Fractionation of Carbon and Oxygen Isotopes and Magnesium between Coexisting Metamorphic Calcite and Dolomite

Simon M. F. Sheppard

Department of Geological Sciences, University of Texas, Austin, Texas

Henry P. Schwarcz

Department of Geology, McMaster University, Hamilton, Ontario, Canada

Abstract. Fractionations of carbon and oxygen isotopes and magnesium between coexisting dolomite and calcite have been determined for marbles and calcareous schists of a wide variety of metamorphic environments from Vermont and the Grenville Province of Ontario. Concordant equilibrium fractionations are given by 83% of the samples. Calibration of the isotopic thermometers using the Mg-calcite solvus thermometer gave in the temperature range: $650° > T° > 100°C$

$$1{,}000 \ln \alpha_{D\text{-}Ct}^{O^{18}} = 0.45 \, (10^6 T^{-2}) - 0.40$$

$$1{,}000 \ln \alpha_{D\text{-}Ct}^{C^{13}} = 0.18 \, (10^6 T^{-2}) + 0.17.$$

These isotopic fractionation expressions differ significantly from the experimentally derived relations, including the dolomite-Mg-calcite C^{13} partial exchange experiments of this study.

Temperature ranges obtained for the metamorphic zones of Vermont are: chlorite zone, 210° to 295° C; biotite zone, 255° to 400° C; staurolite-kyanite zone, 110° to 550° C. In amphibolite-facies rocks the quenched partition relations can be complex. The temperature of quench or recrystallization may be as large as 400° C below the inferred metamorphic maximum. Oxygen isotope disequilibrium in high grade rocks, particularly from the Chester dome area, Vermont, is characterized by large negative $\delta O_D^{18} - \delta O_{Ct}^{18}$ values.

The size of the equilibrium exchange system for carbon and oxygen isotopes and magnesium is small, less than a few inches across the inferred relict bedding. This is attributed to the lack of a mobile pore fluid except in systems undergoing decarbonation. C^{13}/C^{12} ratios in Grenville and Vermont marbles and O^{18}/O^{16} ratios in Grenville and greenschist-facies Vermont carbonates span the range of ancient limestones. Staurolite-kyanite zone calcareous schists and marbles from the Chester dome area, Vermont are depleted in $O^{18}(\delta O^{18} = 12$ to $20^0/_{00})$ due to equilibrium or disequilibrium decarbonation and some partial exchange.

Extrapolation of the dolomite-calcite fractionation expressions to 20° C indicates that dolomite is enriched in O^{18} by about $4.9^0/_{00}$ and in C^{13} by about $2.4^0/_{00}$.

Introduction

Marble is an abundant rock type in many regional metamorphic terrains. Many marbles are composed almost wholly of calcite and/or dolomite. The assemblage calcite-dolomite is stable over a very wide range of physical conditions. Commonly the only major chemical variation through the different environments is the change in the $MgCO_3$ content of the calcite coexisting with dolomite. Petrographically this is not very conspicuous.

Intrinsically this assemblage is of considerable interest because of the potential temperature-sensitive equilibrium properties of the carbon and oxygen isotope fractionations and the temperature-pressure sensitive partitioning of magnesium

between calcite and dolomite. This investigation is more concerned with determining the general behavior of these isotopes and magnesium in marbles from metamorphic environments than with the elucidation of the thermal history in a particular place. A study of the response of the various partitioned properties to changes in the environment is an important prelude to detailed geothermometry. Comparison of the results of isotopic exchange reactions in marbles and associated pelitic rocks which have been subjected to a similar sequence of pressure and temperature fluctuations and tectonic settings is desirable.

Carbon and oxygen isotope variations in metamorphic dolomite-calcite assemblages have been studied by Schwarcz (1966) and Shieh and Taylor (1969). Schwarcz observed apparent discordant quench phenomena, or disequilibrium relations between the O- and C-isotope fractionations and Mg partitioning in many samples of marble and calcareous schist of Vermont. In Shieh and Taylor's study of contact metamorphism they observed that decarbonation reactions liberated CO_2 enriched in O^{18} and C^{13} relative to the carbonate.

Experimental equilibration studies pertinent to carbonates are those of Clayton (1961), O'Neil and Clayton (1964) for calcite-H_2O; Northrop and Clayton (1966) for dolomite-H_2O, dolomite-Mg-calcite and CO_2-calcite, CO_2-dolomite; O'Neil and Epstein (1966) for CO_2-calcite and CO_2-dolomite. There are two critical problems associated with these experimental studies: (1) all experiments involving dolomite have encountered considerable problems in attaining equilibrium; (2) only the fractionation between dolomite and pure calcite can be derived from most of these studies. However, in carbonate-carbonate exchange reactions, with either calcite-dolomite or calcite-magnesite as starting materials, Northrop and Clayton observed that as equilibrium was approached for the temperature range 800° to 500° C

$$-0.03 \leqslant 1{,}000 \ln \alpha_{D\text{-}MgCt}^{O^{18}} \leqslant +0.25.$$

Isotopic data for non-carbonate metamorphic systems indicate that isotopic equilibrium between coexisting minerals was often closely attained (e.g. Garlick and Epstein, 1967). The relatively systematic variation of the isotopic fractionations with grade combined with experimentally determined calibration curves indicate that the quench temperature was similar to the probable peak metamorphic temperature. In certain environments however, equilibrium is not displayed. This may be due either to differential retrograde phenomena (James and Clayton, 1962) or alternatively equilibrium exchange may never have been closely attained, e.g. in some metacherts from the blueschist-facies (Taylor and Coleman, 1968). The isotopic composition of the whole rock is sometimes found to be significantly different from its presumed protolithic value as a consequence of either exchange with a mobile oxygen-bearing pore fluid or dehydration and/or decarbonation processes.

Notation and Isotopic Analysis

The name calcite will refer to magnesian calcite solid solutions having the calcite structure, space group $R\bar{3}c$. Dolomite will refer to the ordered Ca-Mg carbonates with the dolomite structure, space group $R\bar{3}$. Some calcites contain micro- or crypto-exsolution blebs of dolomite. The subscript abbreviations Ct for calcite and D for dolomite are used.

The isotopic composition of a sample is reported in the δ notation, where

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) 1{,}000$$

and R is the O^{18}/O^{16} or C^{13}/C^{12} ratio. The fractionation factor, α, between two phases D and Ct is defined by

$$\alpha_{D\text{-}Ct} = \frac{R_D}{R_{Ct}} .$$

For small differences in δ, $1{,}000 \ln \alpha_{D\text{-}Ct} = \Delta_{D\text{-}Ct} \simeq \delta_D - \delta_{Ct}$.

Analytical Methods and Sample Preparation

Samples, as CO_2 gas, were analyzed on a 6 inch, double-collecting mass spectrometer of the McKinney-Nier type. Reproducibility was routinely $\pm 0.1^0/_{00}$ or a little better for both carbon and oxygen. The corrected δ values are reported relative to the Chicago PDB standard for carbon and standard mean ocean water (SMOW) for oxygen.

Carbon dioxide was liberated from the carbonate by the reaction with 100% phosphoric acid (McCrea, 1950). In this reaction only $2/3$ of the oxygen is liberated. The fractionation factors determined by Sharma and Clayton (1965) were used:

$$\alpha_{CO_2\text{-}D} = 1.01110, \quad \alpha_{CO_2\text{-}Ct} = 1.01025.$$

Whenever possible dolomite and calcite were separated by physical means, using the Franz magnetic separator or heavy liquids on crushed samples sieved to -100, $+200$ mesh. Physical separation of calcite from dolomite was impractical for some chlorite zone samples and in all hydrothermal syntheses. For these samples the technique developed by Epstein *et al.* (1964) was used which exploits the different rates of reaction of dolomite and calcite with phosphoric acid.

Phases were identified by using alizarin Red S stain for calcite or Mg-calcite, refractive index oils and X-ray methods. All separates were checked for purity. In general all samples contained less than 5% contaminant carbonate. Purity of carbonate separates for isotopic analysis are less critical than for chemical analysis, because isotopic fractionations between the phases are small.

The Solvus Geothermometer

Introduction

The subsolidus phase relations in the binary system $CaCO_3$-$CaMg(CO_3)_2$ have been described by Goldsmith and Heard (1961) and Goldsmith and Newton (1969). The magnesium content of calcite coexisting with dolomite forms the basis of a geothermometer. The $MgCO_3$ content of the calcites were determined by an X-ray diffraction method using a 114.59 mm Philips Debye-Scherrer powder camera with Mn-filtered $FeK\alpha$ radiation. The distances between the two (521) and (552, 633) back reflections were measured. With these two measurements and calibration curves of Goldsmith (1962), two determinations of the $MgCO_3$ content were made per photograph. No internal standard is necessary in this method. The $MgCO_3$ content of calcite can be determined to ± 0.2 mol % or better.

A least squares analysis of the solvus data of Goldsmith and Heard (1961) and Goldsmith and Newton (1969) for $400° < T < 1{,}075°C$ gives the relation

$$\log MgCO_3 = 1.727 \times 10^{-3} T - 0.223 \tag{1}$$

12*

where T is the temperature °C. Neither corrections for $FeCO_3$ or $MnCO_3$ in solid solution nor the effect of pressure on the solid solubility were attempted. For a calcite with 1 mol-% $FeCO_3$ in equilibrium with Fe-dolomite the solvus temperature (X-ray method) is too high by 8°C at 600°C (Sheppard, 1966). This error decreases with decrease in temperature. Table 1 presents partial analyses of some calcites from Vermont and the Grenville of Ontario. The influence of the ions Fe^{2+}, Mn^{2+} and Sr^{2+}, with contents less than 1 to 2 mol-%, can be neglected with confidence.

Table 1. *Partial chemical analyses of some selected calcites* [a]

Sample No.	$FeCO_3$ (mol %)	$MnCO_3$ (mol %)	$SrCO_3$ (mol %)
GCS	0.12	0.02	0.017
GLSK	0.06	0.06	0.066
G5-1	0.61	0.10	0.076
G4-5-3	0.19	0.03	0.007
G4-54-1	0.01	0.06	0.007
Vt4-11 B [b]	0.34	0.01	0.019
Vt4-35-1a	0.65	0.06	0.038
Vt4-35-1b	0.70	0.86	0.038
Vt4-35-5	0.30	0.21	0.001
Vt4-37-5	0.99	0.52	0.013

[a] Analyst: J. R. Muysson.
[b] Average of the 9 samples: Vt4-11B-1, -6, -7, -8, -9, -17, -11, -12, -14.

Increase in pressure increases the solubility of $MgCO_3$ in calcite by approximately 1 mol-% per 10 kb (Goldsmith and Newton, 1969). The experimental solvus data to 700°C are for pressures up to 2 kb. For $P \sim 10$ kb, the uncorrected solvus temperature, T_s, is too high by about 25°C. Kyanite in the Chester dome area, Vermont, at temperatures of about 550°C (Garlick and Epstein, 1967) indicates a pressure of $P \sim 4$ to 5 kb (Newton, 1966). If the geothermal gradient was as low as 15°C per km, an upper limit of about 10 kb is given. In the Denbigh area of the Ontario Grenville Province sillimanite is ubiquitous in the pelitic schists with minor staurolite and rare kyanite (Evans, 1964). Probable temperatures in the range 500 to 700°C indicate $P \sim 4$ to 7 kb based on the stability fields of Al-silicates (Newton, 1966).

Exsolution

Exsolution phenomena are common in the higher-temperature metamorphic calcites (Goldsmith, 1960; Sheppard, 1966). Many of the more Mg-rich calcite separates ($MgCO_3 > 4$ mol-%) gave weak dolomite d_{211} reflections. Optical study of the stained calcite separates detected < 2 to 3% of discrete grains of dolomite. This is probably insufficient dolomite to account for the reflection. Exsolved dolomite is the probable major source (Goldsmith, 1960). Exsolution blebs of dolomite were observed in some thin sections and most calcites from the high-grade rocks were cloudy due possibly to very fine exsolved dolomite (Goldsmith, 1960; Shaw *et al.*, 1965, Figs. 4 and 5).

Physical separation of calcite with its exsolved dolomite from that dolomite which originally coexisted with the homogeneous calcite is fraught with problems. In Table 2 the X-ray analysis of the Mg-calcite composition is compared with the chemical analysis of the Mg-calcite plus exsolved dolomite. Note that a larger uncertainty is associated with the chemical analysis because of the problems of mineral separate purity. A 2% dolomite impurity in the chemically analyzed calcite increases the solvus temperature by 50°C. These four selected samples are all high-grade upper amphibolite-facies marbles from the Grenville Province. The difference in the temperature derived from the X-ray and chemical analyses (Table 2) is due in part to the exsolved dolomite and to contamination by discrete grains of dolomite.

Table 2. *Comparison of the determination of mol % $MgCO_3$ in calcite by X-ray method and chemical analysis*

Sample No.	X-ray Chemical (mol % $MgCO_3$)		T_s^a (°C)	T_{sc}^a (°C)	Remarks
GLSK	7.4 4.8	9.8	635	705	D blebs in Ct[b] Ct cloudy
G 5-1	4.6 1.4	9.2	515	690	Ct cloudy with occasional blebs of D
G 4-5-3	5.2 1.3	8.8	545	680	Ct centers cloudy, margins clear
G 4-54-1	4.0 1.3	7.7	480	645	Ct cloudy

Analyst: J. R. Muysson.
[a] T_s = Solvus temperature from X-ray data (uncorrected for pressure). T_{sc} = Solvus temperature from chemical analysis (uncorrected for pressure).
[b] Illustrated in Shaw *et al.* (1965, Figs. 4 and 5).

