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OXYGEN AND CARBON ISOTOPIC COMPOSITION OF GRENVILLE MARBLE, AND AN APPRAISAL OF EQUILIBRIUM IN THE DISTRIBUTION OF ISOTOPES BETWEEN CALCITE AND ASSOCIATED MINERALS, OTTER LAKE AREA, QUEBEC, CANADA

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ABSTRACT

Marble occurs abundantly in a portion of the Grenville Province of the Canadian Shield extending from the Adirondack Mountains, through Ontario, and into the Laurentian Highlands of Quebec, a distance of 300 km. In the Otter Lake area of western Quebec, major marble units, which are obviously metamorphosed limestone, consist of combinations of calcite, dolomite, olivine, humite-group minerals, Ca pyroxene, Ca amphibole, biotite, graphite, and retrograde serpentine and brucite, whereas minor marble units, which are evidently metasomatic rocks, consist of combinations of (pink) calcite, Ca pyroxene, Ca amphibole, biotite, garnet, K-feldspar, scapolite, and titanite. The oxygen and carbon isotopic composition of calcite in the major marble units ($\delta^{18}O_{VSMOW}$ in the range 28 to 17‰; $\delta^{13}C_{PDB-1}$ in the range +6 to –2‰) is the same as in the Adirondacks and in unmetamorphosed Proterozoic limestone; only slight shifts (~1‰) can be attributed directly to metamorphic reactions. In bodies of minor marble, mean concentrations of ^{18}O and ^{13}C are slightly lower (+14.5 and +0.23‰, respectively). Mean fractionation-factors (α), expressed as 1000 ln α, are as follows: ^{18}O, calcite/dolomite, +0.295 ($n = 11$); ^{13}C, calcite/dolomite, –0.346 ($n = 12$); ^{18}O, calcite/biotite, +3.49 ($n = 5$); ^{13}C, calcite/graphite, +3.74 ($n = 5$). Additional (exploratory) results ($n = 1$) on the distribution of ^{18}O are as follows: calcite/olivine, +3.5; calcite/clinohumite, +5.1; calcite/garnet, +2.4; calcite/titanite, +3.1; calcite/Ca pyroxene, +2.0; calcite/Ca amphibole, +2.4, calcite/K-feldspar +1.8; calcite/scapolite, +2.0; calcite/serpentine, +13.9; calcite/brucite, +19.7; a trend of increasing α is related to increasing OH/(O + OH) in the non-carbonates and the preference of OH for ^{16}O. For the first group of mineral pairs ($n \geq 5$), a small *variation* in α across the study area (relative standard deviation ~0.05%) is viewed as an expression of a close approach to isotopic exchange equilibrium, and for certain pairs from the second group ($n = 1$), a temperature estimate close to 700°C (the biotite–garnet temperature of associated gneisses) is also viewed as evidence for equilibrium. Attainment of isotopic exchange equilibrium was facilitated by dynamic recrystallization, which occurred during the peak of metamorphism.

Keywords: marble, oxygen isotopes, carbon isotopes, exchange equilibrium, Grenville Province, Otter Lake, Quebec.

SOMMAIRE

On trouve des séquences de marbre en abondance dans la partie de la Province du Grenville du bouclier canadien traversant de la chaîne des monts Adirondack, vers l'Ontario, jusque dans les Laurentides, au Québec, sur une distance de 300 km. Dans la région du lac Otter, dans la partie occidentale du Québec, des unités majeures de marbre, de toute évidence des séquences de calcaire à l'origine, contiennent des assemblages de calcite, dolomite, olivine, minéraux du groupe de la humite, pyroxène calcique, amphibole calcique, biotite, graphite, ainsi que serpentine et brucite rétrogrades, tandis que les unités mineures de marbre, d'origine métasomatique, contiennent des assemblages de calcite (rose), pyroxène calcique, amphibole calcique, biotite, grenat, feldspath potassique, scapolite, et titanite. La composition isotopique de l'oxygène et du carbone dans la calcite des unités majeures de marbre ($\delta^{18}O_{VSMOW}$ dans l'intervalle entre 28 et 17‰; $\delta^{13}C_{PDB-1}$ dans l'intervalle entre +6 et –2‰) est la même que dans les roches semblables des Adirondacks et dans les calcaires protérozoïques non métamorphisés; on peut attribuer les légers décalages (~1‰) directement aux réactions métamorphiques. Dans les accumulations de marbre dites mineures, les concentrations moyennes de ^{18}O et ^{13}C sont légèrement plus faibles (+14.5 et +0.23‰, respectivement). Les facteurs de fractionnement moyens (α), exprimés sous forme de 1000 ln α, sont comme suit: ^{18}O, calcite/dolomite, +0.295 ($n = 11$); ^{13}C, calcite/dolomite, –0.346 ($n = 12$); ^{18}O, calcite/biotite, +3.49 ($n = 5$); ^{13}C, calcite/graphite, +3.74 ($n = 5$). Des résultats de reconnaissance additionnels ($n = 1$) portent sur la distribution de ^{18}O: calcite/olivine, +3.5; calcite/clinohumite, +5.1; calcite/grenat, +2.4; calcite/titanite, +3.1; calcite/pyroxène calcique, +2.0; calcite/amphibole calcique, +2.4, calcite/feldspath potassique, +1.8; calcite/scapolite, +2.0; calcite/serpentine, +13.9; calcite/brucite, +19.7; le facteur α a une tendance d'augmenter avec le rapport OH/(O + OH) dans les phases non-carbonatées à cause de la préférence qu'a le OH d'incorporer ^{16}O. Pour le premier groupe de paires de minéraux ($n \geq 5$), une légère *variation* en α dans la région étudiée (écart-type relatif d'environ 0.05%) serait l'expression d'un équilibre approximatif par rapport à l'échange isotopique. Dans le cas de certaines paires de minéraux du second groupe ($n = 1$), une température estimée proche de 700°C (température indiquée selon le géothermomètre biotite–grenat des gneiss associés) serait un autre indication de l'équilibre. Que l'équilibre isotopique ait été atteint a été facilité par la recristallisation dynamique, lors du paroxysme métamorphique.

(Traduit par la Rédaction)

Mots-clés: marbre, isotopes d'oxygène, isotopes de carbone, équilibre d'échange, Province du Grenville, lac Otter, Québec.

INTRODUCTION

A belt of Proterozoic marble, gneiss, and quartzite extends from the Adirondack Mountains in New York, into eastern Ontario, and from there across the Ottawa River into Quebec, a distance of 300 km (Fig. 1). Isotopic data on calcite in marble from Ontario were reported by Sheppard & Schwarcz (1970) and by Dunn & Valley (1992, 1996), and from the Adirondacks by Valley & O'Neil (1984), Kitchen & Valley (1995), and others. These authors found that the isotopic composition of calcite in Grenville marble is the same as that in unmetamorphosed limestone of similar age, and that the composition was therefore largely preserved during deformation and metamorphism. The first objective of the present study is to present comparable data from the Otter Lake area in Quebec (Fig. 2), where several varieties of marble occur, including some that are evidently metasomatic in origin, and where the mineral composition of these rocks and the associated gneisses has been examined previously.

Since the earliest studies of the distribution of isotopes between metamorphic minerals, *i.e.,* those of Clayton & Epstein (1958), Taylor *et al.* (1963), Garlick & Epstein (1967), Taylor & Coleman (1968) and Shieh & Taylor (1969), the question of the attainment and preservation of exchange equilibrium has been considered frequently, this being of importance to the use of isotopes as geothermometers. For example, Bottinga & Javoy (1975) and Deines (1977) found that some samples of metamorphic rock have conserved an oxygen isotope equilibrium temperature, whereas in other samples, changes in isotopic composition evidently occurred during cooling. Later, Giletti (1986) and Eiler *et al.* (1992) examined possibilities for isotopic exchange during cooling, using data on the diffusion of oxygen in crystals. A second objective of the present study is to determine if equilibrium in the distribution of oxygen and carbon isotopes between calcite and associated minerals was realized in the study area, where peak temperatures of metamorphism are estimated to have been nearly uniform throughout. Two criteria will be applied: 1) if the observed *variation* in a particular fractionation-factor (*e.g.,* ^{18}O, calcite/dolomite) across the field area is very small, the result will be viewed as evidence for a close approach to exchange equilibrium, and 2) where only a single mineral pair was analyzed (*e.g.,* ^{18}O, calcite/olivine), an isotopic temperature near the estimated peak temperature of metamorphism will also be viewed as evidence for equilibrium. Possible causes for departure from exchange equilibrium will then be considered.

All of the isotope analyses reported here were obtained on high-purity mineral separates. Compositional variation on the 2 to 10 cm scale was investigated in six samples, leaving for the future a study of variation on the scale of 1 μm to 1 mm.

GEOLOGICAL SETTING

Bedrock in the study area (Fig. 2) consists principally of marble (symbol 1, Fig. 2), pelitic to mafic gneisses with sillimanite, biotite, garnet, hornblende, Ca pyroxene, and local orthopyroxene plus minor quartzite (2), metagabbro (3), K-feldspar (veined) gneiss (4) and granite and syenite (5).

