible for gold mineralization.

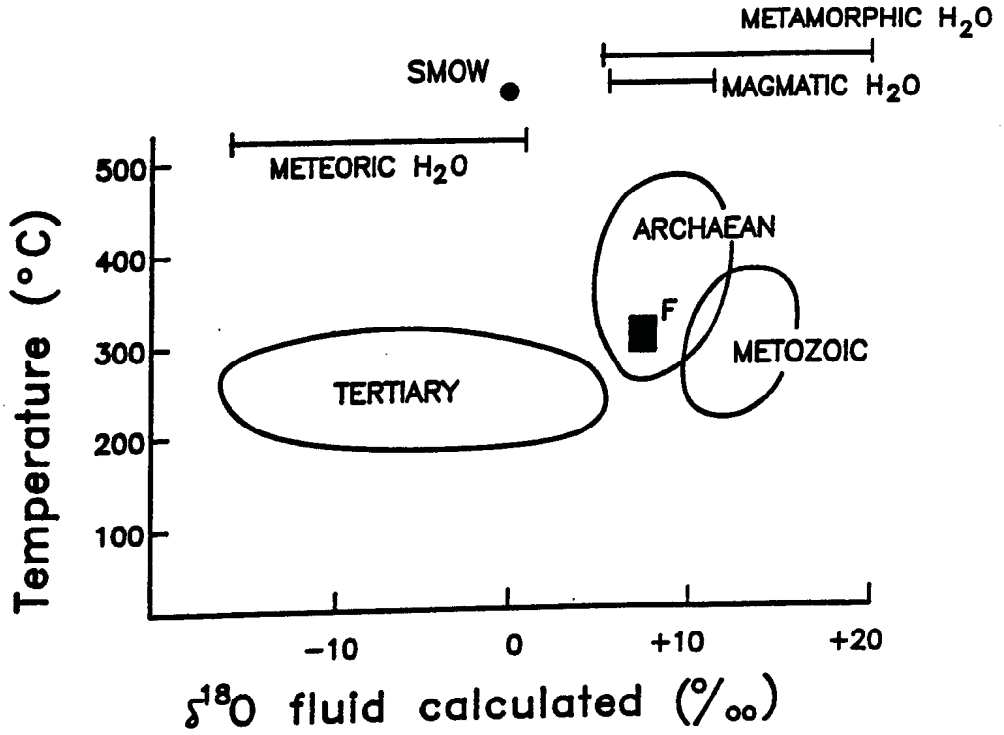

Figure 5.3.1. Calculated $\delta^{18}O_{fluid}$ and the precipitation temperature of the quartz for the albitized intrusions (Position F)

5.4.0. pH Versus fO_2 Diagram

Figure 5.4.1 is a plot of pH versus log fO_2, showing the positions of the $\delta^{34}S$ and $\delta^{13}C$ contours with the stability fields of Fe-S-O minerals at a temperature of 250 °C. The diagram has been calculated using the technique of Ohmoto (1972). A $\delta^{34}S$ value of +1 $^0/_{00}$ as been used in the construction of the $\delta^{34}S$ contours within the log fO_2 versus pH field, as this is the narrow range of values proposed for Archaean deposits (Lambert *et al.*, 1978) and indicated from this study. The $\delta^{13}C$ contour values of the hydrothermal solution are calculated at -7 $^0/_{00}$, as indicated by this study. The sulphide stability fields are calculated using a sulphur content in the fluid of 0.1 and 0.01 moles/ kg H_2O. The calcite stability field is calculated by assuming a CO_2 content in the fluid of 1.0 mole/ kg H_2O. It should be noted that the salt content in fluids also affects the activity coefficients of aqueous species and thus influences the positions of the contours and phase boundaries in this type of diagram. However, since the effects on the position of the contours is smaller than the uncertainties in isotopic enrichment factor, this parameter is ignored (Ohmoto, 1972).

The pyrites and carbonates from the altered intrusions exhibit narrow ranges of $\delta^{34}S$ values and $\delta^{13}C$ values, which indicates a homogeneous isotopic fluid as well as fairly constant physiochemical conditions, with only small amounts of cooling.

With decreasing fO_2, there is also a decrease in the $\delta^{34}S$ values with small changes in the fO_2 resulting in large changes in $\delta^{34}S$. Under conditions of high fO_2, $\delta^{13}C$ values are highly dependent on the pH. The $\delta^{34}S$ values are not greatly influenced by changes in the pH and only change at high fO_2 values. Using the pH-fO_2 diagram and the $\delta^{13}C$, $\delta^{18}O$ contours, the pH-fO_2 conditions of the fluid involved in the mineralization of the intrusions can be approximated. The prevailing conditions calculated at 250°C within the intrusions, is estimated to be fO_2 = log 10^{-37} to 10^{-38} with a neutral to slightly alkaline pH (conditions prevailing in magmatically derived fluids, Ohmoto ,1972). At these pH-fO_2 fluid conditions, calcite is stable and sulphates are unstable (see Figure 5.4.1). In this particular pH-fO_2 environment, both the sulphide and carbonate minerals precipitating from the solution would exhibit uniform isotopic compositions throughout the paragenetic sequence unless modified by late, low temperature effects. The conditions prevailing within the pyritic schists however appear, on the basis of the isotope data (ie. decreasing $\delta^{34}S$ values and constant $\delta^{13}C$ values), to indicate increasing fO_2 conditions.