Many calcites from the high-grade rocks display considerable peak broadening of the high-angle back reflections. This has been interpreted as the coexistence of two or more calcites with differing Mg contents. It is not due to fine grain size or strain. Goldsmith *et al.* (1955) attribute this effect to a once homogeneous calcite which has locally segregated into lower Mg-calcite-dolomite regions within the higher Mg-calcite host. The broadening may represent a range in Mg content but often two weak maxima are observed. It is inferred that the low Mg peak represents the calcite surrounding the exsolved dolomite blebs and it is depleted in Mg by the exsolution process. The temperature is derived from the highest $MgCO_3$ content.

Solvus Geothermometry

Table 3 presents the solvus temperatures from all the calcites, coexisting with dolomite, which were analyzed isotopically. The description of the geological setting of these samples from Vermont and the Grenville Province is deferred to later. The metamorphic grade given in Table 3 was inferred from the mineral
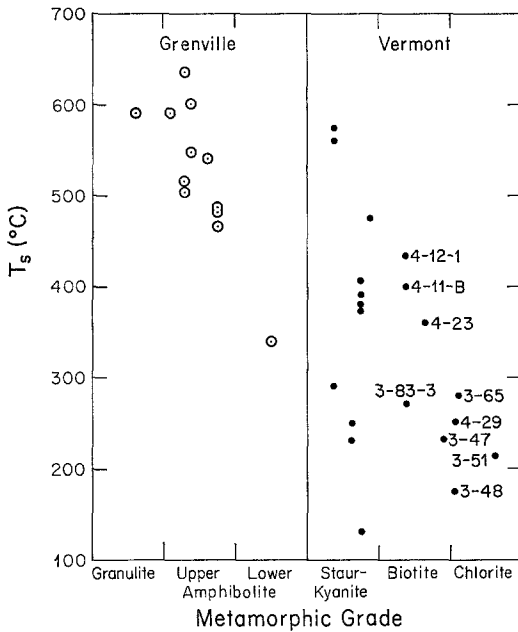
Fig. 1. Relationship between the solvus temperature and the metamorphic grade in calcite-dolomite assemblages of Vermont and the Grenville Province. Samples in the chlorite and biotite zones are placed in their approximate relative position within the zone

assemblages in nearby pelitic schists. The relationship between grade and T_s is illustrated in Fig. 1. This emphasizes a characteristic feature of the system: a good correlation between the maximum value of T_s and the metamorphic grade, except from some high-grade assemblages.

The five coexisting calcite-dolomite pairs from the Kent Quarry core, South Dorset, Vermont, Vt4—11B—6, —8, —9, —12, —15, are samples taken from within a 60 foot section of the core which is inclined to the relict bedding. These calcites quenched in at essentially identical temperatures: $MgCO_3 = 2.85$ mol-%, $\sigma = 0.09\%$, $T_s = 400 \pm 25°C$. The percentage of calcite to total carbonate ranges from 95% to 12% and there are minor variations in the content of other phases (Table 3). Apparently these minor variations of the environment have had little direct influence on the quench process.

Conclusions

The data of Table 3 are consistent with the hypothesis that the *maximum* $MgCO_3$ content of calcite coexisting with dolomite reflects the preservation of equilibrium, albeit sometimes on a very local scale, at a temperature similar to the metamorphic maximum as inferred from associated pelitic schist mineral assemblages. A few high-grade samples, e.g. Vt4—35—5, Vt3—74, Vt3—75 (Table 3) apparently recrystallized at a low temperature. Some samples, e.g. G4—54—1, G4—6, G4—55, may have quenched at a temperature of about 100°C less than the probable metamorphic maximum.

Table 3. *Modes, $MgCO_3$ content of calcites and solvus temperatures of dolomite-calcite marbles*
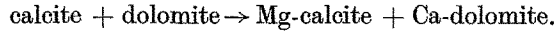
Sample	Mode[a]					Calcite (mol % $MgCO_3$)	T_s (°C)	Remarks[a]
	D	Ct	Qtz	Mg-sil	Op			
Chlorite Zone								
Vt3-51	41	52	7		tr	1.4	215	Black meta-lst; CS
Vt3-48	30	57	12		1	1.2	175	Black meta-lst; CS
Vt4-29	76	27	6		1	1.6	250	Grey meta-lst; CS
Vt3-65	45	52	2		1	1.8	280	Veinlets of Ct;
Biotite Zone								
Vt3-47	47	42	8	2	1	1.5	230	Grey meta-lst
Vt4-23	4	96	tr	tr	tr	2.5	360	White; plicated D layers
Vt3-83-3	80	5	12	3	tr	1.8	270	Qtz-Ct patches in D
Vt4-12-1	17	71	10	3	tr	3.4	435	D-Ct and Ct-Qtz layers
Vt4-11B-6	2	98	tr	tr		2.8 ⎫		
-8	4	85	1	10	tr	2.8 ⎪		Core from Kent quarry;
-9	14	82	1	3	tr	3.0 ⎬ 400		white and grey
-12	80	13	1	5	1	2.8 ⎪		banded marbles
-15	6	93	tr	1		2.9 ⎭		
Staurolite-Kyanite Zone (Retrograde)								
Vt4-35-1a	53	33	tr	14		5.5, 4.9	560 ⎫	-1a and -2a from same
-1b	34	48	tr	18		5.7 (b)	565 ⎪	schist band, 5 inches apart;
-2a	53	33	tr	14		5.9, 4.2	575 ⎬	-1b and -2b are from ad-
-2b	34	48	tr	18		5.9, 4.2	575 ⎪	jacent band 1/2 inch below;
-5	70	25	2	3		1.9	290 ⎭	-5 is 4 feet across foliation from -1a
Vt4-37-1	94	3	2	1		1.0	130 ⎫	
-2	93	4	3	tr		2.6	375 ⎪	
-3	6	86		8		2.7	380 ⎬	D-Qtz coexist,
-4	76	22	2	tr		2.8, 1.7	390 ⎪	Ct rich bands.
-5	69	26	2	tr		3.0	405 ⎭	
Vt3-74	71	26	1	2		1.6	250	D-Qtz and Ct-Qtz layers.
Vt3-75	88	3	3	1		1.5	230	Microcline = 5%, D-Qtz.
Vt3-76	63	34	tr	2		3.9	475	D-Qtz coexist.
Lower Amphibolite								
G Ch-14	70	14		16		2.3 (b)	340	Ct cloudy; Ct-serp layers.
Upper Amphibolite								
G4-54-1	94	4		2	tr	4.0, 1.3	480	Serpentinized Fo.
G4-55	96	3		2	tr	3.8, 1.6	465	Ct cloudy, D bleds in Ct
G4-6	96	2			1	4.0, 1.5	480	Trace of serpentinization
M16	37	50		13		5.1, 4.2	540	Ct-chond layers, Ct cloudy
G4-5-3	31	44		25	tr	5.2, 1.3	545	Ct cloudy; serp. Fo
G4-3	6	85		8	1	6.5, 4.4	600	D blebs in cloudy Ct
GLSK	36	44		20		7.4, 4.8	635	D blebs in cloudy Ct
G5-1	35	36		29	tr	4.6, 1.4	515	D blebs in cloudy Ct
-1b	59	37		4		4.4, 1.5	505	Ct cloudy; serp. Fo
Granulite								
G3-11-1	32	66		2		6.2, 3.3	590	D blebs in cloudy Ct

[a] Abbreviations: D = dolomite; Ct = calcite; Qtz = quartz; Mg-sil = phlogopite, actinolite, sericite, chlorite, forsterite, chondrodite, serpentine; Op = opaques. CS = chemical separation (Epstein *et al.*, 1964). (b) = broad peak.
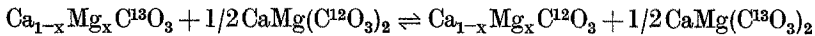
Exchange Reactions Studies

Calcite-Dolomite Exchange Reactions

Exchange experiments were performed to determine the equilibrium carbon isotope fractionation between calcite and dolomite as a function of temperature. Ideally the direct determination of the fractionation between coexisting calcite and dolomite avoids the problems of correcting for the $MgCO_3$ content of the calcite. Reactions between calcite and dolomite were studied:

$$\text{calcite} + \text{dolomite} \rightarrow \text{Mg-calcite} + \text{Ca-dolomite}.$$

The isotopic exchange reaction may be written:

$$Ca_{1-x}Mg_xC^{13}O_3 + 1/2\,CaMg(C^{12}O_3)_2 \rightleftharpoons Ca_{1-x}Mg_xC^{12}O_3 + 1/2\,CaMg(C^{13}O_3)_2$$

where x depends upon temperature according to expression (1). These exchange reactions have the advantage that a limited degree of cation exchange takes place without creating or destroying any phase. Reactions involving the production or destruction of phases may be associated with kinetic isotope effects. In studies of the oxygen isotope and cation exchange chemistry of feldspars O'Neil and Taylor (1967) have shown that cation exchange is accompanied by and may promote isotopic exchange.

Experimental Results

The method of graphical interpolation described by Northrop and Clayton (1966) was used to determine the equilibrium fractionation from sets of partial exchange reaction runs. The method requires that the starting materials are identical in all respects except for their isotopic composition. The present experiments do not satisfy this requirement in so far as the different solid starting materials had differences in grain size, defect density etc., and one of the calcite starting materials was a physical mixture of two different calcites of different origin. This calcite was treated as an homogeneous phase because it recrystallized during each run.

The experimental details and data are described in Appendix I. The fractionations determined from the sets of partial exchange reactions are given in Table 4. Cation equilibration was closely approached in all runs excepting at the lowest temperatures used (T=320° C) as shown by the similarity between the solvus and measured temperatures. Incomplete isotopic exchange was characteristic for all run temperatures. Equivalent runs CtD I and CtD VB using the Haley and Bamle dolomites respectively gave different values for the extrapolated fractionation at 590°C. Northrop and Clayton (1966) also noted a disparity in O^{18} partial

Table 4. *The dolomite-calcite carbon isotope fractionation determined from sets of incompletely exchanged dolomite-calcite samples*

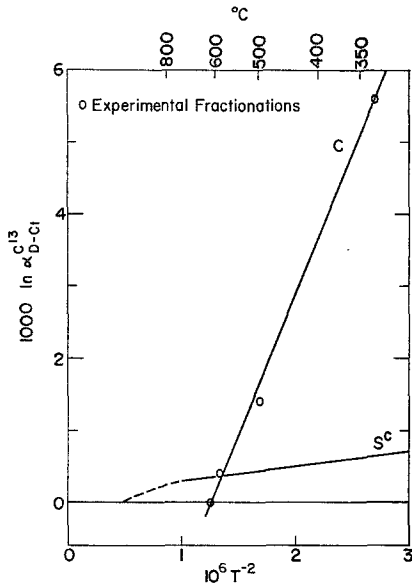| Run	Dolomite	Temp. (°C)	Solvus temp. (°C)	Time (hrs)	$10^3 \ln \alpha_e^{C13}$	-1/B[a]
CtD II	Haley	335	25	803	5.6	0.13
CtD III	Haley	500	485	346	1.4	0.54
CtD I	Haley	590	570	240	0.4	0.76
CtD IV	Haley	610	580	113	0.0	0.79
CtD V	Bamle	590	565	113	− 2.4	0.62

[a] See Appendix I.

Fig. 2. Experimental dolomite-calcite carbon isotope fractionations and least-squares curve, Line C. Curve S^c is the carbon isotope fractionation curve derived from natural dolomite-calcite assemblages (see Fig. 14 and text for discussion). The Bamle dolomite run is omitted

exchange studies which included using the Bamle dolomite. Although the extrapolated equilibrium values closely approximate to a linear relation of the form $1{,}000 \ln \alpha_{D\text{-}Ct}^{C^{13}} = AT^{-2}+B$ (Fig. 2, line C) this is not necessarily indicative of equilibrium. It will be shown below that there is a large disparity between these experimentally determined fractionations and fractionations in natural coexisting dolomite-calcite assemblages formed at $T < 600°$ C.

Geology and Isotopic Results

Samples were collected from three large areas of regional metamorphic rocks: Southwestern Vermont (15×80 sq. miles); Southeastern Vermont (12×25 sq. miles); Grenville Province, Ontario (100×160 sq. miles). This scale of sampling was dictated largely by the need for coexisting carbonate pairs covering as wide a range of metamorphic environments as possible. Localities and sample descriptions are given in Appendix II and Table 3.

Southwestern Vermont

The general geology of this area has been described by Bain (1933), Dale (1912), Doll (1961), Fowler (1950), Hewitt (1961), Skehan (1961), Thompson (1952) and Zen (1960). The crystalline complex forming the core of the north-south trending Green Mountain anticlinorium (Fig. 3) was metamorphosed to the lower or upper amphibolite-facies in the Precambrain. The north-south striking Cambro-Ordovician miogeosynclinal sediments in the Vermont Valley and the eugeosynclinal sediments in the Taconic Range comprising jointly the Middlebury synclinorium were metamorphosed to the greenschist-facies, chlorite and biotite zones, during the Taconic orogeny. At the northeast border of this area, Lincoln Mountain, the amphibolite-facies was attained (Cady *et al.*, 1962). The Precambrian Green Mountain complex suffered retrogradation towards the greenschist-facies. The metamorphic zones deduced from the mineral assemblages in the

pelitic schists are taken from Doll *et al.* (1961) (Fig. 3). The metamorphic grade increases from west to east. The location of the biotite isograd in west Vermont is not firmly established (Albee, personal communication, 1968).