On the basis of mineral content, the marble can be classified as shown in Table 1, where varieties referred to as Major marble are by far the most common. They are locally interlayered with biotite–garnet gneiss and quartzite, and are obviously metamorphosed limestone. Varieties of marble referred to as Minor marble in Table 1 occur as conformable layers, one to a few meters thick,

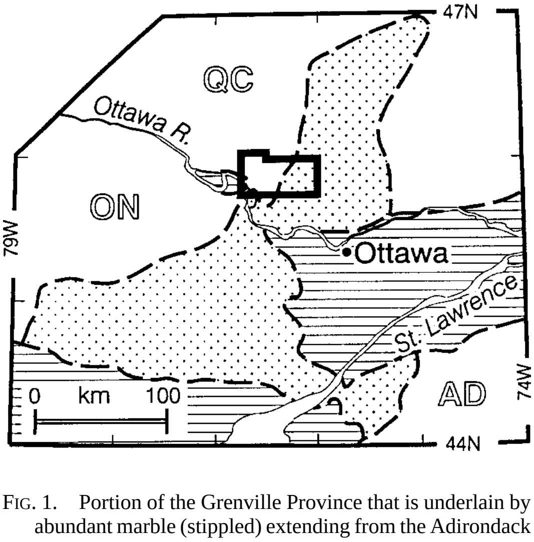

FIG. 1. Portion of the Grenville Province that is underlain by abundant marble (stippled) extending from the Adirondack Mountains in New York (AD) through Ontario (ON) and into Quebec (QC); horizontal line pattern delineates Paleozoic cover; from Baer *et al.* (1971). Study area (Fig. 2) is located.

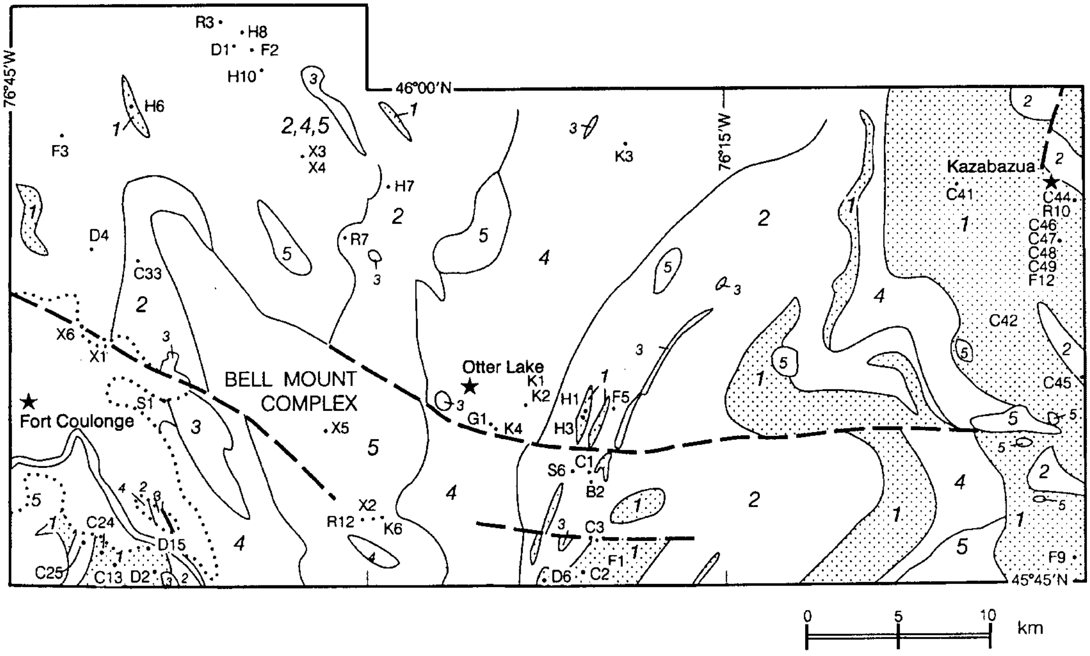

FIG. 2. Simplified geological map of the study area; dominant rock-types are as follows: 1 marble, 2 gneiss and amphibolite, 3 metagabbro, 4 K-feldspar (veined) gneiss, 5 granite and syenite; all samples are located with the exception of the following, which lie to the north, C 27 (46° 12.3'N, 76° 39.8'W), R 1 (46° 09.2', 76° 36.7'), R 4 (46° 06.7', 76° 30.6'), R 5 (46° 11.9', 76° 37.7'), K 5 (46° 12.8', 76° 37.9'), and one to the south, C 50 (45° 44.1'N, 76° 23.7'W); samples X1 to X6 are skarn, veins, breccia (Fig. 4). Some of the geological data in the eastern third of the area are from Baker (1956), and in the southwestern corner (Calumet Island), from Shaw (1956).

TABLE 1. VARIETIES OF MARBLE, OTTER LAKE AREA, QUEBEC

Major marble	
C	Common calcite and calcite–dolomite marble (calcite > dolomite) with graphite, biotite, Ca amphibole, Ca pyroxene
D	Dolomite marble (dolomite >> calcite)
F	Olivine-bearing marble
H	Marble containing humite-group minerals
S	Serpentine-rich marble
B	Brucite-bearing marble
Minor (pink calcite) marble; dolomite and graphite are absent	
R	Calcite – Ca pyroxene – Ca amphibole – biotite marble
K	Calcite – Ca pyroxene – K-feldspar – scapolite marble
G	Calcite – garnet marble

associated with veined gneiss, or as irregular bodies adjacent to or within granite–syenite complexes (Kretz 1980). Marble samples chosen for isotopic study are listed in Tables 2, 3, and 4, and sample locations are indicated in Figure 2.

On the basis of work by Skippen (1974), Käse & Metz (1980) and others, mineral assemblages in marble of the study area are considered to be stable at the amphibolite–granulite facies boundary, *i.e.*, at approximately 650 to 700°C, 6.5 to 7.0 kbar, allowing for some variation in the activity of H_2O and CO_2 in the crystal-boundary phase, as discussed elsewhere by the writer (Kretz 1980). The obvious exception is the local presence of minor quartz with dolomite (Table 2) (resulting evidently from the low-temperature introduction of silica), and the presence of epidote, serpentine, and brucite (Tables 2 to 4), which are products of retrograde metamorphism. Similar conclusions apply to the gneisses of the study area. Thus, excluding a down-faulted block of the Ottawa rift structure (in the southwest corner of the study area) where metamorphic grade is slightly lower, a variation in metamorphic grade across the study area cannot be demonstrated, on the basis of mineral associations.

The microstructure of the marble units varies greatly. The diameter of calcite and dolomite crystals in single samples commonly ranges from less than 1 mm to 5 mm [(*e.g.*, Fig. 3, also Fig. 4 of Kretz (1996)], and locally is 3 cm or more. Biotite crystals commonly have a mean diameter of 1 mm with a range, in single samples, that extends from 0.1 to 2.5 mm. Other silicates are of comparable size. Tabular crystals of biotite and graphite are

TABLE 2. ASSEMBLAGES AND PROPORTIONS OF MINERALS, AND ISOTOPIC COMPOSITION OF CARBONATES IN SAMPLES OF MARBLE C AND D, OTTER LAKE AREA, QUEBEC

	Cal	Dol	Cpx	Cam	Bt	Qtz	Mgt	Py	Po	Gr	Ap	Other	Calcite $\delta^{18}O$	Calcite $\delta^{13}C$	Dolomite $\delta^{18}O$	Dolomite $\delta^{13}C$
C 1	93			4	3		<<1	<<1	<<1		<<1		22.63	+ 5.60		
C 2	84	13		<<1	1		<<1	<<1		<1	<<1		26.06	+ 4.80		
C 3	80	12	1	3	2					1	<1		24.45	+ 1.51		
C 13	96	<1		1	3					1	<<1		22.16	+ 1.70		
C 24	79	18		<1	2	<1				<1		Ttn <<1	26.46	+ 2.47		
C 25	82	14		1	2				<<1	<1	<<1	Ttn <<1	25.23	+ 3.44		
C 27	74		9	9	9	1		<<1			<<1	Kfs <1	20.15	+ 2.15		
C 33	60	38			1					<1			23.61	+ 2.74	24.32	+3.34
C 41	87	10		<1	1	<1			<<1	<1	<<1	Ttn, Pl <<1	23.94	+ 4.55		
C 42	89	10			<1			<<1		<1			26.08	+ 3.60		
C 44	99		<<1	<<1						1	<<1		27.92	+ 3.61		
C 45	79	20	<1	<1	1					<1			25.24	+ 4.68		
C 46	89	6	<1	1	3					<1		Hu <1	23.65	+ 2.52		
C 47a	88		1	3	8	<1			<1	<1			23.32	+ 2.15		
C 47b	72		6	6	16	<1			<1	<1			23.20	+ 1.78		
C 48	64	6			31			<1					21.58	+ 2.19		
C 49	86	10			2	<1				<1		Kfs <1	24.40	+ 3.60		
C 50a	92	7	<1	<1	1	1				1			25.64	+ 4.08		
C 50b	90	10			<1					<1		Hu <1			24.42	+3.56
D 1	10	74			9				1	<1		Srp 6	20.65	–1.73	20.73	–1.33
D 2	7	76		17									25.55	–0.36	25.68	+0.75
D 4	1	99								<1					26.75	+2.63
D 6	<1	96		4	<1			<<1							25.60	+2.83
D 15a	<1	99													27.71	–0.36
D 15b	<1	99													27.94	–0.23

Mineral symbols: Ap apatite, Bt biotite, Cal calcite, Cam Ca amphibole, Cpx Ca pyroxene, Dol dolomite, Ep epidote, Gr graphite, Grt garnet-group minerals, Hu humite-group minerals, Kfs K-feldspar, Mgt magnetite, Ol olivine, Pl plagioclase, Po pyrrhotite, Py pyrite, Qtz quartz, Scp scapolite, Ttn titanite, Spl spinel, Srp serpentine, Tur tourmaline, Zrn zircon. Mineral proportions are expressed in vol.%, and isotopic composition, in ‰. See Table 1 for definition of marble C and D.

commonly aligned somewhat to define a foliation. Crystal distribution ranges from uniform to layered, the layering being defined by differences in modal proportions of calcite and dolomite (Fig. 3), or in the percent of silicates.