The marble belt is in the Vermont Valley and pelitic schists are rare in this sequence. Several inliers of the Precambrian basement crop out in the synclinorium. Igneous activity during the Taconic orogeny and after is notably absent in this area except for sparse camptonite dikes. Retrograde effects in the Paleozoic metasediments are minor when observed.

In all the samples analyzed (Table 5) carbonates and quartz constitute 90 per cent or more of the rock. Samples from the chlorite zone and a few from the low biotite zone, Vt3-48, 3-51, 3-65, 4-29 and 3-47, are dark grey to black metalimestones. The other samples are white to light grey and more thoroughly recrystallized.

Table 5. *Isotopic data for samples from southwestern Vermont*

Sample No.	$\delta\,O^{18}_{D}$ ($^0/_{00}$)	$\delta\,O^{18}_{Ct}$ ($^0/_{00}$)	$10^3\ln\alpha^{O^{18}}_{D\text{-}Ct}$	$\delta\,C^{13}_{D}$ ($^0/_{00}$)	$\delta\,C^{13}_{Ct}$ ($^0/_{00}$)	$10^3\ln\alpha^{C^{13}}_{D\text{-}Ct}$
Vt3-51	24.91	23.45	1.43	0.25	−0.70	0.95
Vt3-48	21.44	20.58	0.85	−0.56	−0.56	0.00
Vt4-29	23.86	22.83	1.01	−2.01	−2.72	0.71
Vt3-65	23.78	21.97	1.77	2.36	1.60	0.76
Vt3-47	22.51	21.30	1.19	−2.03	−2.68	0.65
Vt4-23	22.70	22.00	0.68	1.32	0.62	0.70
Vt3-83-3	23.64	22.41	1.21	−0.34	−1.14	0.80
Vt4-12-1	22.32	21.13	1.17	0.02	−1.11	1.13
Vt4-11B-6	22.74	22.19	0.54	1.26	0.67	0.59
Vt4-11B-8	22.74	22.20	0.53	0.64	0.18	0.46
Vt4-11B-9	22.53	22.02	0.48	0.79	0.05	0.74
Vt4-11B-12	22.73	22.20	0.52	0.66	0.04	0.62
Vt4-11B-15	22.33	21.79	0.53	1.16	0.64	0.52

In Fig. 1 the variation of the solvus temperature with metamorphic grade is shown for these samples from southwestern Vermont. The samples are placed in their approximate relative positions within the chlorite and biotite zones. Excluding Vt3-48, there is a progressive increase in temperature on traversing up through the chlorite zone into the biotite zone.

The variation of the carbon and oxygen isotope fractionations between dolomite and calcite with solvus temperature are shown in Fig. 4. The temperature function $10^6\,T^{-2}$ is chosen rather than T as the ordinate. Many isotope fractionations between cogenetic mineral pairs show an approximately linear dependence against T^{-2} for temperatures in the metamorphic range (e.g. see Epstein and Taylor, Fig. 1, 1967). In all these assemblages dolomite concentrates both C^{13} and O^{18} relative to calcite. Also, with few exceptions both the carbon and oxygen isotope fractionations decrease systematically with increase in solvus temperature. These systematics for carbon and oxygen isotopes and magnesium partitioning between coexisting dolomite and calcite suggest that equilibrium was closely attained for many but not all of these samples.
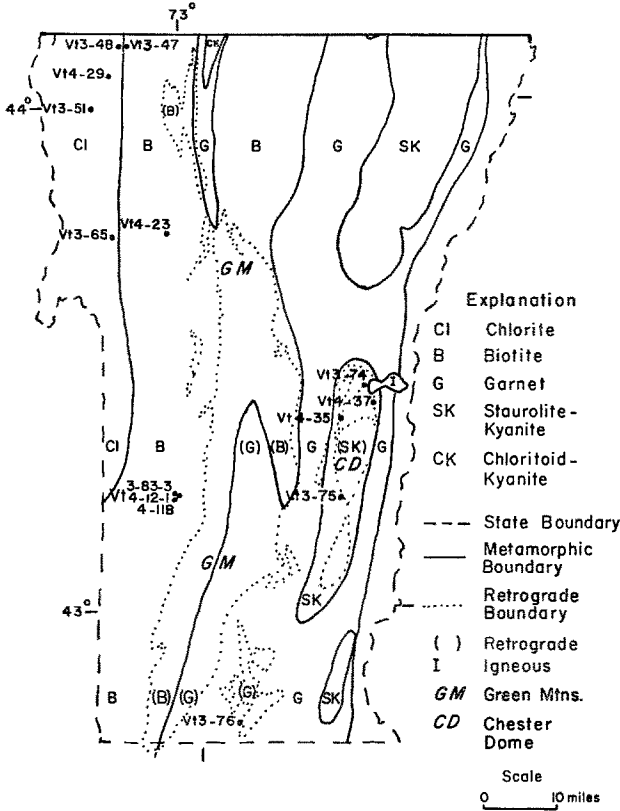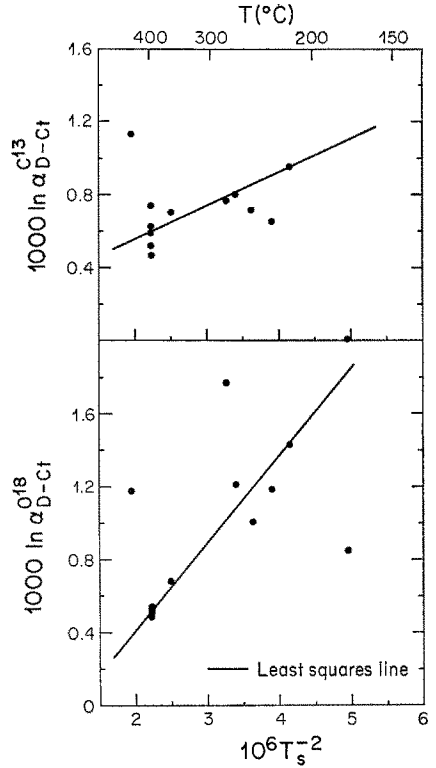
Fig. 3

Fig. 4

Fig. 3. Map of southern Vermont showing the metamorphic geology and sample locations (after Doll *et al.*, 1961)

Fig. 4. Relationship between the carbon and oxygen isotope fractionations and the temperature based on the solvus thermometer for greenschist-facies samples of southwest Vermont

South Dorset Area, Southwestern Vermont

More detailed sampling was made in the quarries of the South Dorset area. The general geology of this area within the Vermont Valley is shown in Fig. 5 after Hewitt (1961).

The Dorset anticline (Fig. 5) is composed of a multitude of small isoclinal and recumbent folds (Dale, 1912, Fig. 14). Locally the marble is intensely plicated but flow folding is characteristic. There is a pre-metamorphic thrust fault between the allocthonous Mount Anthony phyllites and the Bascom-Beldens formation (Thompson, 1959).

The Kent, Valley, Plateau and Bennington quarries are all within the Shelburne Marble of the Lower Ordovician. These white to light grey marbles in the biotite zone may contain up to a few per cent of one or more non-carbonates (Table 3). The degree of decarbonation is minor. Coarse vein calcite (width < 1 inch), like Vt4-11B-11 from the Kent Quarry, occurs locally in the marbles.
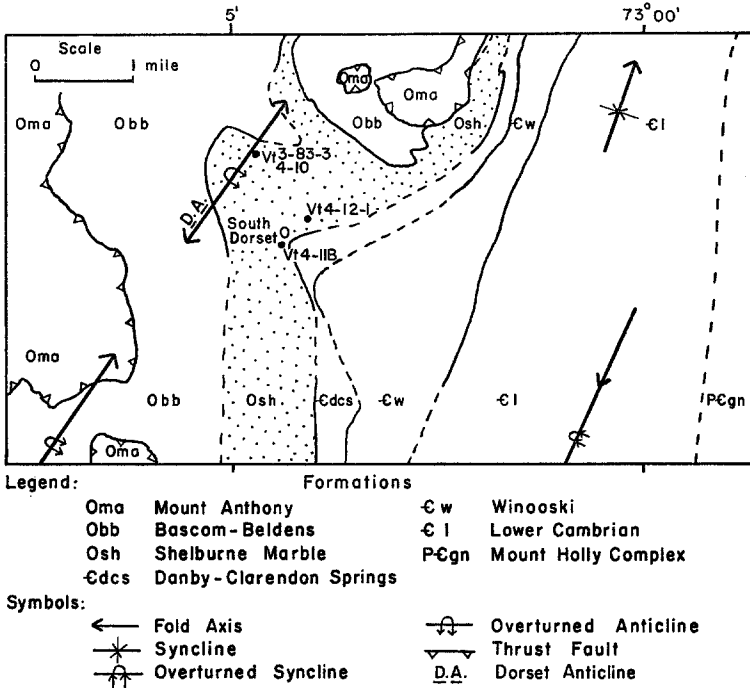
Fig. 5. Map of the South Dorset area, Equinox quadrangle, Vermont, showing the geology and sample locations (after Hewitt, 1961). Kent Quarry: Vt4-11 B; Valley Quarry: Vt3-83-3, Vt4-10; Bennington Quarry: Vt4-12-1

From Kent Quarry, 17 small samples (1 to 1.5 cm³) were taken from a 130 ft core steeply inclined to the inferred relict bedding. Five of these samples contain more than 1 to 2 per cent of both calcite and dolomite. The $MgCO_3$ content of the calcites, δC^{13} and δO^{18} analyses of the carbonates are given in Table 6 and shown with reference to their location in the core in Fig. 6. The five calcites coexisting with dolomite give the single value for their $MgCO_3$ content of 2.85 mol-%, $\sigma = 0.09$ mol-%. The $MgCO_3$ content of the other 12 samples with no detectable dolomite (less than 1 to 2% dolomite) have contents less than or equal to this same maximum value of 2.85 mol-%. Equilibrium partitioning of Mg between coexisting calcite and dolomite was attained and preserved at a single temperature for these five samples with $T_s = 400° \pm 25°$C.

Although there are significant but small variations in δO^{18} through the core, the five coexisting dolomite-calcite samples give a single value for the fractionation, $\varDelta O^{18}_{\text{D-Ct}} = 0.53\%_{00}$, $\sigma = 0.02\%_{00}$. This is a necessary condition for oxygen isotope equilibrium between coexisting dolomite and calcite at a single temperature as supported by the $MgCO_3$ solvus data.

The C^{13} data, Fig. 6, are a little more irregular. First, more sizeable $\delta C^{13}_{\text{Ct}}$ gradients than those for $\delta O^{18}_{\text{Ct}}$ are observed, presumably reflecting the more restricted size of the C-isotope equilibrium exchange system. The dolomite-calcite fractionations, $\varDelta C^{13}_{\text{D-Ct}}$, show a spread which is a little larger than the precision. This perhaps is due to either C-isotope equilibrium being attained on a
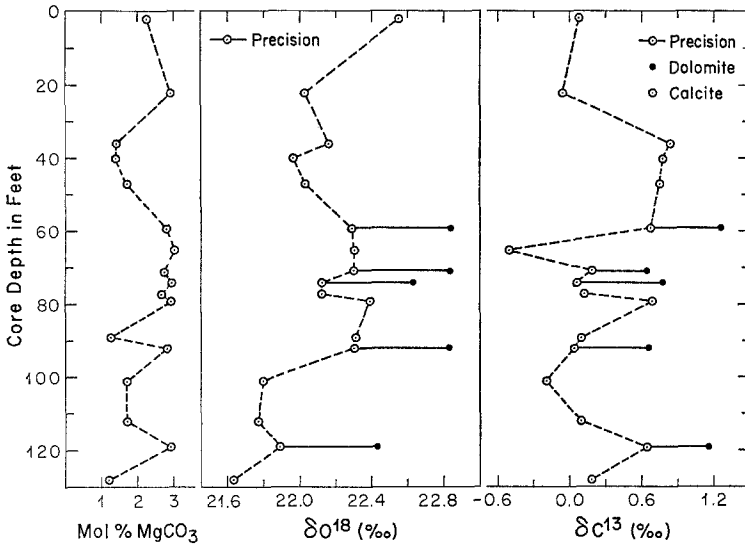
Fig. 6. The variations of the $MgCO_3$ content of calcite, and the oxygen and carbon isotope compositions of calcite and dolomite in the Kent Quarry core, Vt4-11 B. The full horizontal lines connect the isotopic compositions of coexisting dolomite and calcite. The dashed line between the sample locations represents the minimum gradient between samples

Table 6. *Kent quarry core: isotopic data and $MgCO_3$ content of calcites*

Sample	Depth (feet)	δO^{18}_D ($^0/_{00}$)	δO^{18}_{Ct} ($^0/_{00}$)	$10^3 \ln \alpha^{O^{18}}_{D\text{-}Ct}$	δC^{13}_D ($^0/_{00}$)	δC^{13}_{Ct} ($^0/_{00}$)	$10^3 \ln \alpha^{C^{13}}_{D\text{-}Ct}$	$MgCO_3$ (mol %)
Vt4-11 B								
1	2		22.45			0.07		2.25
2	22		21.93			—0.06		2.90
3	36		22.06			0.83		1.40
4	40		21.86			0.79		1.40
5	47		21.93			0.77		1.70
6	59	22.74	22.19	0.54	1.26	0.67	0.59	2.80
7	65		22.20			—0.52		3.00
8	70.5	22.74	22.20	0.53	0.64	0.18	0.46	2.75
9	74	22.53	22.02	0.48	0.79	0.05	0.74	2.95
17	77		22.02			0.12		2.65
10	79		22.29			0.68		2.95
11	89		22.21			0.09		1.25
12	92	22.73	22.20	0.52	0.66	0.04	0.62	2.80
13	101		21.70			—0.15		1.70
14	111.5		21.67			0.10		1.70
15	118.5	22.33	21.79	0.53	1.16	0.64	0.52	2.90
16	128.5		21.53			0.18		1.20

scale less than the sample size, or preservation of equilibrium fractionations over a range of temperatures — improbable in light of the behaviour of O^{18} and Mg — or to some, as yet, undetected process. The large δC^{13}_{Ct} gradients between sample

locations is suggestive, but not proof that the sample size could be greater than the size of the equilibrium system with regard to C^{13}. The coarse vein calcite, Vt4-11B-11 appears to be isotopically similar to calcite of the host marble in which it is emplaced.

A necessary criterion for equilibrium is the observation of consistent fractionations for a set of dolomite-calcite pairs from a volume of rock sufficiently small to assume uniformity in the physicochemical conditions, despite variations in the isotopic compositions of the carbonates. The effect of differential or partial exchange processes producing consistent fractionations can be detected as long as the carbonate isotopic compositions and proportions are different. These conditions are satisfied in the Kent Quarry samples.

The significant gradients in δO^{18} and δC^{13} shown in Fig. 6 coupled with the uniform fractionations and $MgCO_3$ content in the 5 dolomite-calcite assemblages are compelling arguments for equilibrium. Thus, identifying T_s with the temperature of isotopic equilibration, the equilibrium fractionations at $400° \pm 25°C$ are: $1{,}000 \ln \alpha_{D\text{-}Ct}^{C^{13}} = 0.59°/_{00}$; $1{,}000 \ln \alpha_{D\text{-}Ct}^{O^{18}} = 0.53°/_{00}$.

Southeastern Vermont

The geology of southeastern Vermont has been described by Skehan (1961) and Thompson (1952). The Chester dome is the largest of a series of gneiss-cored domes occurring along an axis approximately parallel with the Green Mountain axis but 15 miles or so to the east (Fig. 3). This dome is composed mainly of Precambrian gneisses which have been plastically remobilized and uplifted into the overlying Paleozoic schists. The mantling schists are intensely deformed and exhibit major thinning around the domes of probable tectonic origin. Contiguous metamorphic zonation is essentially concentric about the dome with the node, staurolite-kyanite zone, centered on the dome core, retrograded from possible sillimanite to staurolite-kyanite zone. All samples (Appendix II) come from the Cavendish formation which exhibits prominent retrograde features. Dolomitic marbles predominate with extensive decarbonation to diopside-actinolite assemblages locally. However, dolomite-quartz is a common assemblage in the marbles implying a high CO_2 activity (Table 3).

Vt3-76 is from the Sherman Marble, Cavendish formation, near the Ray Pond or Sadawaga dome to the south south-west of the Chester dome (Fig. 3). A complex metamorphic history including retrogradation is characteristic here also.

Minor ultramafic intrusives are found in and around the Chester dome but antedate the last metamorphism. The Mount Ascutney alkalic stock, hornblende-biotite diorite and syenite, on the north-east edge of the dome outcrops 1/2 to 2 miles from sample localities Vt3-74 and Vt4-37-1 to -5. It is post-metamorphic.

The isotopic fractionation data (Table 7) from these retrograde staurolite-kyanite zone samples are variable. In this region the dolomite-calcite oxygen isotope fractionation ranges from $+0.2$ to $-2.2°/_{00}$. The sets of samples Vt4-35-1 to -5 and Vt4-37-1 to -5 which are taken from within a few feet of each other display a similar range in fractionations. Although dolomite invariably is enriched in C^{13} compared to calcite an appreciable range in the fractionation is observed also from these sample sets. These results are indicative of complex quench or annealing phenomena and possible alteration processes.
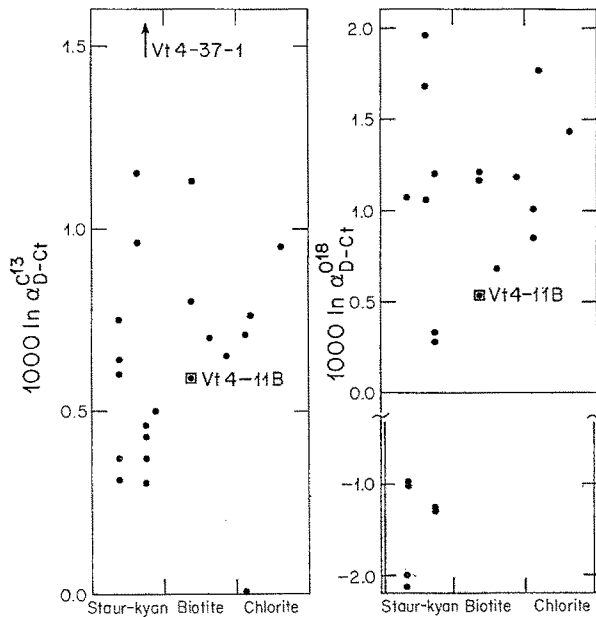
Fig. 7. Relationship between the carbon and oxygen isotope fractionations and the metamorphic grade for carbonates from Vermont. Chlorite and biotite zone samples are placed in their approximate relative position within the zone

Variation of Isotopic Fractionations vs Metamorphic Grade, Vermont

The carbon and oxygen isotope fractionations, for all the samples from southwest and southeast Vermont, are compared in Fig. 7 with their metamorphic grade. No well defined relation is seen for either isotopic fractionation. Nevertheless, for carbon, the minimum value for the fractionation decreases on going

Table 7. *Isotopic data for samples from southeastern Vermont*

Sample No.	δO_{D}^{18} ($^0/_{00}$)	δO_{Ct}^{18} ($^0/_{00}$)	$10^3 \ln \alpha_{D-Ct}^{O^{18}}$	δC_{D}^{13} ($^0/_{00}$)	δC_{Ct}^{13} ($^0/_{00}$)	$10^3 \ln \alpha_{D-Ct}^{C^{13}}$
Vt4-35-1a	13.79	14.83	−1.03	−1.77	−2.37	0.60
Vt4-35-1b	12.53	14.71	−2.16	−2.53	−2.84	0.31
Vt4-35-2a	13.52	14.54	−1.00	−1.61	−2.25	0.64
Vt4-35-2b	12.55	14.62	−2.04	−2.28	−2.65	0.37
Vt4-35-5	18.92	17.83	1.07	1.84	1.09	0.75
Vt4-37-1	18.84	17.62	1.20	1.57	−1.13	2.70
Vt4-37-2	15.50	16.83	−1.31	1.53	1.23	0.30
Vt4-37-3	14.78	14.50	0.28	−0.07	−0.44	0.37
Vt4-37-4	17.35	16.02	0.33	1.88	1.42	0.46
Vt4-37-5	16.04	17.36	−1.30	1.68	1.25	0.43
Vt3-74	19.10	17.39	1.68	1.27	0.31	0.96
Vt3-75	18.17	16.18	1.96	0.08	−1.07	1.15
Vt3-76	18.59	17.52	1.06	1.72	1.22	0.50

from the chlorite to the staurolite-kyanite zone. Samples in the biotite and chlorite zones are placed in their approximate relative position within the zone. Similarly for oxygen, the minimum value for the fractionation decreases from the chlorite to the staurolite-kyanite zone if the large negative fractionations are excluded (see below). Note that the Kent Quarry samples, represented by a single point (Vt4-11B), fall on these two trends of minimum values. The considerable spread in the data could be a consequence of either: (1) equilibrium fractionations being preserved at temperatures different from the metamorphic high; or (2) some disequilibrium processes.

Southeastern Ontario

The Grenville Province of southeastern Ontario is composed of a wide variety of igneous, metavolcanic and metasedimentary rocks including widespread marbles. Although the metamorphic history is extremely involved, there is a broad zonation, shown in Fig. 8 after Lumbers (1964), centered on a northeast-southwest trending low of greenschist-facies rocks. The metamorphic grade increases to the west, north and east attaining upper amphibolite to granulite-facies. In the high grade areas migmatite is common. Throughout a 300 my period (Silver and Lumbers, 1965) various intrusive series were emplaced and many structures are related to the emplacement of the numerous batholithic masses.

The general regional metamorphic pattern probably was established before the emplacement of some of the earliest igneous rocks (Lumbers, 1964).

The marbles outside of the greenschist-facies area (Fig. 8) are white to light grey, medium to coarse grained (2 to 5 mm medium grained; >5 mm coarse grained) with variable amounts of silicate minerals (Table 3). Large tracts of the marbles contain less than 5 per cent of non-carbonates. The distribution of coexisting calcite and dolomite appears to be irregular. The graphite distribution is variable and in the higher-grade marbles may be segregated into clots of well crystallized plates a few mm in size. X-ray diffraction studies of $d_{(002)}$ (French, 1964) indicate that the graphite is ordered in samples G4-54 and G5-1 from intermediate and high-grade areas respectively.

The location of the samples is given in Fig. 8 with the exception of G5-1 and -1b from the Seguin River, near Parry Sound, and GLSK described by Shaw *et al.* (1965). Geological information for the Seguin River area and the Renfrew area (G4-3, G4-5-3) is limited and the metamorphic grade is known only very broadly. Comparison between Grenville marbles and Vermont marbles from a similar temperature environment indicate that the grain size is larger and the mineralogy more variable in the Grenville samples.

The dolomite-calcite oxygen isotope fractionations range from +0.70 to −0.80 (Table 8). On the other hand the carbon isotope fractionations between dolomite and calcite are positive and have the range +0.98 to 0.00. The three samples G4-54-1, G4-55 and G4-6 from the Denbigh area are from a $^3/_4$ mile length of a single marble unit within the sillimanite-almandine-muscovite subfacies (Evans, 1964). The carbon and oxygen isotope fractionations and the solvus temperature are similar for all three samples. These calcites are cloudy and chemically not homogeneous (Table 2) and presumably reflect the complex quench history.
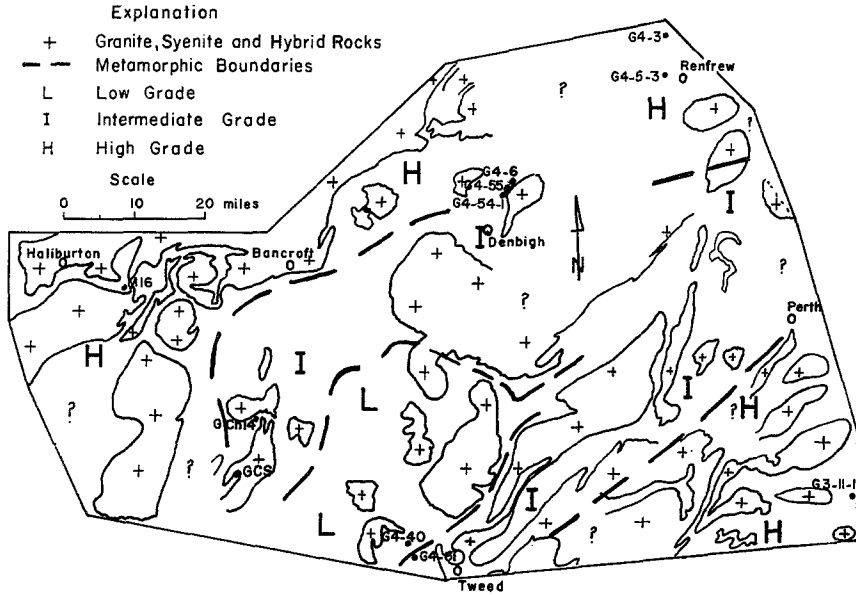
Fig. 8. Map of part of the Grenville Province of Ontario showing the metamorphic geology and sample locations (after Lumbers, 1964; Wynne-Edwards, 1959)

Table 8. *Isotopic data for samples from the Grenville Province*

Sample No.	δO_D^{18} $(^0/_{00})$	δO_{Ct}^{18} $(^0/_{00})$	$10^3 \ln \alpha_{D\text{-}Ct}^{O^{18}}$	δC_D^{13} $(^0/_{00})$	δC_{Ct}^{13} $(^0/_{00})$	$10^3 \ln \alpha_{D\text{-}Ct}^{C^{13}}$
GCS		18.48			0.64	
G4-40		23.31			0.87	
GCh-14	17.60	17.72	−0.12	4.55	3.86	0.69
G4-54-1	23.16	22.45	0.70	−1.51	−2.09	0.58
G4-55	22.95	22.47	0.48	3.55	3.13	0.42
G4-6	26.05	25.60	0.54	2.56	2.00	0.56
M16	21.08	20.83	0.25	2.57	2.01	0.56
G4-5-3	22.63	22.11	0.51	3.66	3.20	0.46
G4-3	25.99	25.34	0.64	3.83	3.25	0.58
G5-1	19.68	20.50	−0.80	−0.17	−1.15	0.98
G5-1b	20.49	20.33	0.16	−0.75	−0.75	0.00
GLSK	22.99	22.83	0.16	0.84	0.33	0.51
G3-11-1	21.65	21.75	−0.10	5.11	4.76	0.35