The pressure of metamorphism for the study area is estimated at 7 kbar, on the basis of the equilibrium: anorthite = grossular + sillimanite + quartz (eight widespread samples, mean 6.9 kbar; Kretz 1994, p. 217). The peak temperature is estimated at approximately 700°C, based on Mg–Fe^{2+} exchange between biotite and garnet, taking into consideration the effect of Ca in garnet [nine widespread samples, range (viewed as being insignificant) of 690 to 720°C, mean 710°C; equation 139, p. 228 of Kretz (1994), using data from Kretz (1990)]. The calcite–dolomite thermometer gives a temperature greater than 640°C (Kretz 1980). These estimates are supported by the findings of Perkins *et al.* (1982), who found 5 to 7 kbar and 675°C. For isotopic exchange, temperature is the dominant variable, and 700°C will, in the first analysis, be taken as the temperature of equilibrium.

Evidence for ductile deformation in most rock types, and particularly in marble and gneiss, is widespread, and the strain was locally of a very large magnitude. In marble, the evidence exists mainly in the form of folded and disjointed layers of more competent silicate rock.

General information on the Grenville Province was presented by Baer (1976) and Rivers *et al.* (1989), and on the study area, by Kretz (1977, 1997).

METHODS AND NOTATION

In an attempt to avoid gradients in isotopic concentration of the kind described by Cartwright & Valley (1991), nearly all samples were collected a few meters or more from adjoining bodies of silicate rock. Mineral proportions were determined by point counting in thin sections and on cut surfaces that were stained with Alizarin red S to distinguish dolomite from calcite. These estimates, which are reported in Tables 2 to 4, are based on a counting of at least 400 points.

Fragments of rock 5 cm in diameter were selected for mineral separation. Adequate (>98% pure) separa-

TABLE 3. ASSEMBLAGES AND PROPORTIONS OF MINERALS, AND ISOTOPIC COMPOSITION OF CARBONATES IN SAMPLES OF MARBLE F, H, S AND B, OTTER LAKE AREA, QUEBEC

															Calcite		Dolomite	
	Cal	Dol	Ol	Hu	Cpx	Cam	Bt	Spl	Mgt	Py	Po	Gr	Ap	Srp	δ¹⁸O	δ¹³C	δ¹⁸O	δ¹³C
F 1	39	19	17				3		1	<<1				21	16.47	-1.88		
F 2	28	37	2		<1		2		<<1	<<1				30	20.30	+2.39		
F 3	62	9	1	<1			3		<<1				<<1	23	18.67	-0.19	17.25	-0.33
F 5	60	22	3		1	1	<1	<1					<1	14	18.02	+1.79	17.43	+2.21
F 9	41	24	<1				2		<<1					33	17.23	+1.01		
F 12a	30	50	16	<1	1		<1	<<1		2		<<1	<<1	<1	21.46	+1.25	21.11	+1.62
F 12b	8	85	5	1	1		1	<1		<<1		<<1					21.11	+1.60
H 1	85	13		1	2	<1	2					1	<<1		26.07	+3.21	26.09	+3.76
H 3	69	29		1		1	<1	<1			<1	1	<<1		24.62	+2.82	24.46	+3.15
H 6	14	64		11			11					<<1	<<1		22.44	+1.49	22.29	+1.95
H 7	4	85		2			6			<<1				<1			21.59	+3.31
H 8	70	26		2			2	<1			<1	<<1			19.48	+2.21	18.00	+1.44
H 10	81	12		6			2							<1	19.49	+0.47		
S 1	52	15					1							32	22.25	+0.16		
S 6	72	10					1							17	23.58	+1.96	26.76	+2.38
B 2*	58	7		4				<<1						1	20.13	+0.65	20.04	+1.06

Symbols are defined in Table 2. Mineral proportions are expressed in vol.%, and isotopic composition, in ‰. See Table 1 for definition of marble F, H, S and B. * Sample B 2 also contains 26% brucite.

TABLE 4. ASSEMBLAGES AND PROPORTIONS OF MINERALS, AND ISOTOPIC COMPOSITION OF CALCITE IN SAMPLES OF MARBLE R, K AND G, OTTER LAKE AREA, QUEBEC

	Cal	Cpx	Cam	Bt	Grt	Ttn	Kfs	Pl	Scp	Ep	Qtz	Mgt	Py	Gr	Ap	δ¹⁸O	δ¹³C
R 1	90	4	1	5									<1		<<1	21.37	+1.65
R 3	94	1	1	4							<1		<<1	<<1		20.93	+2.18
R 4	91	1	2	6							<1				<<1	14.71	–0.23
R 5	91	2	1	6				<<1			<1				<<1	18.37	+1.43
R 7	85	8	7													17.11	+0.19
R 10*	99														<<1	18.68	+2.53
R 12	84	7		9												14.15	–2.30
K 1	65	9				1	11		13		1	<<1	<<1			12.32	–0.33
K 2	60	11	<1			<1	15		10	<1	3		<<1		<<1	11.88	–0.54
K 3	84	10				<1	3		4	<1	<1		<<1		<<1	14.55	–1.63
K 4	81	6				<1	1		11	<1		<<1	<<1		<<1	12.40	–0.66
K 5	84	8		2		<1	2		5			<<1	<<1		<<1	22.35	+1.99
K 6	50	19	<1			2	5		18		5				<<1	13.72	–0.70
G 1	75	6			9	1			2	<<1	7					11.00	–0.34

* with 5% pods of silicate minerals (Cpx, Cam, Ttn, Ep, Qtz, Ap, Tur, Zrn). Mineral proportions are expressed in vol.%, and isotopic composition, in ‰. See Table 1 for definition of marble R, K and G.

tion was achieved by hand sorting, magnetic separation, and heavy liquids. Calcite and dolomite of particle size 0.2 to 0.4 mm were separated from each other by use of bromoform, the sink–float operation repeated two or more times; purity was monitored by immersing particles in Alizarin red S and observing the color change under a binocular microscope. Sampling for local (2 to 10 cm) variation in the composition of calcite was carried out by use of a small diamond drill. Exsolved plates and rods of dolomite in calcite appear in one-quarter of the samples of Major marble (Kretz 1988); the effect of exsolution on calculated fractionation-factors is considered below.

Oxygen and carbon isotopic analyses of calcite and dolomite separates were obtained in the Hatch Isotope Laboratory at the University of Ottawa. CO_2 was ex-

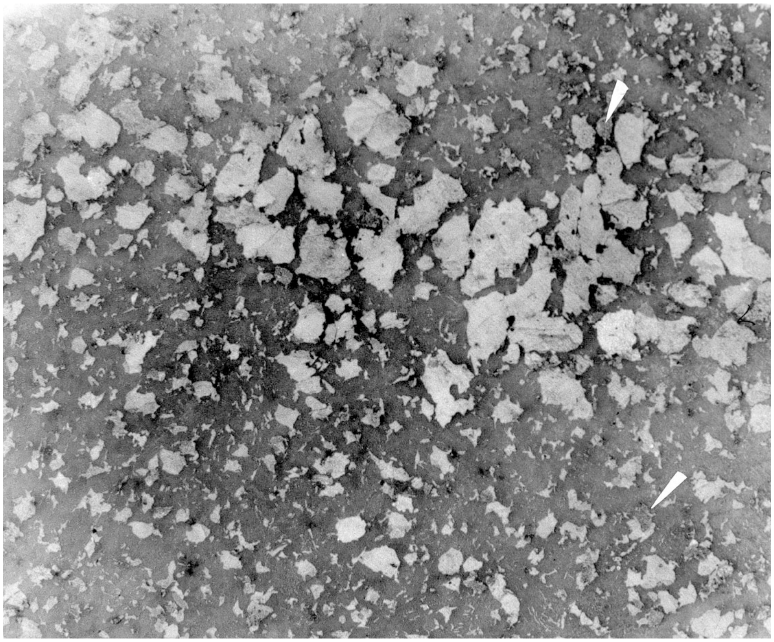

FIG. 3. Sample H3, showing the distribution of calcite (dark, stained with Alizarin red S) and dolomite (white). Also present is minor clinohumite (*e.g.*, at arrows) and very minor amounts of other minerals (Table 3). Width of photo = 6.5 cm.

tracted from calcite (at 25°C) and from dolomite (at 50°C) by use of 100% phosphoric acid (McCrea 1950). Carbon in graphite separates was changed to CO_2 by heating with copper oxide at 800°C. CO_2 obtained from carbonates and graphite was analyzed by use of a triple collector VG SIRA–12 mass spectrometer.