Discussion of Results

General Relations

Various relations between the isotopic and X-ray data are presented in Figs. 9—11. If equilibrium is generally preserved a correlation between one or more of these variables may be expected. The simultaneous quenching of two or more of the parameters carbon and oxygen isotope fractionations and magnesium partitioning
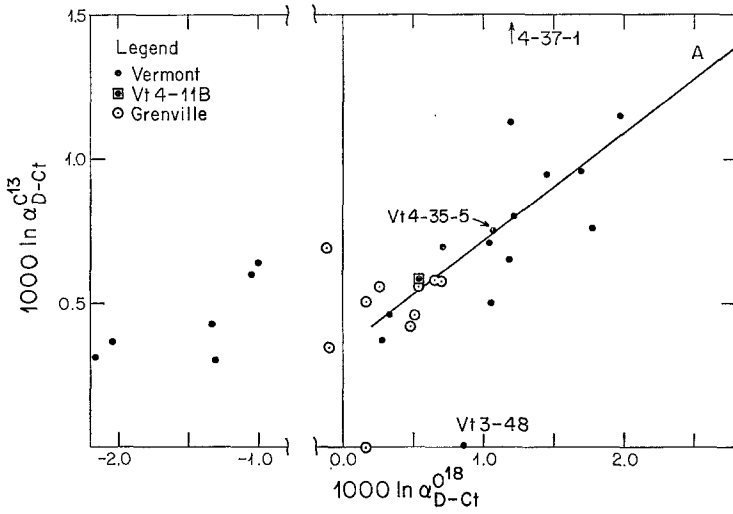
Fig. 9. Relationship between the carbon and oxygen isotope fractionations. Curve A is the regression line fitted to data points in the positive fractionation quadrant, excluding Vt4-37-1 and Vt3-48

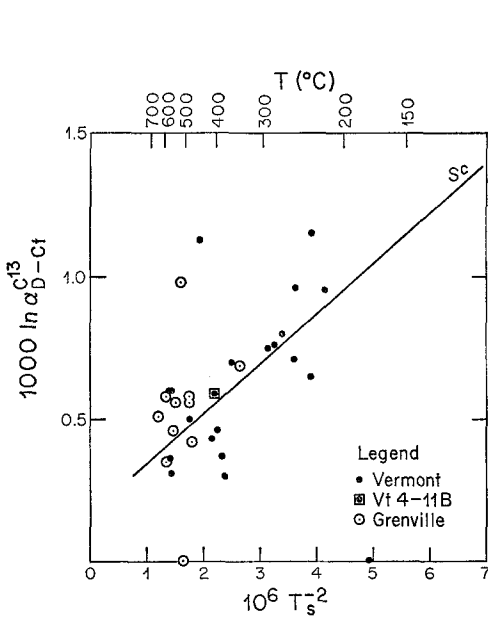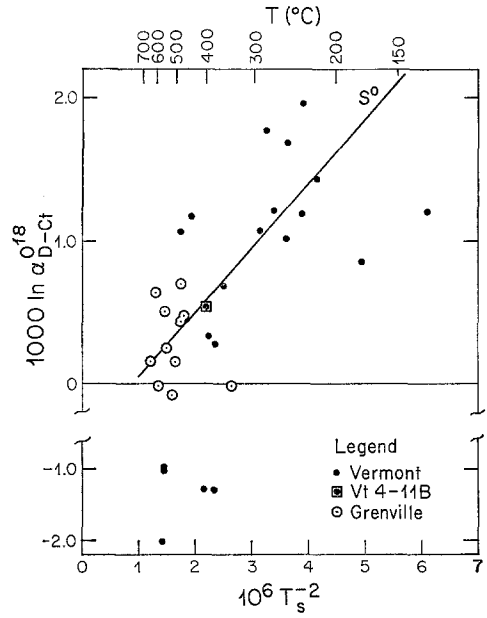Fig. 10   Fig. 11

Fig. 10. Variation of the carbon isotope fractionation with solvus derived temperature for carbonates from Vermont and the Grenville Province. Curve S^c is the fractionation curve derived from the selected data (see Fig. 14 and text for discussion)

Fig. 11. Variation of the oxygen isotope fractionation with solvus derived temperature for carbonates from Vermont and the Grenville Province. Curve S^o is the fractionation curve derived from the selected data (see Fig. 13 and text for discussion)

between coexisting dolomite and calcite at a single temperature will be called concordant equilibrium. There is no *a priori* reason why the exchange of carbon and oxygen isotopes and magnesium between dolomite and calcite should have frozen in concordantly at the same temperature. However, at Kent Quarry, as emphasized above, we probably have concordant equilibrium relations.

$1,000 \ln \alpha_{D-Ct}^{C^{13}}$ vs $1,000 \ln \alpha_{D-Ct}^{O^{18}}$. A marked positive correlation between these variables is shown in Fig. 9 when the large negative oxygen isotope fractionations are excluded. Line A is the regression line using those data points falling in the positive fractionation quadrant. This correlation (correlation coefficient r = 0.95) indicates that for many marbles the carbon and oxygen isotope fractionations are closely coupled. The Kent Quarry data fall on this line. The smallest fractionations are given by the highest-grade rocks. The expression for A is:

$$1,000 \ln \alpha_{D-Ct}^{C^{13}} = 0.37 \ (1,000 \ln \alpha_{D-Ct}^{O^{18}}) + 0.35. \tag{2}$$

Samples which lie about A are assumed to have closely approached concordant equilibrium with respect to carbon and oxygen isotope exchange.

$1,000 \ln \alpha_{D-Ct}^{C^{13}}$ and $1,000 \ln \alpha_{D-Ct}^{O^{18}}$ vs $10^6 T_s^{-2}$. The isotopic fractionations are plotted against the temperature function $10^6 T_s^{-2}$ derived from the solvus thermometer (Table 3) in Figs. 10 and 11. A rather diffuse correlation is observed for both carbon and oxygen when the large negative oxygen isotope fractionations are excluded. However, for the greenschist-facies data of southwest Vermont the correlations are more well defined as noted above (Fig. 4).

Carbonate Systems With Large Negative Oxygen Isotope Fractionations

Many of the large negative O-isotope fractionations (Figs. 7, 9 and 11) are given by high-grade calcareous schists. Five samples from the Cavendish Formation, Chester dome, which are closely related spatially, were analyzed in detail. The four samples Vt4-35-1a, -1b, -2a, -2b, are from two cores taken from a single hand specimen: -1a and -2a are from the same carbonate rich schist band but 5 inches apart, while -1b and -2b are from a carbonate poor schist band immediately adjacent to -1a and -2a respectively. Vt4-35-5 is from a massive marble unit (non-carbonates < 5%) 4 feet across the foliation from Vt4-35-1 and -2. Some pertinent features of these samples are summarized and contrasted in Fig. 12. The large negative O-isotope fractionations in -1a, b and -2a, b coupled with the uniformity of δO_{Ct}^{18} between -1a and -1b are indicative of disequilibrium. The C-isotope fractionations are consistent with equilibrium. The marble, Vt4-35-5 has concordant C- and O-isotope fractionations (Fig. 9). However the quench temperature apparently was considerably lower than that of the metamorphic maximum (staurolite-kyanite zone). Thus there is evidence from the Mg-partitioning alone of some retrograde metamorphism at this locality. The discordant isotopic fractionations may have been generated during this retrogressive episode.

Dolomite-calcite fractionations in retrograde assemblages depend on factors such as the relative exchange rates, the cooling history and the isotopic composition and nature of the exchanging mediums. The observed oxygen isotope shift could result from the more rapid exchange of calcite with an isotopically heavier aqueous-rich fluid common to both -1a and -1b and an oxygen reservoir. The
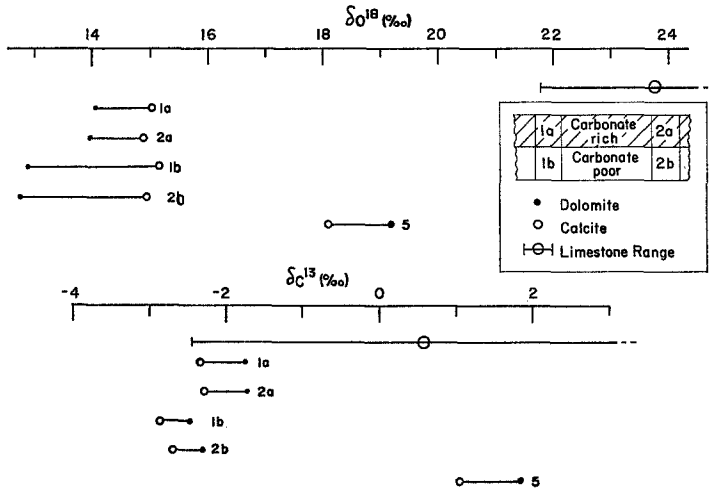
13*

Fig. 12. Comparison of the isotopic composition of carbonates Vt 4-35-1a, -1b, -2a, -2b, -5 from the Chester dome area, Vermont and average limestone and its range

differences between δO_D^{18} in -1a and -1b may indicate that dolomite was relatively inert to exchange.

Disequilibrium relations are particularly characteristic of calcareous schists and some marbles from the Chester dome area, Vermont. However, not all calcareous schists give disequilibrium oxygen isotope relations. Some high-grade samples from the Grenville (GLSK, M16, G4-5-3), whose mineralogy (Table 3) is indicative of dedolomitization like Vt4-35-1a, exhibit neither negative oxygen isotope fractionations nor oxygen isotope lightening. Apparently calcite-dolomite assemblages respond in a variety of ways to changes in their metamorphic environment.

The Isotopic Geothermometers

Derivation of Carbon and Oxygen Isotope Fractionation Expressions

Analysis of the above data can be used to derive expressions for the fractionation of carbon and oxygen isotopes between coexisting dolomite and Mg-calcite as a function of the temperature of quenching of Mg-exchange as determined from the dolomite-calcite solvus relations. All the data cannot be employed indiscriminantly during this operation. From inspection of Figs. 4, 9—11 it is evident that approximate linear relations exist between the two isotope fractionations and T_s^{-2} over the larger part of the temperature range of interest. Samples which fall close to the main trend on each of the plots ($10^6 T_s^{-2}$ vs 1,000 ln α_{D-Ct}^{C13} and 1,000 ln α_{D-Ct}^{O18}, and 1,000 ln α_{D-Ct}^{C13} vs 1,000 ln α_{D-Ct}^{O18}) are referred to as being concordant with respect to that plot. Some samples fall far from these trends. It is noted that samples falling far from the concordant trend on Fig. 9 (curve A) tend to be discordant with respect to both the carbon isotope fractionation vs T_s^{-2} trend and the oxygen isotope fractionations vs T_s^{-2} trend. All such doubly or triply discordant samples are discarded from the subsequent analysis. Such
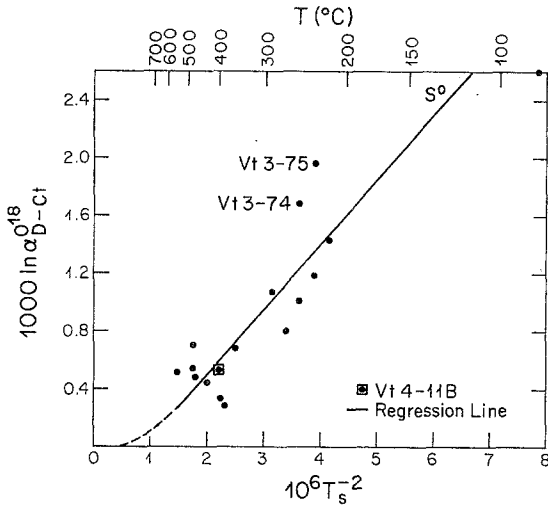
Fig. 13. Relationship between the oxygen isotope fractionation and the solvus temperature for the selected data
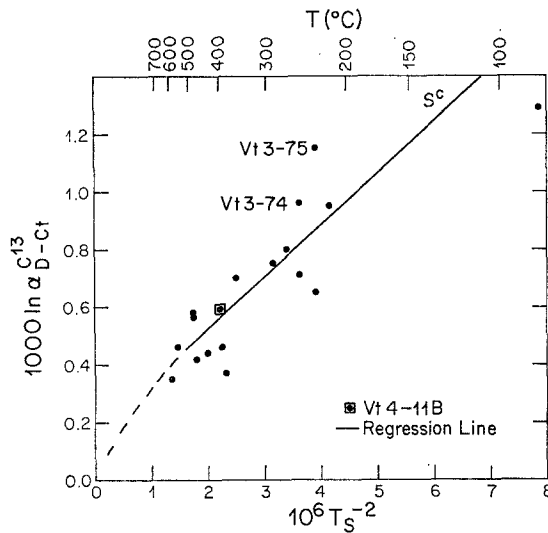

Fig. 14. Relationship between the carbon isotope fractionation and the solvus temperature for the selected data

discordant samples are principally from rocks of high grade (staurolite-kyanite or higher). They include those samples with large negative oxygen isotope fractionations which are in oxygen isotope disequilibrium.

These criteria were designed to select those samples which most closely approached triply concordant equilibrium quenching of Mg, carbon and oxygen isotopes. They fall about a line with small dispersion in $1{,}000 \ln \alpha_{D\text{-}Ct}^{C^{13}}$, $1{,}000 \ln \alpha_{D\text{-}Ct}^{O^{18}}$, $10^6 T_s^{-2}$ space. Forty five percent of the calcite-dolomite pairs including the data of Schwarcz (1966) were rejected in this way. Those pairs selected are given in Table 9. The regression line fitted to these data is shown as Line S^o in Fig. 13 and Line S^c in Fig. 14, where

$$S^o \qquad 1{,}000 \ln \alpha_{D\text{-}Ct}^{O^{18}} = 0.45\,(10^6\,T^{-2}) - 0.40 \qquad (r = 0.92)$$

$$S^c \qquad 1{,}000 \ln \alpha_{D\text{-}Ct}^{C^{13}} = 0.18\,(10^6\,T^{-2}) + 0.17 \qquad (r = 0.87).$$

Comparing Figs. 9—11 greater dispersion in the data is seen in Figs. 10 and 11. This is in part a consequence of the problems associated with the solvus thermometer. The neglect of any correction for pressure would add "noise" to the fractionation vs $10^6 T_s^{-2}$ plots without affecting the correlation between the carbon and oxygen isotope fractionations (Fig. 9) which are essentially independent of pressure.

The $MgCO_3$ content of calcites from the greenschist-facies rocks are known with greater relative certainty because the high angle back reflections are sharp well defined single peaks. Also, the pressure correction for these samples is probably minimal. However, since the solvus curve is extrapolated to temperatures below the region of experimental data for some of these samples there may be a consistent, but small, calibration error.

Regression lines fitted to the greenschist-facies data alone yield curves for both carbon and oxygen isotope fractionations that are indistinguishable, within the limits of precision of the analytical data, from lines S^o and S^c. Considering the oxygen isotope fractionation the correlation coefficient is a little higher for the greenschist-facies data (r = 0.95) compared with that for the selected data (r = 0.92).

The selected data points have been fitted by linear relations. These lines must be curves at least at the high temperature end where $1,000 \ln \alpha \to 0$ as $T \to 1,075° C$. For the calcite-dolomite solvus the critical temperature is approximately $T_c = 1,075° C$ (Goldsmith and Heard, 1961).

The fractionation expressions for oxygen isotopes determined experimentally by Northrop and Clayton (1966), line NC_1, and O'Neil and Epstein (1966), line OE_1, are contrasted in Fig. 15 with line S_o. Line NC_1 is the fractionation relation for dolomite-pure calcite derived from the calcite-water and dolomite-water relations. In all the dolomite-water experiments oxygen isotope equilibrium was not attained. Northrop and Clayton derived the equilibrium fractionation by graphical extrapolation from a set of incompletely exchanged runs. There are certain as yet incompletely understood problems with this method (Northrop and Clayton, 1966; Sheppard, 1966). Line OE_1 is the dolomite-pure calcite fractionation relation derived from CO_2-calcite and CO_2-dolomite exchange experiments. Because of experimental problems CO_2-dolomite fractionations were determined for two temperatures only, 400° and 350° C. O'Neil and Epstein stated that they did not consider that their relation was accurate enough for geothermometry. Line OE_2 is for dolomite-Mg-calcite and has been derived here from OE_1 and the solvus relations assuming a linear relation between the isotopic fractionation and $MgCO_3$ content at constant temperature.

Line NC_2 is taken from the carbonate-carbonate exchange reactions of Northrop and Clayton (1966) neglecting all runs with evidence for chemical or phase disequilibrium. It is not a well determined line because disequilibrium is prevalent in many of their experiments.

Fractionations given by the Mg-calcite-dolomite exchange experiments, line NC_2, are closer to the values inferred from the natural dolomite-Mg-calcite assemblages than those given by the indirectly derived expressions, lines OE_1 and NC_1. Although the reasons for these discrepancies are not apparent, it may not be satisfactory to assume that such indirect methods of determining equi-
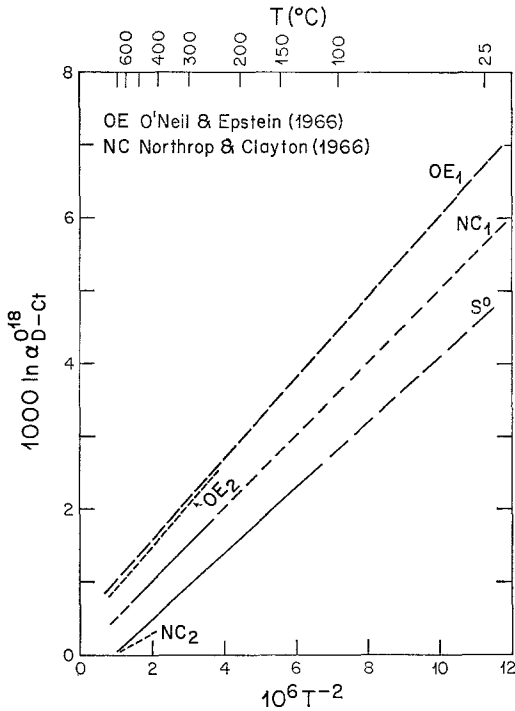
Fig. 15. Comparison of the experimentally determined oxygen isotope fractionation curves with curve S^o from the natural data (see text for discussion)

librium fractionations are always valid. Application of these three different thermometric relations, OE_1, NC_1 and S^o, to the Kent Quarry data give:

$$OE_1 \qquad T > 1,000°C$$

$$NC_1 \qquad T \sim 700°C$$

$$S^o \qquad T = 400°C.$$

The temperatures given by OE_1 and NC_1 are geologically quite unrealistic for biotite zone assemblages. In the light of the compelling arguments for assuming that the Kent Quarry data represents concordant relations between the carbon and oxygen isotope fractionations and magnesium partitioning, we conclude that relation S^o most probably represents the temperature dependence of the equilibrium oxygen isotope fractionation between dolomite and Mg-calcite.

Similarly curve S^c for carbon isotopes is considered the most probable equilibrium fractionation expression. Again the experimentally determined fractionation expression (Fig. 2) deviates markedly from S^c, except for $T \sim 600°C$. Again, temperatures calculated from the experimental expression are geologically unreasonable. These discrepancies between geologically and experimentally obtained isotopic fractionations indicate the need for further experimental isotopic study of the system dolomite-calcite.

Discordant Relations

It was noted that 45% of the samples were rejected during the selection operation because they did not have apparent concordant C- and O-isotope and $10^6 T_s^{-2}$

Table 9. *Selection analysis of samples with concordant Mg, C-and O-isotope fractionations*[a]

Sample No.	Large neg. ΔO^{18}	ΔO^{18} vs. ΔC^{13}	ΔC^{13} vs. $10^6\ T_s^{-2}$	ΔO^{18} vs. $10^6\ T_s^{-2}$	Selected
Vt3-51		C	C	C	C
Vt3-48					
Vt4-29		C	C	C	C
Vt3-65			C		
Vt3-47		C	C	C	C
Vt4-23		C	C	C	C
Vt3-83-3		C	C	C	C
Vt4-12-1					
Vt4-11B (5)		C	C	C	C
Vt4-35-1a (2)	×				
Vt4-35-1b (2)	×		C		
Vt4-35-5		C	C	C	C
Vt4-37-1					
Vt4-37-2	×				
Vt4-37-3		C	C	C	C
Vt4-37-4		C	C	C	C
Vt4-37-5	×		C		
Vt3-74		C	C	C	C
Vt3-75		C	C	C	C
Vt3-76			C		
GCh14			C		
G4-54-1		C	C	C	C
G4-55		C	C	C	C
G4-6		C	C	C	C
M16				C	
G4-5-3		C	C	C	C
G4-3		C			
G5-1	×				
G5-1b				C	
GLSK				C	
G3-11-1		C	C	C	C
Vt26[b]		C	C	C	C
Vt II 6[b]		C	C	C	C

[a] Samples with a large negative ΔO^{18}_{D-Ct} are marked: X. Samples with probable concordant relations are marked: C.
[b] From Schwarcz (1966).

relations (Table 9). One third of these samples have large negative O-isotope fractionations, showing that they have suffered conspicuous partial O-isotope exchange. The remaining samples fall into two groups:

Low Grade Samples. Vt3-48 is a black meta-limestone which has both a disequilibrium C-isotope fractionation and a calcite with a very low $MgCO_3$ content. There is little evidence for recrystallization. Although this sample comes from the upper chlorite zone (Fig. 3), neither cation nor C-isotope equilibrium was attained.

Vt3-65 from the chlorite zone has textural evidence for more than one generation of calcite. It is observed to have discordant O-isotope fractionation relations with both the C-isotopes and the solvus thermometer. However, the C-isotope frac-

tionation and the solvus relations are concordant. It is concluded that the O-isotope fractionation is probably not an equilibrium value.

Vt 4-12-1 comes from South Dorset (Fig. 5). The $MgCO_3$ content is similar to those from the Kent Quarry suite, Vt 4-11 B. The C- and O-isotope fractionations are discordant and probably out of isotopic equilibrium.

High-Grade Samples. The discordant relations observed in some marbles and calcareous schists from the Chester dome area indicate that oxygen or oxygen and carbon isotope exchange occurred which resulted in disequilibrium fractionations. These oxygen isotope fractionations are typically negative (e.g. Vt 4-35-1 b). Some of the carbon isotope fractionations in these same samples are consistent with equilibrium (e.g. Vt 4-35-1 b). It is possible that equilibrium carbon isotope fractionations may be preserved in these high grade rocks that have undergone subsequent incomplete oxygen isotope exchange.

Some Grenville samples have solvus temperatures that are appreciably higher than the isotopic temperatures. One interpretation is that carbon and oxygen continued to exchange between dolomite and calcite down to a lower temperature than magnesium. Alternatively, the high $MgCO_3$ content of the calcites may represent equilibrium distributions concordant with the isotope fractionations under pressures higher than the experimental pressures used to determine the $MgCO_3$ saturation solubility in calcite.

Geothermometry

Table 10 tabulates the temperatures determined from the carbon and oxygen isotope fractionations, expressions S^o and S^c, and the chemical and X-ray solvus data. An average temperature is given when the two isotope thermometers are concordant ($|T^o - T^c| < 75^\circ C$). We note

1. Apparent concordancy between all three properties is given by 55% of all the samples.

2. Excluding those samples with petrographic evidence for disequilibrium relations, 62% of the samples are triply concordant.

3. Double and triple concordancy is given by 83% of the samples lacking petrographic evidence for disequilibrium relations.

4. For the metamorphic zones in Vermont the following temperature ranges are observed

Chlorite Zone	(5 samples)	210° to 295°C
Biotite Zone	(12 samples)	255° to 400°C
Staurolite-Kyanite Zone	(16 samples)	110° to 550°C.

5. Many high-grade samples recrystallized at a temperature considerably less than the probable metamorphic maximum. This temperature difference may be as large as 400°C (e.g. Vt 3-75). Calcites are sometimes cloudy in these retrograde rocks (e.g. Vt 4-35, G 4-55).

6. Rocks with textural evidence for disequilibrium, such as presence of more than one generation of calcite (e.g. Vt 3-65), give discordant relations.

7. Carbon isotope equilibrium may never be closely attained in some low grade rocks (Vt 3-48, Vt 69 F).

Table 10. *Temperatures of metamorphic dolomite-calcite assemblages*

Sample	Grade	T_s (°C)	T_{sc} (°C)	T^o (°C)	T^c (°C)	T_{av} (°C)
Vt3-51	Chl	215		215	200	210
Vt3-48		175		325	d	
Vt4-29		250		285	300	295
Vt3-65		280		175	275	
Vt69F[a]		215		210	340	
Vt3-47	Bi	230		250	330	290
Vt4—23		360		360	305	335
Vt3-83-3		270		250	255	255
Vt4-12-1		435		255	150	
Vt4-11B		400		400	400	400
Vt60[a]		155		230	285	260
Vt41[a]		95		450	d	
Eq-K[a]		195		230	285	260
VtII36[a]	Gt	565		d	625	
Vt4-35-1a	S-K	560		d	360	
Vt4-35-1b		565		d	625	
Vt4-35-5		290		280	280	280
Vt4-37-1		130		255	d	
Vt4-37-2		375		d	625	
Vt4-37-3		380		545	555	550
Vt4-37-4		390		505	480	495
Vt4-37-5		405		d	505	
Vt26[a]		430		460	490	475
Vt1[a]		215		d	d	
VtII6[a]		85		115	125	110
Vt32[a]		535		d	625	
Vt34[a]		250		d	430	
Vt3-74		250		190	195	195
Vt3-75		230		160	150	155
Vt3-76		475		285	430	
GCh-14	L. Amph.	340		d	305	
G4-54-1	U. Amph.	480	645	365	385	375
G4-55		465		440	515	480
G4-6		480		400	390	395
M16		540		555	520	540
G4-5-3		545	680	420	490	455
G4-3		600		385	380	385
GLSK		635	705	625	440	
G5-1		515	690	d	190	
G5-1b		505		625	d	
G3-11-1	Gran.	590		d	580	

[a] Data from Schwarcz (1966).

Column headings: T_s is solvus temperature, X-ray method, and uncorrected for pressure; T_{sc} is solvus temperature, chemical method (Table 2); T^o: from expression S^o; T^c: from expression S^c; T_{av}: average temperature when T^o and T^c are concordant. d = disequilibrium.

The maximum temperature observed in each zone is consistent with other geological thermometry where comparable. Well defined geothermometric data for the chlorite zone is essentially lacking. A temperature of 300°C was inferred for the biotite isograd in the Dalradian of Scotland by McNamara (1965). This was based on (a) quartz segregations; (b) anatase-rutile transition; (c) synthesis fields for muscovite, chlorite, kaolinite. This temperature must be considered as approximate.

Size of the Equilibrium Exchange System

In the Kent and Valley Quarries, South Dorset, samples were collected to provide a three dimensional picture of the possible isotopic gradients on a local scale. The data for the carbon and oxygen isotope compositions and the $MgCO_3$ content of the calcites of 17 samples taken from an 130 ft. core steeply inclined to the inferred relict bedding in Kent Quarry are given in Table 6. These data are shown in Fig. 6 with reference to their location within the core. Significant variations in δO_{ct}^{18}, δC_{ct}^{13} and Mg between the samples are observed. The dotted lines between the sample locations (Fig. 6) are no more than guides to a minimum value for the gradient. The maximum observed gradients are: $0.13^0/_{00}$/foot for O^{18}, $0.28^0/_{00}$/foot for C^{13}, and 0.16 %/foot for Mg.