Oxygen isotopic analyses of silicate separates (finely ground) were obtained in the Isotope Laboratory at the University of Western Ontario. Oxygen was extracted by use of BrF_5, as described by Clayton & Mayeda (1963), and quantitatively converted to CO_2 over red-hot graphite (Beyth *et al.* 1997). The co-analysis of standard NIST–28 (formerly NBS–28) produced a value of 9.52‰, and three analyses of a quartz internal standard gave 11.4‰ (average), which corresponds to 9.6‰ for NIST–28 (F. Longstaffe, pers. commun.).

In the present study, the oxygen isotopic composition of a mineral is expressed as the atomic ratio, $^{18}O/^{16}O$, denoted R, and by use of the variable δ defined as

$$\delta_{\text{sample}} = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) 1000\,, \qquad (1)$$

where $R_{\text{standard}} = R_{\text{VSMOW}} = 0.00200520 \pm 0.00000045$, as determined by Baertschi (1976). From (1),

$$R_{\text{sample}} = R_{\text{standard}} \left(1 + \frac{\delta_{\text{sample}}}{1000} \right), \qquad (2)$$

which can be used to calculate R from δ. Similarly, the carbon isotopic composition of a mineral is expressed as the atomic ratio $^{13}C/^{12}C$ and by use of equation (1) with $R_{\text{standard}} = R_{\text{PDB–1}} = 0.0112372 \pm 0.0000029$, as given by Craig (1957) and Hoefs (1997).

With regard to carbonates the precision assigned to $\delta^{18}O$ and $\delta^{13}C$ is s (standard deviation) = 0.05‰; thus for a single determination, the 0.95 confidence limits are $\pm c = \pm 2s = \pm 0.10$‰. This was confirmed by twice submitting to the laboratory (masked) portions ($n = 10$) taken from a single finely ground sample of calcite. The uncertainty, propagated to the ratio R is $\pm 0.002 \times 10^{-4}$ for oxygen and $\pm 0.001 \times 10^{-3}$ for carbon. Corresponding numbers for $\delta^{13}C$ in graphite are larger by a factor of two.

For silicates, the value of s assigned to $\delta^{18}O$ was estimated from replicate analyses (two of biotite, two of garnet, two of serpentine and three of quartz) to give $s = 0.24$‰; thus for a single determination, $\pm c = \pm 0.48$‰.

TABLE 5. PARTIAL COMPOSITION OF MINERALS SELECTED FOR ISOTOPIC ANALYSIS, OTTER LAKE, QUEBEC

		FeO	Fe_2O_3	MgO	MnO	Al_2O_3	TiO_2	CaO	Na_2O	K_2O	F	Cl
C 33	Calcite	0.02		1.06	0.03			53.5				
D 1	Calcite	0.08		2.57	0.06			51.0				
F 3	Calcite	0.18		3.41	0.04			50.6				
H 1	Calcite	0.05		1.40	0.00			55.7				
C 33	Dolomite	0.25		21.4	0.08			30.0				
D 1	Dolomite	0.23		21.6	0.07			30.8				
F 3	Dolomite	0.50		21.3	0.06			30.2				
H 1	Dolomite	0.28		21.0	0.01			30.0				
C 3	Biotite	1.18		27.0	0.02	13.7	0.90	0.02	0.17	11.1	2.26	0.085
F 3	Biotite	0.78		28.1	0.01	12.8	0.37	0.05	0.91	9.61	2.47	0.047
H 1	Biotite	0.32		28.3	0.01	13.4	0.47	0.01	0.60	10.3	3.73	0.060
R 1	Biotite	5.02		23.3	0.01	15.1	1.11	0.02	0.16	10.6	1.01	0.086
R 4	Biotite	3.79		25.1	0.02	13.7	0.90	0.03	0.20	10.7	2.29	0.057
F 12a	Olivine	2.38		55.2	0.06	0.0		0.02				
H 6	Clinohumite	1.57		52.8	0.08							
G 1	Garnet	3.3	9.4	0.30	0.21	16.2		33.6				
K 6	Titanite	1.98		0.17	0.02	4.3		27.5				
R 7	Ca pyroxene	3.4	1.5	14.9	0.07	2.4		24.0	0.32			
R 7	Ca amphibole	5.4	5.6	15.3	0.05	15.1		12.1	2.0	1.7		
S 6	Serpentine	0.88		40.3	0.03							
K 6	K-feldspar					20.0		0.57	2.39	12.7		
K 2	Scapolite					25.2		16.5	3.53	0.75		
B 2	Brucite	1.93		62.4	0.02							

Where there is no entry in the Fe_2O_3 column, total Fe is expressed as FeO; data for biotite and olivine were obtained by electron-microprobe analysis (mean of 3 or 4 spot determinations). The remainder are from Kretz (1980), where additional carbonate compositions are reported. Compositions are expressed in wt%.

RESULTS

Information on the elemental composition of minerals in samples selected for isotopic study is presented in Table 5, and results of all isotopic analyses are listed in Tables 2 to 4, above. In these tables, all δ values are relative to standards VSMOW (oxygen) and PDB–1 (carbon).

Figure 4 displays the concentrations of ^{18}O and ^{13}C that were measured in calcite in the varieties of marble listed in Table 1. Also plotted are results for six samples of calcite from other rocks (skarn, vein, breccia) and, for comparison, the range (±3*s*) of δ values in calcite of the Mesozoic Oka carbonatite (200 km to the east), which was studied by Deines (1970).

ISOTOPIC COMPOSITION OF CALCITE IN THE MAJOR MARBLE UNITS

Regional and local variation

Figure 4 (open symbols) illustrates the isotopic composition of calcite in Major marble (C, D, F, H, S, B, Table 1), *i.e.*, in those bodies of marble that are, without doubt, metamorphosed limestone. *Mean* concentrations of ^{18}O and ^{13}C are similar to those in the Adirondacks (Table 6), and the *range* of concentration encountered for both isotopes is also very similar. In examining these results, it is well to bear in mind that large differences in δ values correspond to very small differences in concentration. For example, a decrease in $\delta^{18}O$ from 28 to 16‰ corresponds to a decrease in $^{18}O/^{16}O$ from 0.002061 to 0.002037, *i.e.*, by 1.2%.

In the study area, $\delta^{13}C$ in dolomite marble (D) is relatively low (Table 2, Fig. 4). Valley (1986) and others have noted that the presence of organic matter (with $\delta^{13}C \approx -25$‰) will lead to low $\delta^{13}C$ values in the associated carbonates, and this may possibly explain the present results.

Variation on the outcrop scale was examined at site C47, south of Kazabazua (Fig. 2) where, on a 30 m traverse normal to layering (five samples), variations in $\delta^{18}O$ and $\delta^{13}C$ are "in phase" and amount to 2 to 3‰ units. Variation on the scale of 2 to 10 cm was examined in four samples that are homogeneous or faintly layered, and on this scale, variation in $\delta^{18}O$ and $\delta^{13}C$ of calcite is either not detectable (taking analytical error into consideration) or very small. Results illustrated in Figure 5 are representative.

Overall, the isotopic composition (both *mean* and *range*) of calcite in the Major marble units of the study area is similar to that found in unmetamorphosed Prot-

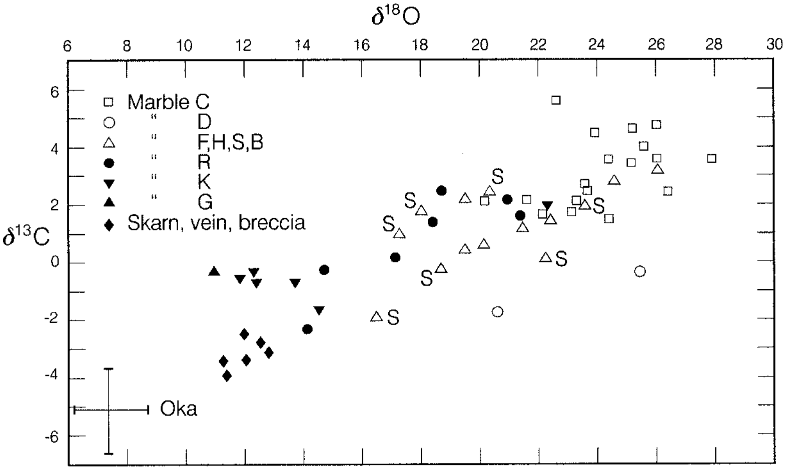

FIG. 4. δ–δ plot of all analyzed samples of calcite (see Table 1) and, for comparison, data from the Oka carbonatite, as reported by Deines (1970). Samples labeled S contain 14–33% serpentine.