They signal the small size of the equilibrium exchange system across the inferred relict bedding for these properties. The size of the equilibrium system for carbon is smaller than that for oxygen. Thus, the 130 ft core system attained thermal equilibrium at a single temperature, $T = 400°C$, as argued above, but equilibrium exchange across the relict bedding for Mg, C^{13} and O^{18} was restricted to a few inches at most. The percent exchange cannot be determined here.

Four samples were collected from Valley Quarry; three from within and one from across a single bedding unit (Table 11). The isotopic composition for both carbon and oxygen is uniform over the distance of 100 ft. Significant gradients across the bedding are again observed.

Table 11. *Isotopic composition of calcite along and across the inferred relict bedding plane in Valley Quarry, South Dorset, Vermont*

Sample No.	δO_{Ct}^{18} $(^0/_{00})$	δC_{Ct}^{13} $(^0/_{00})$	Comments
Vt4-10-2	21.33	−0.35	Reference sample
Vt4-10-3-1	21.41	−0.30	12 ft. along inferred relict bedding plane from 10-2
Vt4-10-4	21.44	−0.31	100 ft. along inferred relict bedding plane from 10-2
Vt4-10-3-2	21.89	−0.03	4 inches across inferred relict bedding plane from 10-3-1

These data attest to the lack of an efficient communicating fluid in these systems. The variations in δO_{Ct}^{18} and δC_{Ct}^{13} may be largely relict variations inherited from the sedimentary protolith. Similar conclusions were reached from an isotopic and chemical study of the meta-iron formations of Quebec by Sharma *et al.* (1965) and Anderson (1967). In contrast, from an isotopic study in pelitic schists from Lincoln Mountain quadrangle, Vermont, Taylor *et al.* (1963) and

Garlick and Epstein (1967) found evidence for isotopic homogenization, through a presumed widespread oxygen bearing fluid, over distances of a few hundred meters.

Variation of Isotopic Composition with Metamorphic Grade

In Fig. 16 δC_D^{13} and δO_D^{18} from the metamorphic carbonates are compared between themselves and with the average isotopic composition of diagenetically altered limestone and its range. For δC_D^{13} neither a variation with grade nor a significant deviation from the marine limestone range is noted. The isotopic composition of the one greenschist-facies Grenville calcite, G4-40, (Table 8) also falls into this general pattern. Seven calcites from the Grenville of the Adirondacks, New York, have been analyzed by Craig (1953) and Taylor (1969). They observed

$$\text{Lowlands} \quad (3) \qquad \delta C_{Ct}^{13} = \quad 1.5 \text{ to } 3.1^0/_{00} \qquad \text{mean } 2.4^0/_{00}$$

$$\text{Highlands} \quad (4) \qquad \delta C_{Ct}^{13} = -1.6 \text{ to } 1.0^0/_{00} \qquad \text{mean } 0.0^0/_{00}.$$

With so few samples it is too early to say anything definitive about these apparent differences between the C^{13}/C^{12} ratios from the Highland and the Lowland carbonates. It is noted that many Grenville carbonates tend to be enriched in C^{13} compared with average limestone. Recent sediments with similar high values for C^{13}/C^{12} ratios are aragonites and calcites of algal, coralline and oolitic origin occurring in the Bahamas, Bermuda and the West Indies (Craig, 1953; Lowenstam and Epstein, 1957; Keith and Weber, 1964; Weber, 1967). It seems reasonable to assume, with no evidence to the contrary, that the C^{13}/C^{12} ratio for essentially pure marble is largely inherited from the sedimentary precursor.

    In Vermont, δO_D^{18} decreases from the biotite and chlorite zone, where the isotopic compositions are similar to limestones, to the staurolite-kyanite zone. The latter group from the Chester dome area show an appreciable range in composition: $\delta O_D^{18} = 12$ to $20^0/_{00}$. In contrast, the high grade Grenville carbonates cluster around the limestone range. In the Adirondacks, Taylor (1969) observed similar O^{18}/O^{16} ratios to those observed here except for one sample from the Highlands with $\delta O_{Ct}^{18} = 13.8^0/_{00}$. One of the most O^{18} depleted samples analyzed here is GCS from within a pure calcite unit immediately to the east of the Blue Mountain nepheline syenite. It would be interesting to determine whether there are widespread significant decreases in the O^{18}/O^{16} ratio, compared with average limestone, of carbonates adjacent to igneous bodies, especially since Taylor (1969) has postulated the importance of oxygen isotope exchange between the Highland marbles and the anorthosite complex.

    All samples with petrographic evidence for dedolomitization are plotted against the percent of Mg-silicate present (Fig. 17). For the Chester dome samples a trend is noted for both δC_D^{13} and δO_D^{18} vs modal percent of Mg-silicate. Grenville carbonates show no such systematic variation. Two processes, either singly or in combination, could produce these observed trends for the Chester dome samples: *1. Decarbonation.* At equilibrium for metamorphic temperatures, CO_2 is isotopically heavier than the carbonates for both oxygen and carbon (Northrop and Clayton, 1966; O'Neil and Epstein, 1966; Bottinga, 1968). If the liberated CO_2 tends to be in equilibrium with the carbonates then progressive isotopic enrichment of the
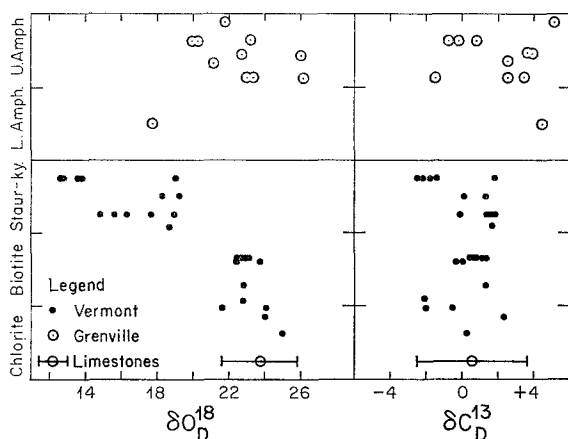
Fig. 16. Variation of the isotopic composition of dolomites from Vermont and the Grenville Province with metamorphic grade. The range of isotopic compositions of normal marine limestones is included

carbonate in C^{12} and O^{16} occurs to an extent dependent on the degree of decarbonation and the fractionation factor for the process. In thermal decomposition experiments with dolomite Sharma and Clayton (1965) report a kinetic isotopic effect, decreasing with increasing temperature, which also enriches the liberated CO_2 in O^{18}. Although the nature of the natural decarbonation processes are not known, the trends noted in the rock data are consistent with either equilibrium or disequilibrium loss of CO_2 by decarbonation. Shieh and Taylor (1969) have similarly observed that the CO_2 liberated during contact metamorphic decarbonation reactions is enriched in C^{13} and O^{18} relative to the carbonates.

2. *Mixing.* The siliceous dolomitic marbles and schists are metamorphosed mixtures of carbonate of a composition similar to Paleozoic limestones ($\delta O^{18} = 24 \pm 2^0/_{00}$; Keith and Weber, 1964) and psammo-pelitic siliceous sedimentary rocks ($\delta = 11$—$18^0/_{00}$; Taylor and Epstein, 1964). Closed-system metamorphism of such a mixture would result in a negative correlation between O^{18}/O^{16} ratio of dolomite and modal abundance of silicates.

Similarly, there might also be some carbonaceous material ($\delta C^{13} = -25$ to $-30^0/_{00}$; Craig, 1953) mixed with the pelitic fraction of the protolith. Graphite is in fact observed as a minor accessory in many of the marbles and calcareous schists. Isotopic exchange between the reduced carbon phase and carbonate would result in a lightening of the latter, which would be proportional to silicate content assuming a roughly constant carbon-content in the pelitic component.

3. *Exchange.* Exchange between the carbonates and some non-carbonate medium whose isotopic composition may be determined in part or in whole externally to the system. Some marbles (e.g. Vt4-37-2) have undergone partial exchange since they contain almost no silicates and cannot have been decarbonated.

Calcareous non-dolomitic rocks from Vermont studied by Schwarcz, Clayton and Mayeda (1970) display a similar correlation between silicate content and δO^{18} of calcite (line B in Fig. 17), although their data are more dispersed about line "B" than are the present data about curve "A". This variation of δO^{18}_{Ct} cannot be due to decarbonation reactions since only a small fraction of the silicates (principally quartz, mica and feldspar) in these non-dolomitic rocks have been formed by reactions between carbonates and silicates. Schwarcz et al. attribute
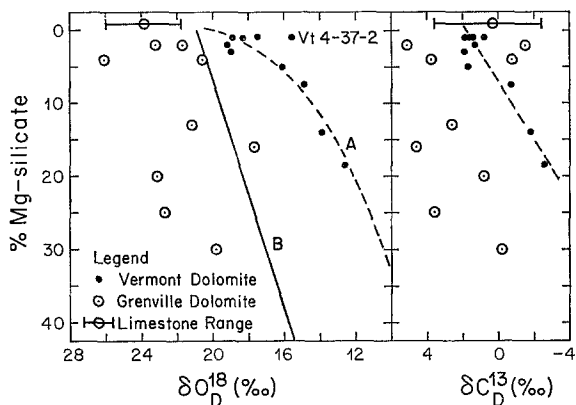
Fig. 17. Variation of the isotopic composition of dolomites from Vermont and the Grenville Province with the modal abundance of Mg-silicates (wt %). The dashed curve (A) is the trend shown by the Chester dome samples. Curve B, taken from Schwarcz et al. (1970) is for non-dolomitic marbles, calcareous quartzites and schists of Vermont

the trend to closed system carbonate-silicate isotopic exchange. In contrast curve "A" cannot be simply explained by mixing psammo-pelitic sediment ($\delta O^{18} \simeq 11$—$18^0/_{00}$) with limestone ($\delta O^{18} \simeq 24^0/_{00}$) because it extrapolates to a δO^{18} value lighter than that of any probable admixed sedimentary protolith. Although it is possible that trend "A" may be due to exchange with a light oxygen-rich reservoir external to the carbonate-silicate system, the absence of any such exchange in the calcitic marbles and schists suggests that it is not important here. In conclusion, the most probable explanation of trend "A" is the loss of O^{18}-enriched CO_2 during decarbonation coupled with some exchange with admixed silicate material.

Whatever the process, decarbonation, mixing and/or exchange, the communication across the foliation apparently was limited as judged from samples Vt4-35 and Vt4-11 B. More effective exchange processes may have smoothed out the differences between the marbles and silicate-marbles from the Grenville Province. Comparison of petrographic features of Grenville marbles with Vermont marbles from a similar temperature environment also suggests that more extensive recrystallization occurred in the former since their texture is coarser and they contain more abundant pegmatitic material.

Summary and Conclusions

From the analyses for $MgCO_3$ in calcite and the carbon and oxygen isotope relations in dolomite-calcite assemblages from marbles of Vermont and the Grenville, and the experimental equilibration studies, the following statements and conclusions may be made:

1. Samples from the metamorphic zones of Vermont gave the following temperature ranges:

Chlorite Zone	210° to 295° C
Biotite Zone	255° to 400° C
Staurolite-Kyanite Zone	110° to 550° C.

2. Although there is some spread of solvus derived temperatures at each metamorphic grade and particularly at the higher grades the maximum temperature correlates well with the metamorphic grade.

3. Calibration of the isotopic thermometers using the solvus thermometer gave the expressions: $(600° > T > 200°C)$

$$S^o \qquad 1,000 \ln \alpha_{D\text{-}Ct}^{O^{18}} = 0.45 \, (10^6 T^{-2}) - 0.40$$

$$S^c \qquad 1,000 \ln \alpha_{D\text{-}Ct}^{C^{13}} = 0.18 \, (10^6 T^{-2}) + 0.17.$$

4. Apparent concordancy between two or more of the three thermometric properties is given by 83% of the samples lacking textural evidence of disequilibrium.

5. Oxygen isotope disequilibrium occurs in some high grade samples, particularly from the Chester dome area, Vermont. Many of these are characterized by large negative $\delta O_D^{18} - \delta O_{Ct}^{18}$ values.

6. Rocks showing textural evidence for disequilibrium, such as calcite veins filling fractures, give discordant isotope relations.

7. In high grade rocks, the complexity of the metamorphic history, both thermal and structural-tectonic, is reflected in the variability of the temperature of quench or recrystallization. This temperature may be as much as 400°C below the probable metamorphic maximum.

8. No unequivocal criterion (texture, mineral assemblage, etc.) has been found to select a high-grade rock which will yield an isotopic or solvus temperature (X-ray method) close to the probable metamorphic maximum, except actual measurement of one of the thermometric properties.

9. Analysis of the suite of samples from the biotite zone, southwestern Vermont demonstrates that, although thermal equilibrium was closely attained at a single temperature (400°C) for all samples as shown by the magnesium, and carbon and oxygen isotope fractionations, the size of the equilibrium exchange system was small, less than a few inches, across the inferred relict bedding. The scarcity of pore fluid may be responsible for this restricted communication.

10. C^{13}/C^{12} ratios of Grenville and Vermont carbonates and O^{18}/O^{16} ratios of Grenville and greenschist-facies carbonates of Vermont span the range of diagenetically altered limestones. Staurolite-kyanite zone carbonates from the Chester dome area are depleted in O^{18} due to equilibrium or disequilibrium decarbonation and partial exchange.