TABLE 6. ISOTOPIC COMPOSITION OF CALCITE IN MAJOR MARBLE (C, F, H, S, B), IN ADIRONDACK MARBLE, AND IN UNMETAMORPHOSED PROTEROZOIC LIMESTONE

	$\delta^{18}O$		$\delta^{13}C$		
	range	mean	range	mean	n
Quebec (present study)	27.9 to 16.5	22.7	5.6 to −1.9	+2.3	32
Adirondacks[1]	27.2 to 12.3	19.8	5.0 to −7.2	+0.1	75
Unmetamorphosed[2]	23.8 to 16.3	20.6	6.1 to −2.6	+1.7	10

[1] Valley & O'Neil (1984); data compiled for Ontario localities are similar.

[2] Veizer & Hoefs (1976); Proterozoic (1000 Ma) Bitter Springs Formation, Amadeus Basin, Australia.

erozoic limestone, as determined by Veizer & Hoefs (1976) and Veizer *et al.* (1992); results from the Bitter Springs Formation in Australia (Table 6) are representative. Thus, evidence for large changes in isotopic composition during metamorphism could not be detected. Some small changes are, however, to be expected.

Changes resulting from decarbonation

Most occurrences of Major marble contain less than 10 vol.% of Mg-bearing silicates (Tables 2, 3), which were evidently produced by reactions of the kind dolomite + quartz → diopside + CO_2. Provided that only a portion of the dolomite at reaction sites is consumed, then because CO_2 favors ^{18}O, the residual dolomite is expected to become depleted in ^{18}O (enriched in ^{16}O), resulting in a decrease in $\delta^{18}O$ of dolomite. The problem was analyzed by Rumble (1982) and others, and reviewed by Valley (1986).

The decrease in R^{Dol} (= $^{18}O/^{16}O$ in dolomite) as a function of the extent of reaction can be expressed by two equations (Pfann 1966), a "closed-system" equation, which applies where all CO_2 accumulates at reaction sites, and an "open-system" equation, which applies where CO_2 is continuously removed from these sites. Assuming open-system conditions, the equation is,

$$R^{Dol} = R^{Dol\ (initial)}\ (1 - f)^{\alpha - 1}, \qquad (3)$$

where f is the fraction of total CO_2 in the CO_2 gas (extending from zero when the reaction begins to 1.0 when all dolomite is consumed), and α is the ^{18}O fractionation factor (CO_2/dolomite), which at 600°C (a reasonable estimate of the temperature of reaction) is approximately 1.005 (Chacko *et al.* 1991), assuming that $\delta^{18}O$ in associated calcite and dolomite are nearly equal (Table 3). By this equation, $\delta^{18}O$ of residual dolomite will decrease significantly as reaction progresses, for example from 24 to 12‰ as f changes from zero to 0.9.

But the equation does not take into consideration the presence of calcite in the vicinity of reaction sites, and ^{18}O – ^{16}O exchange between this calcite and residual dolomite, which will prevent $\delta^{18}O$ of dolomite from decreasing by the prescribed amount. Consider, for example, a volume of calcite–dolomite marble in which 70% of the original dolomite (initial $\delta^{18}O$ of both carbonates = 24‰) was consumed by reaction with quartz to produce diopside. In the absence of exchange, $\delta^{18}O$

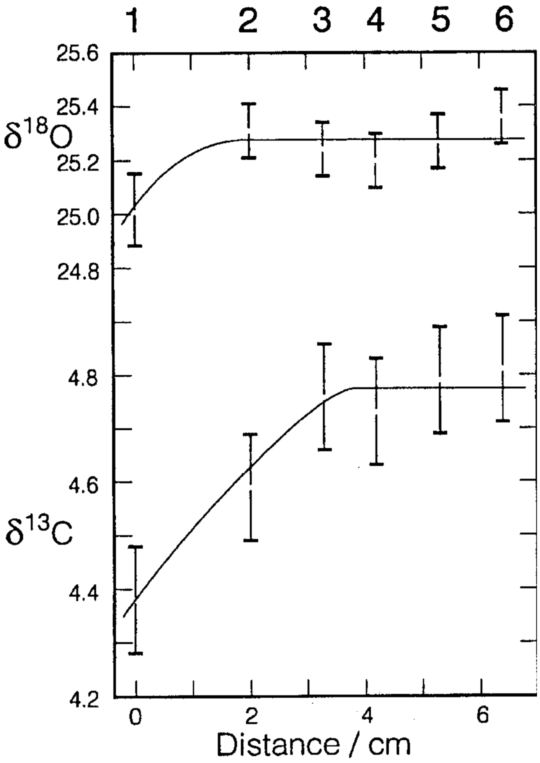

FIG. 5. Local variation in the isotopic composition of calcite in sample C 45, presumably inherited from sedimentation or diagenesis. Error bars represent 0.95 confidence limits, analytical precision.

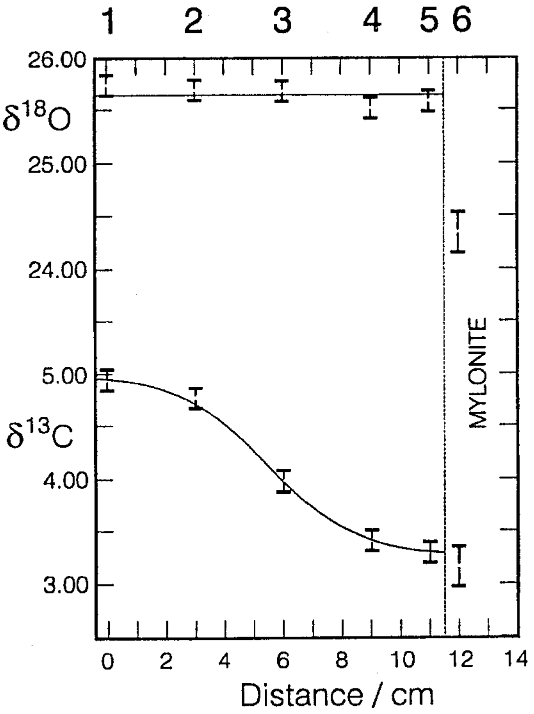

FIG. 6. Local variation in the isotopic composition of calcite in sample C50, in relation to a narrow zone of mylonitic marble. Only dolomite porphyroclasts were analyzed in mylonite; the composition of the fine-grained calcite is assumed to have achieved equilibrium with these clasts. Error bars represent 0.95 confidence limits, analytical precision.

will have decreased to 18‰, but a calculation shows that exchange with a volume of calcite exceeding that of residual dolomite by a factor of four will cause $\delta^{18}O$ of dolomite (and calcite) to decrease by only 1.0‰.

Reactions that release CO_2 are similarly expected to result in a decrease in the proportion of ^{13}C in carbonate crystals, but α (CO_2 / calcite) is smaller ($\approx$ 1.0036 at 600°C, as reported by Chacko *et al.* 1991), and a decrease in $\delta^{13}C$ of 1.0‰ or less presumably occurred during decarbonation.

An attempt was made to detect the decarbonation effect. Sample F12 (Table 3) contains a layer of marble (F12a) 2.1 cm thick with 16 vol.% olivine, bounded on both sides by marble (F12b) with 5 vol.% olivine. Both $\delta^{18}O$ and $\delta^{13}C$ of dolomite were found to be uniform throughout, possibly because of exchange between adjacent portions, resulting in homogenization. At site D15 (bottom left of Fig. 2), diopside-rich reaction zones have formed at contacts between quartz veins and dolomite marble, but the $\delta^{18}O$ and $\delta^{13}C$ values of dolomite immediately adjacent to diopside and 2.5 m away (samples D15a and D15b, Table 2) are virtually identical.

Changes resulting from hydration

Locally in the study area, H_2O was introduced to volumes of marble to produce Ca amphibole, which commonly occurs as a mantle about crystals of Ca pyroxene. Elsewhere, larger amounts of H_2O were consumed to produce serpentine from olivine or from Ca pyroxene, and brucite, presumably from periclase. But calcite in samples containing between 14 and 33 vol.% of serpentine is not conspicuously low in ^{18}O (Fig. 4), nor is that associated with 26% of brucite (Table 3). Thus evidence for a large-magnitude passage of H_2O through serpentine and brucite marble was not found, and the flux may have been small, occurring by way of crystal-boundary diffusion.

Changes facilitated by deformation

Mylonite zones 0.5 to 20 cm wide occur locally in the Major marble units (Kretz 1996). In sample C50, calcite in marble adjoining a mylonite zone is homogeneous in $\delta^{18}O$, but $\delta^{13}C$ decreases progressively as the zone is approached (Fig. 6). Within the mylonite, a dolomite porphyroclast is distinctly low in ^{18}O and ^{13}C, and by inference, so is the very fine-grained calcite, which was not analyzed.

The low ^{18}O and ^{13}C concentrations *within* the mylonite can be explained by the transport of CO_2 through the zone, but results in the adjacent non-mylonitic marble (*i.e.*, a change in ^{13}C but not in ^{18}O) are not understood. One possibility is that the decrease in ^{13}C was caused by exchange with methane, which penetrated the marble from the mylonite.