Since exsolution processes are least important in the greenschist-facies rocks these thermometers are well suited for studying the temperature regime through the greenschist-facies. Such a study could determine the importance of variations of a_{H_2O} and a_{CO_2} on the temperature of a given reaction because the three thermometers are independent of these variables. In high-grade calcareous rocks a variety of apparent temperatures may be given including values similar to the presumed maximum value. Interpretation of the retrograde temperatures that are significantly lower than the maximum metamorphic temperature in terms of some specific geologic event occurring within the cooling history must await detailed isotopic and other studies. It would be important to establish whether retrograde temperatures from a given metamorphic area tend to cluster around certain values as possibly suggested by Vt3-74 and Vt3-75, and G4-45-1, G4-55 and G4-6. A detailed study of the exsolution processes may clarify relations here too.

The fractionation relations S^o and S^c can possibly be extrapolated to lower temperatures and applied to calcite-ordered dolomite assemblages. For temperatures between 25° and 0° C S^o gives fractionations between 4.7 and 5.7⁰/₀₀ respectively, and S^c gives values between 2.2 and 2.6⁰/₀₀. Comparison of these fractionation relations, S^o and S^c, with dolomite-calcite fractionation data from telethermal alteration haloes (Friedman and Hall, 1963), diagenetic dolomites (Fritz, 1967) or syngenetic dolomites (Degens and Epstein, 1964) indicates that in these environments oxygen and carbon isotope disequilibrium is prevalent. Relations S^o and S^c are not strictly applicable to disordered or Ca-rich dolomites. Also the phosphoric acid-carbonate fractionation factor may vary with the state of disordering in the dolomite. However, these disorder phenomena probably do not have a large effect on the isotopic properties of dolomite.

Weber (1964) observed fractionations in fine-grained lacustrine limestones ranging from 5.3 to 7⁰/₀₀. These may represent equilibrium between the two carbonates. Such data, however, must be treated with caution since dolomite-calcite oxygen isotope fractionations between 2 and 7⁰/₀₀ have been attributed to differential, non-equilibrium exchange of one or both phases during their diagenetic history (Berner, 1965; Gross and Tracey, 1966).

Recently for carbonate sediments from Deep Springs Lake, California, Clayton *et al.* (1968) have presented isotopic evidence for the direct crystallization of dolomite from solution without the $CO_3^=$ group being inherited from a calcite precursor. Their measured dolomite-water fractionation combined with the calcite-water fractionation gives a dolomite-calcite fractionation of 5.4⁰/₀₀ at about 20° C. This agrees more closely with the value derived here by extrapolation of S^o than with the values derived from the various extrapolations of the experimental data of O'Neil and Epstein (1966) and Northrop and Clayton (1966).

Appendix I

Calcite-Dolomite Exchange Experiments

All the carbonate exchange reactions were carried out using conventional hydrothermal apparatus. Cold seal bombs (O.D.=2.0″, I.D.—0.5″) (Tuttle, 1949) holding three gold capsules (d=6 mm, l=3.8 cm) were run at the selected temperature and 1,000 bars water pressure. The pressure is read directly off a gauge connected to the bomb. The temperature was measured by a chromel-alumel thermocouple placed in a well in the bomb wall close to the sample. The temperature is recorded to ±5°C. Quenching was completed in a few minutes at constant pressure using a cold air blast until T<400°C, followed immediately by a cold water bath.

In each charge an intimate mixture of calcite and dolomite of known composition was sealed in a gold capsule with a known quantity of water plus salts. The isotopic compositions of the starting materials were chosen so that the exchange reactions for two of the three charges would approach the equilibrium fractionation from a distance, but from opposite sides, while the third charge had an initial composition quite close to the anticipated equilibrium value. The composition of the water plus salt was dictated by the following considerations:

1. H_2O water was added to aid the exchange reactions.
2. $CaCl_2$ above about 100°C dolomite is incongruently soluble in water (Morey, 1962; Rosenberg and Holland, 1964). Addition of small quantities of Ca^{++} ions prevents this decomposition of dolomite. It was felt important to prevent the formation of other phases such as magnesite in order to restrict the partial equilibration studies to simple exchange reactions.

3. NH_4HCO_3 dolomite decomposes to brucite plus calcite in water at high temperatures and low P_{CO_2}. The minimum quantity of NH_4HCO_3 was added sufficient to prevent brucite formation.

4. NH_4Cl exchange rates are increased in carbonate systems by the addition of NH_4Cl (Clayton, 1959).

A description, isotopic composition of the starting materials and, partial chemical analyses of the dolomites are given in Tables 12 and 13 respectively. In all runs, with $T > 320°C$, the fluid phase probably can be considered as an aqueous rich single phase (Takenouchi and Kennedy, 1964). X-ray examination of the solid phases at the conclusion of all runs revealed only Mg-calcite and dolomite. No magnesite nor brucite was detected.

Table 12. *Description and isotopic composition of the starting materials*

Sample		δO^{18} ($^0/_{00}$)	δC^{13} ($^0/_{00}$)	Description
Calcites:	A-calcite	13.35	− 7.07	Reagent grade $CaCO_3$ (B.D.H.)
	H-calcite	8.74	8.80	$CaCO_3$ synthesized from Tivoli travertine
	L-calcite	4.80	− 28.07	$CaCO_3$ synthesized from tank CO_2
Dolomites[a]:	H-dolomite	27.37	2.94	A white metamorphic dolomite from Haley, Ontario; well-defined order reflections
	B-dolomite	11.20	− 8.00	A natural hydrothermal dolomite from Bamle, Norway; from the same hand specimen as that used by Northrop and Clayton (1966)
Others:	$CaCl_2$			A solution of 4.22 g of reagent grade $CaCl_2 \cdot 2H_2O$ in 100 cc. H_2O
	NH_4HCO_3	3.21[b]	− 25.80	Reagent grade (B.D.H.)
	NH_4Cl			Reagent grade (Fisher)
	H_2O			Laboratory distilled water

[a] Partial chemical analyses are given in Table 13.
[b] Using $\alpha_{CO_2-NH_4HCO} = 1.01025$.

Table 13. *Partial chemical analyses of dolomite starting materials*

Sample	$FeCO_3$	$MnCO_3$	$SrCO_3$
Haley dolomite	0.00	0.02	0.023
Bamle dolomite	5.69	0.15	0.003

Analyst: J. R. Muysson.

Recrystallization of the calcite was conspicuous in all runs except the one at 335°C. Cation (Mg-Ca) equilibrium was closely attained in all the exchange runs except CtD II at 335°C (Table 14). Some calcite crystals were as large as 1 mm across. Recrystallization of the dolomite, if any, was less apparent and difficult to judge because of the presence of intimately mixed finger-grained calcite. Absence of the very fine fraction was noticeable.

The experimental data for C^{13} were analyzed using the graphical interpolation method of Northrop and Clayton (1966). Their relations are

$$\ln \alpha_i = \ln \alpha_e + B\,(\ln \alpha_f - \ln \alpha_i)$$

where $1{,}000 \ln \alpha_i$ = initial fractionation (observed)
$1{,}000 \ln \alpha_f$ = final fractionation (observed)
$1{,}000 \ln \alpha_e$ = equilibrium fractionation (determined)
B = constant.

The initial and final isotopic analyses of each charge in a set were plotted as $(\ln \alpha_f - \ln \alpha_i)$ against $\ln \alpha_i$. The method predicts that this plot should give a straight line of slope B and with an intercept of $\ln \alpha_e$. Northrop and Clayton (1966, p. 179) state that "the fact that so many different sets of samples run under widely varying conditions yielded linear plots is a good indication that this method is valid". The accuracy of the method is greatly enhanced by an increase in the percentage of exchange. The percentage of exchange is measured by $-100/B$, if some exchange occurs throughout the whole crystal (Table 4).

Three charges were run together in a single bomb in order to have identical thermal histories. The results from these sets of charges are given in Table 14. The extrapolated equilibrium fractionations derived from these data are presented in Table 4 and Fig. 2.

Table 14. *Experimental data for sets of dolomite-calcite samples*

Run	D	Temp. (°C)	Time (hrs)	Solvus Temp. (°C)	$10^3 \ln \alpha_i$	$10^3 \ln \alpha_f$	$10^3 (\ln \alpha_f - \ln \alpha_i)$	δO_{Ct}^{18} (°/₀₀)
CtD II	H	335	803	~25	− 5.24	− 3.57	1.67	7.34
					31.36	28.13	− 3.23	6.97
					1.00	1.32	0.32	9.21
CtD III	H	500	346	485	− 3.58	− 1.01	2.57	1.20
					31.24	14.70	− 16.54	0.06
					1.46	1.46	0.00	1.46
CtD I	H	590	240	570	− 2.66	− 0.69	1.97	0.52
					31.19	7.77	− 23.42	0.20
					2.08	0.98	− 1.10	1.23
CtD IV	H	610	113	580	− 2.83	− 0.67	2.16	0.50
					2.10	0.39	− 1.71	2.28
CtD V	B	590	113	565	− 13.62	− 7.36	6.26	− 0.14
					20.22	6.55	− 13.67	− 0.40
					− 8.72	− 4.53	4.19	+ 0.08

The composition of a typical initial charge was: H_2O, 83.5 mg; $CaCl_2$(sol), 16.4 mg; NH_4Cl, 6.7 mg; NH_4HCO_3, 5.1 mg; $CaCO_3$, 65.0 mg; $CaMg(CO_3)$, 65.0 mg. A small correction was made for the NH_4HCO_3 content of each run.

As noted in the text the present experiments do not satisfy all the requirements of the method as described by Northrop and Clayton. The starting materials consisted of a mixture of solid phases and not of a single crystalline phase identical in all sets of three charges plus an homogeneous isotopic reservoir. In each set of charges the same dolomite starting material was used. However, different calcites with possible significant differences in composition, defect density and surface properties were used. Because the analysis of a charge run for a few hours at 500°C demonstrated that the calcite recrystallized rapidly it was assumed that these differences in the calcites would not seriously violate the above requirements. The disparity between the experimental estimates of $\alpha_{D-Ct}^{C^{13}}$ and the geological estimates given in the text suggest that this assumption is not fully justified. Also the extrapolation technique may not be satisfactory when the changes in C^{13}/C^{12} ratios are very small (see O'Neil and Taylor, 1969).

Appendix II

Sample Localities

1. Southwestern Vermont

Vt3-51	Middlebury quadrangle, 3.5 miles W. of Middlebury on U.S. 125 Highway. Burchards formation
Vt3-48	Middlebury quadrangle, 0.25 mile W. of New Haven Junction on U.S. 17 Highway. Bascom formation
Vt4-29	Middlebury quadrangle, 1 mile E. of Weybridge along Otter Creek. Beldens formation
Vt3-65	Bomoseen quadrangle, 1.1 mile E. of Hortonville. Hortonville formation
Vt3-47	Middlebury quadrangle, 0.7 mile E. of New Haven Junction on U.S. 17 Highway. Burchards formation
Vt4-23	Brandon quadrangle, Landon quarry, 3 mile S. 15 E. of Brandon. Shelburne formation
Vt3-83-3	Equinox quadrangle, Valley quarry, South Dorset. Shelburne formation
Vt4-10	Valley quarry
Vt4-12-1	Equinox quadrangle, Bennington quarry, South Dorset. Shelburne formation
Vt4-11 B	Equinox quadrangle, Kent quarry, South Dorset. Shelburne formation

2. Southeastern Vermont

Vt4-35	Ludlow quadrangle, Duttonsville Gulf, 3 miles N. of Gassetts. Cavendish formation
Vt4-37	Ludlow quadrangle, 0.5 mile S. of Amsden by Black River. Cavendish formation
Vt3-74	Ludlow quadrangle, 1 mile S. of Felchville on U.S. 106 Highway. Cavendish formation
Vt3-75	Saxtons River quadrangle, on Vermont State Highway 35, 0.7 mile S. of Williams River, Grafton Gulf. Cavendish formation
Vt3-76	Wilmington quadrangle, 2 mile S. 20 W. of Whitingham. Cavendish formation

3. Grenville Province — Ontario and Quebec

G Ch-14	Chandos Twp., Ont., 2.5 miles E. of Lasswade on dirt road
G4-54-1	Denbigh Twp., Ont., 1 mile N.E. of Hydes Creek on Highway 41
G55	Denbigh Twp., Ont., 0.4 mile N.E. of Hydes Creek on Highway 41
G4-6	Griffith Twp., Ont., 1.2 miles N.E. of Hydes Creek on Highway 41
M16	Monmouth Twp., Ont., boundary between Lots 13—14, Con. XIV. Collected by H. S. Armstrong
G4-5-3	Renfrew Co., Horton Twp., Ont., 0.5 mile N.E. of Payne
G4-3	Renfrew Co., Ross Twp., Ont., 1.5 miles E. of Haley Station
GLSK	Pontiac Co., Pontefract Twp., Gibb Lake, Quebec
G5-1	Parry Sound District, Seguin River, Ont., E. side of bridge
G5-1b	Parry Sound District, Seguin River, Ont., W. side of bridge
G3-11-1	Leeds Co., Bastard Twp., Ont., 0.8 mile S. 20 E. of Philipsville
G4-40	Madoc Twp., Ont., 1 mile N. on Highway 62 from Madoc
GCS	Methuen Twp., Ont., in contact zone to east of Blue Mountain nepheline syenite
Haley	Renfrew Co., Ross Twp., Ont., Haley dolomite quarry

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Dr. S. M. F. Sheppard
Department of Geological Sciences
University of Texas
Austin, Texas 78712, U.S.A.