In summary, only very small changes have occurred in the isotopic composition of the Major marble, resulting directly from metamorphic reactions affecting the minerals.

Isotopic Composition of Calcite in the Minor Marble Units

The following properties of the Minor marble (R, K, G, Tables 1 and 4) distinguish it from the Major marble, described above. a) It occurs only as small bodies associated with granitic and syenitic rocks (groups 4 and 5), b) dolomite, olivine, and graphite are absent, whereas K-feldspar and scapolite are locally abundant (Table 4), and c) concentrations of Fe, Mn, and Sr in calcite and of Fe in silicates are relatively high (Kretz 1980).

Most samples of marble unit R have ^{18}O and ^{13}C concentrations that fall in the same range as that defined by Major marble (Fig. 4), and layers of this kind could represent beds of limestone in which impurities account for higher Fe/(Mg + Fe) values in silicates, and for higher Fe, Mn, and Sr in calcite. But the *average* ^{18}O and ^{13}C concentrations are relatively low, such that an alternative interpretation is that these rock layers are metasomatic in the sense that the sedimentary isotopic and elemental composition has changed slightly during metamorphism. Field evidence for metasomatism on a small scale exists immediately south of Kazabazua (site C44, Fig. 2) where, at a contact with a body of syenite, coarse white graphite-bearing marble (C44, Table 2), within 0.1 to 1 m of the contact, has changed to graphite-free pink marble R10, Table 4), accompanied by a decrease in δ^{18}O from 27.9 to 18.7‰, and in δ^{13}C from +3.61 to +2.53‰; this shift was recently confirmed by Wilk (1998). Evidently an introduction of "light" O, occurred, possibly as H_2O, causing a change in the isotopic composition of calcite and the oxidation of graphite.

Bodies of marble K (with Ca pyroxene, scapolite, K-feldspar) were previously viewed by the writer (Kretz 1980) as deformed beds of sedimentary limestone, affected by metasomatism, but compared with other varieties of marble (including marble R), the δ^{18}O of calcite is generally lower, and the same as that of calcite that has evidently replaced silicate rock, *i.e.*, calcite-rich skarn and veins, and calcite in the matrix of the Coulonge meta-breccia (Fig. 4). The average δ^{13}C value is low, but there is overlap with other varieties of marble.

One of the samples (K6) is from a body at least a few m across within the Bell Mount Complex, which consists in part of heterogeneous granite (with K-feldspar, plagioclase, Ca pyroxene, titanite). This body of marble was possibly formed by the partial replacement of granite by calcite, accompanied by the alteration of plagioclase to scapolite. A similarity in the Fe content of Ca pyroxene in marble and granite supports this interpretation. If correct, complex metasomatic reactions must have occurred. One possible source for CO_2 is that released by decarbonation in metasedimentary limestone elsewhere, the δ^{18}O values having been lowered by exchange with silicate rock during transport.

The lowest δ^{18}O of calcite here reported (11.0‰) is from a single sample of garnet-bearing marble (marble G). This rock possibly also was produced by the metasomatic alteration of silicate rock, *e.g.*, garnet gneiss. Further field and laboratory studies of marble R, K and G are in progress.

Using the Oka carbonatite as a model (Fig. 3), it seems unlikely, from isotopic evidence, that the bodies of Minor marble are carbonatite.

Isotopic Exchange Equilibrium

The isotopic composition of crystals of dolomite, biotite, and other minerals relative to that of associated calcite is now considered from the viewpoint of thermodynamic equilibrium. The aim is to determine if the results are consistent with a close approach to equilibrium, or with departures from equilibrium of a small, medium, or large magnitude. Initially, the equilibrium temperature will be taken as the peak temperature of metamorphism, which, as noted above, is estimated at 700°C.

Theory

The theory of isotopic exchange was discussed by Urey (1947) and reviewed by Clayton (1981). For example, the distribution of ^{18}O and ^{16}O between associated calcite and dolomite is described by the exchange reaction

$$\mathrm{Ca}_{1/3}\mathrm{C}_{1/3}{}^{16}\mathrm{O} + \mathrm{Ca}_{1/6}\mathrm{Mg}_{1/6}\mathrm{C}_{1/3}{}^{18}\mathrm{O} = \mathrm{Ca}_{1/3}\mathrm{C}_{1/3}{}^{18}\mathrm{O} + \mathrm{Ca}_{1/6}\mathrm{Mg}_{1/6}\mathrm{C}_{1/3}{}^{16}\mathrm{O}. \qquad (4)$$

At equilibrium,

$$\left[\frac{{}^{18}\mathrm{O}/\left({}^{18}\mathrm{O}+{}^{16}\mathrm{O}\right)}{{}^{16}\mathrm{O}/\left({}^{18}\mathrm{O}+{}^{16}\mathrm{O}\right)}\right]^{\mathrm{Cal}}\left[\frac{{}^{16}\mathrm{O}/\left({}^{18}\mathrm{O}+{}^{16}\mathrm{O}\right)}{{}^{18}\mathrm{O}/\left({}^{18}\mathrm{O}+{}^{16}\mathrm{O}\right)}\right]^{\mathrm{Dol}} = A\,exp\left(-\Delta G/\mathrm{R}T\right) \qquad (5)$$

or,

$$\left[\frac{{}^{18}\mathrm{O}}{{}^{16}\mathrm{O}}\right]^{\mathrm{Cal}} / \left[\frac{{}^{18}\mathrm{O}}{{}^{16}\mathrm{O}}\right]^{\mathrm{Dol}} = A\,exp\left(-\Delta G / RT\right) \qquad (6)$$

where atomic ratios appear in square brackets, A is a quotient of four activity coefficients expected to remain constant at constant temperature, ΔG is the Gibbs energy change for (4), R is the gas constant, and T is absolute temperature. The quotient on the left is the distribution coefficient or fractionation factor,

$$\alpha(\mathrm{Cal} / \mathrm{Dol}) = [{}^{18}\mathrm{O} / {}^{16}\mathrm{O}]^{\mathrm{Cal}} / [{}^{18}\mathrm{O} / {}^{16}\mathrm{O}]^{\mathrm{Dol}}, \qquad (7)$$

and the expression on the right is a function of temperature. In terms of the δ notation, we have, in place of (7),

$$\alpha\left(\mathrm{Cal}/\mathrm{Dol}\right) = \frac{\left\{0.0020052\left[1+\left(\delta/1000\right)\right]\right\}^{\mathrm{Cal}}}{\left\{0.0020052\left[1+\left(\delta/1000\right)\right]\right\}^{\mathrm{Dol}}}, \qquad (8)$$

or,

$$\alpha\left(\mathrm{Cal}/\mathrm{Dol}\right) = \frac{\left(1000+\delta\right)^{\mathrm{Cal}}}{\left(1000+\delta\right)^{\mathrm{Dol}}}, \qquad (9)$$

as derived by Clayton & Epstein (1958). In this treatment, the presence of ^{17}O atoms (~0.037% of total oxygen) is disregarded. The fractionation factor is usually found to be very close to 1.000 [this results from ΔG in equation (5) being very small], and the expression 10^3 ln α is commonly used in addition to or in place of α.

TABLE 7. DISTRIBUTION OF OXYGEN AND CARBON ISOTOPES BETWEEN CALCITE AND DOLOMITE, OTTER LAKE AREA, QUEBEC

Sample	Oxygen (^{18}O, ^{16}O) α(Cal/Dol)	Carbon (^{13}C, ^{12}C) α(Cal/Dol)
C 33	0.999 306	0.999 402
D 1	0.999 922	0.999 599
* D 2	0.999 873	0.998 891
* F 3	1.001 396	1.000 140
* F 5	1.000 580	0.999 581
F 12a	1.000 343	0.999 631
H 1	0.999 981	0.999 452
* H 3	1.000 156	0.999 671
* H 6	1.000 147	0.999 541
* H 8	1.001 454	1.000 769
S 6	0.996 903	0.999 581
B 2	1.000 088	0.999 590
	mean: 1.000 295§	mean: 0.999 654

* exsolved dolomite particles in calcite microscopically visible. § omitting S 6.

The variable $\delta_{\text{mineral A}} - \delta_{\text{mineral B}}$, which is approximately equal (numerically) to 10^3 ln α (A/B), will not be used.

All fractionation factors here reported are calculated as (1000 + δ) of calcite *divided* by (1000 + δ) of associated mineral, as in equation (9), hence the notation α (calcite / associated mineral).

The following assumptions are now introduced; a) the isotopic composition of crystals in the study samples was *determined* during the peak of metamorphism, b) prograde metamorphism and deformation were *coeval*, and c) apart from local changes that might have occurred in the margins of crystals during cooling, the isotopic composition of crystals was largely preserved during uplift and erosion.

Calcite–dolomite

The distribution of ^{18}O and ^{16}O between associated calcite and dolomite in twelve samples selected for study is illustrated in Figure 7, which is a plot of $\delta^{18}\mathrm{O}^{\mathrm{Dol}}$ against $\delta^{18}\mathrm{O}^{\mathrm{Cal}}$ (from Tables 2, 3); fraction factors, calculated by use of equation (9), are reported in Table 7. Also plotted are data obtained by Sheppard & Schwarcz (1970) from Grenville marble south of the Ottawa River (in Ontario) in a terrane of similar metamorphic grade. In view of equation (6), equilibrium at a given temperature is represented in this figure by a straight line. Similarly, the distribution of ^{13}C and ^{12}C is illustrated in

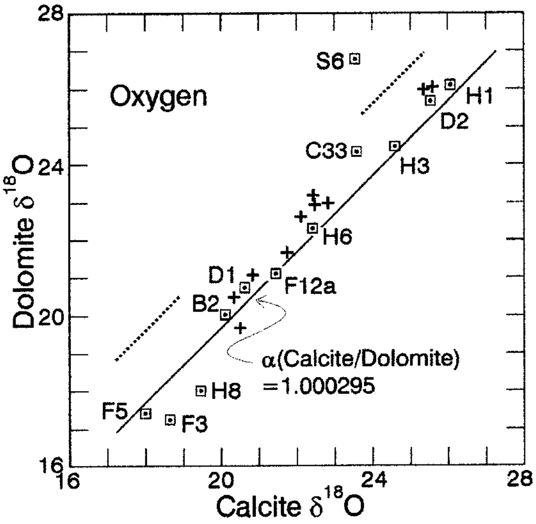

FIG. 7. Distribution of ^{18}O and ^{16}O between calcite and dolomite; crosses are the data of Sheppard & Schwarcz (1970) from Grenville marble in Ontario. Size of symbols indicates 0.95 confidence limits, analytical precision. The full line is for α (Cal/Dol) = 1.000295 (Table 7); the dotted line (α = 0.9985) represents experimental results of Northrop & Clayton (1966) at 300°C.

Figure 8, and fractionation factors are listed in Table 7. The observed variation in fractionation factors is shown in histogram form (Fig. 9).

With regard to oxygen (Fig. 7), one data point (S6) is identified as an outlier (Fig. 9); excluding this one, the mean α (Cal/Dol) is equal to 1.000295 (*i.e.*, 1000 ln α = +0.295), which is the equation of the full straight line in Figure 7. With regard to carbon (Figs. 8, 9), samples D2 and H8 could be viewed as outliers [by application of Chauvenet's criterion (Neville & Kennedy 1976, p. 180)], but they are here retained, to give mean α (Cal/Dol) = 0.999654, (*i.e.*, 1000 ln α = –0.346), which is the equation of the straight line in Figure 8.

The above result for oxygen differs from that expected by extrapolation of the Northrop & Clayton (1966) experimental data to 700°C (which gives α = 0.999472; 1000 ln α = –0.5) and from that proposed by Sheppard & Schwarcz (1970; 1000 ln α = –0.1). The result for carbon agrees well with the Sheppard & Schwarcz proposal of 1000 ln α (at 700°C) = –0.350) (*see* Friedman *et al.* 1977, Figs. 26, 33).

In view of the observed *variation* in α (Table 7, Fig. 9) expressed as a scatter of data points in Figures 7 and 8, the following points may be noted.

1) The variation cannot be attributed to analytical error, which is very small (*cf.* Figs. 7, 8).

2) The variation cannot be attributed to exsolution. Exsolved microcrystals of dolomite are visible in half of the samples (Table 7), and these were present in the calcite separates that were analyzed. But evidently (Kretz 1988), a fraction (roughly one-half) of the total exsolved dolomite migrated beyond calcite boundaries, resulting in a bulk Mg content lower than the 4.9% MgO expected for calcite in equilibrium with dolomite at 700°C (Goldsmith & Newton 1969). A calculation shows that a loss of 10 vol.% of exsolved dolomite from calcite at 500°C, assuming that α (Cal/Dol) = 0.99916 (Northrop & Clayton 1966) causes an immeasurable error in $^{18}O/^{16}O$ of calcite, for example a change from 20.500×10^{-4} to 20.498×10^{-4} . The decrease is expected to be even less because the removal of dolomite to beyond the grain boundaries of calcite most likely occurred during the initial stage of exsolution, when temperatures were only slightly lower than 700°C (Kretz 1988), and α differed only slightly from that at 700°C.

3) Similarly, the presence of up to 2 vol.% of dolomite impurity in calcite separates and of a calcite impurity in dolomite separates is expected to cause a negligible error in δ (measured) and hence in α.

4) Sample S6 is highly anomalous in oxygen (Fig. 9) but not in carbon, and the anomalous α value in this sample cannot be related to the presence of a retrograde hydrous mineral. Sample S6 contains 17% of serpentine, but samples F3 and F5, which contain as much or more serpentine, are not anomalous, nor is B2, with 26% of brucite.

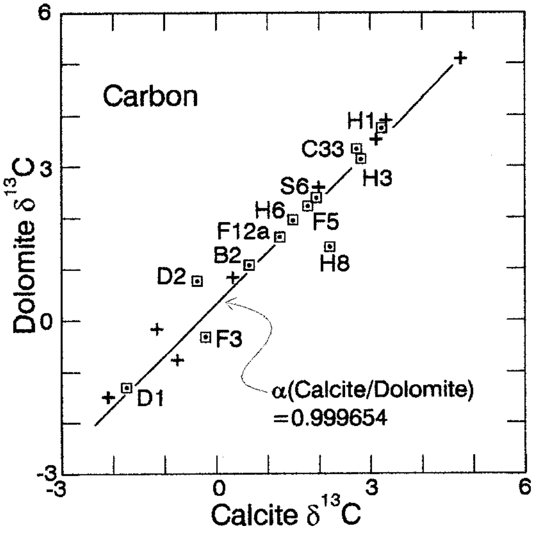

FIG. 8. Distribution of ^{13}C and ^{12}C between calcite and dolomite; crosses are data of Sheppard & Schwarcz (1970) from Ontario. Size of symbols indicates 0.95 confidence limits, analytical precision. The line is for α (Cal/Dol) = 0.999654 (Table 7).

TABLE 8. DISTRIBUTION OF OXYGEN AND CARBON ISOTOPES BETWEEN CALCITE AND ASSOCIATED MINERALS, AND ESTIMATES OF TEMPERATURE, OTTER LAKE AREA, QUEBEC

Sample	Mineral	Mineral	Calcite	α Cal/Mineral	1000 ln α	mean	T °C	Ref
		$\delta^{18}O$						
F 12a	olivine	17.89	21.46	1.00351	+3.501		700	1
H 6	clinohumite	17.22	22.44	1.00513	+5.119		400	2
G 1	garnet	8.59	11.00	1.00239	+2.387		~800	3
K 6	titanite	10.55	13.72	1.00314	+3.132			
R 7	Ca pyroxene	15.07	17.11	1.00201	+2.008		810	1
R 7	Ca amphibole	14.66	17.11	1.00241	+2.412		690	4
C 3	biotite	20.82	24.45	1.00356	+3.550	+3.49	450	5
F 3	biotite	14.69	18.67	1.00392	+3.915			
H 1	biotite	23.20	26.07	1.00280	+2.801			
R 1	biotite	17.63	21.37	1.00368	+3.668			
R 4	biotite	11.17	14.71	1.00350	+3.495			
K 6	K-feldspar	11.94	13.72	1.00176	+1.757			
K 2	scapolite	9.84	11.88	1.00202	+2.018			
S 6	serpentine	9.46	23.58	1.01399	+13.89			
B 2	brucite	0.21	20.13	1.01992	+19.72			
		$\delta^{13}C$						
C 2	graphite	+0.79	+4.80	1.00401	+3.999	+3.74		
C 46	graphite	–0.90	+2.52	1.00342	+3.417			
D 1	graphite	–5.22	–1.73	1.00351	+3.502		690	6
H 1	graphite	–0.56	+3.21	1.00377	+3.765		730	7
H 3	graphite	–1.18	+2.82	1.00400	+3.997			

References: 1 Chiba *et al.* (1989), 2 Zheng (1993), 3 Kieffer (1982), 4 Zheng *et al.* (1994), 5 Fortier *et al.* (1994), 6 Dunn & Valley (see Kitchen & Valley 1995), 7 Chacko *et al.* (1991).

TABLE 8. DISTRIBUTION OF OXYGEN AND CARBON ISOTOPES BETWEEN CALCITE AND ASSOCIATED MINERALS, AND ESTIMATES OF TEMPERATURE, OTTER LAKE AREA, QUEBEC

Sample	Mineral	Mineral	Calcite	α Cal/Mineral	1000 ln α	mean	T °C	Ref
		$\delta^{18}O$						
F 12a	olivine	17.89	21.46	1.00351	+3.501		700	1
H 6	clinohumite	17.22	22.44	1.00513	+5.119		400	2
G 1	garnet	8.59	11.00	1.00239	+2.387		~800	3
K 6	titanite	10.55	13.72	1.00314	+3.132			
R 7	Ca pyroxene	15.07	17.11	1.00201	+2.008		810	1
R 7	Ca amphibole	14.66	17.11	1.00241	+2.412		690	4
C 3	biotite	20.82	24.45	1.00356	+3.550			
F 3	biotite	14.69	18.67	1.00392	+3.915			
H 1	biotite	23.20	26.07	1.00280	+2.801	+3.49	450	5
R 1	biotite	17.63	21.37	1.00368	+3.668			
R 4	biotite	11.17	14.71	1.00350	+3.495			
K 6	K-feldspar	11.94	13.72	1.00176	+1.757			
K 2	scapolite	9.84	11.88	1.00202	+2.018			
S 6	serpentine	9.46	23.58	1.01399	+13.89			
B 2	brucite	0.21	20.13	1.01992	+19.72			
		$\delta^{13}C$						
C 2	graphite	+0.79	+4.80	1.00401	+3.999			
C 46	graphite	−0.90	+2.52	1.00342	+3.417			
D 1	graphite	−5.22	−1.73	1.00351	+3.502	+3.74	690	6
H 1	graphite	−0.56	+3.21	1.00377	+3.765		730	7
H 3	graphite	−1.18	+2.82	1.00400	+3.997			

References: 1 Chiba *et al.* (1989), 2 Zheng (1993), 3 Kieffer (1982), 4 Zheng *et al.* (1994), 5 Fortier *et al.* (1994), 6 Dunn & Valley (see Kitchen & Valley 1995), 7 Chacko *et al.* (1991).

5) Disregarding sample S6, the variation that exists in α (oxygen and carbon) could conceivably result from a variation from place to place within the study area, in the peak temperature of metamorphism, although (as noted above) temperature gradients could in general not be detected, on the basis of mineral assemblages and geothermometry. Experimental data on the temperature-dependence of α ($^{18}O/^{16}O$; Cal/Dol) near 700°C are not available, but Northrop & Clayton (1966) have determined that α, as here defined, increases from 0.99890 at 400°C to 0.99934 at 600°C (see also Friedman *et al.* 1977, Fig. 26), or 0.00044 units per 200 degrees of temperature. The range in α detected in the study area (Table 7, Fig. 9) is comparatively large (0.0021 α units) and, therefore, the observed variation in α ($^{18}O/^{16}O$) cannot be attributed entirely or principally to temperature. Moreover, samples with relatively high and low α (oxygen) values occur together (*e.g.*, F3, H8 high, D1, C33 low) in the northwestern part of study area (Fig. 2), and samples with relatively high or low α values are not spatially associated with bodies of metagabbro, with faults, or other geological features. Experimental data for α ($^{13}C/^{12}C$; Cal/Dol) are not available.

A further discussion of O and C isotopic exchange between calcite and dolomite appears below.

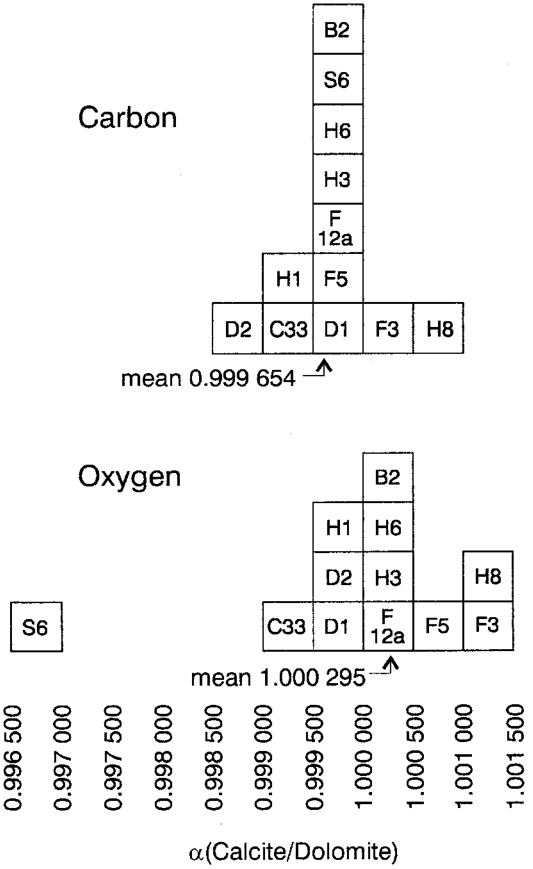

FIG. 9. Variation in fractionation factors (Table 7) presented in histogram form.

Calcite–biotite

The distribution of ^{18}O and ^{16}O between calcite and biotite in five samples is illustrated in Figure 10. Taking analytical precision into consideration, a variation in α within the group of five samples cannot be demonstrated. The mean fractionation factor, α (Cal/Bt) is 1.00349 (1000 ln α = 3.5, Table 8), which is the equation for the straight line drawn in Figure 10. In the Adirondacks (Valley & O'Neil 1984), 1000 ln α (mean) is also 3.5, but the range was found to be larger, from 1.8 to 4.9.

Fortier *et al.* (1994) have shown experimentally that α is a function of F/(OH + F) in biotite, which for samples of the present study (Table 5) is calculated as 0.25, 0.28, 0.45, 0.11, 0.26, with an uncertainty, based on replicate analyses, of ±0.02 (0.95 confidence), or a mean value of 0.27. This sampling gives a temperature of only 450°C (Table 8).

Bottinga & Javoy (1975) and others have noted that isotopic temperatures involving biotite are commonly found to be too low. By use of measurements of oxygen diffusion in biotite, Fortier & Giletti (1991), showed that ^{18}O – ^{16}O exchange between crystals of biotite and those of associated quartz (and calcite) is expected to occur during cooling from 700°C of regional metamorphic terranes, and this retrogression may explain the anomalous biotite – calcite results presented here. *In situ* analyses at biotite–calcite boundaries in the study samples are now needed to search for complementary stranded diffusion-gradients which, if present, would confirm that exchange did indeed occur during cooling.

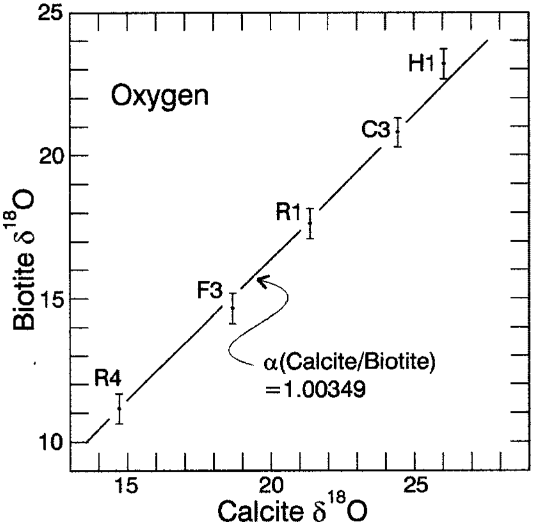

FIG. 10. Distribution of ^{18}O and ^{16}O between calcite and biotite; 0.95 confidence limits (analytical precision) are indicated. $\alpha(Cal/Bt)_{mean}$ = 1.00349 (1000 ln α = 3.49, Table 8).

Calcite–graphite

The distribution of ^{13}C and ^{12}C between calcite and graphite in five samples selected for study is illustrated in Figure 11. A close approach to equilibrium is evident, with mean α (Cal/Gr) = 1.00374 (Table 8). Present results agree well with those obtained by Kitchen & Valley (1995) in their very thorough study of graphite in Adirondack marble to the south. The Dunn & Valley (1992) proposal for a relation between α and *T*, which was used by Kitchen & Valley (1995), yields 690°C, whereas the relation of Chacko *et al.* (1991) gives 730°C (Table 8).

Calcite – various silicate minerals and brucite

Exploratory results ($n = 1$) on the distribution of ^{18}O and ^{16}O between calcite and various minerals are presented in Table 8. Note (Fig. 12) that 1000 ln α (Cal/mineral) appears to be determined largely by the presence of OH ions, which are known to concentrate ^{16}O relative to ^{18}O (Hamza & Epstein 1980, Zheng 1993).

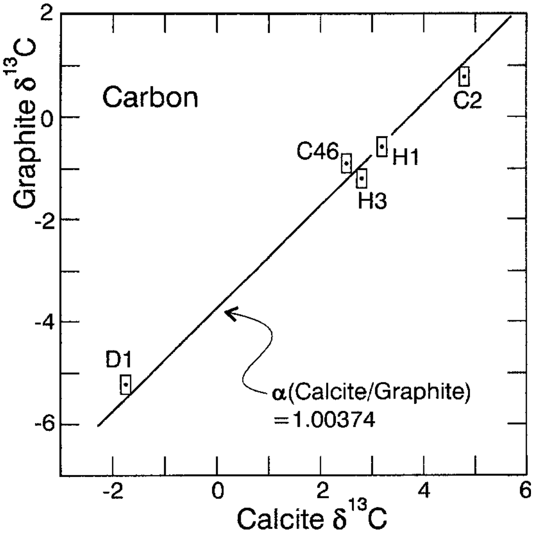

FIG. 11. Distribution of ^{13}C and ^{12}C between calcite and graphite. Size of symbols indicates 0.95 confidence limits, analytical precision. $\alpha(Cal/Gr)_{mean}$ = 1.00374 (1000 ln α = +3.74, Table 8).

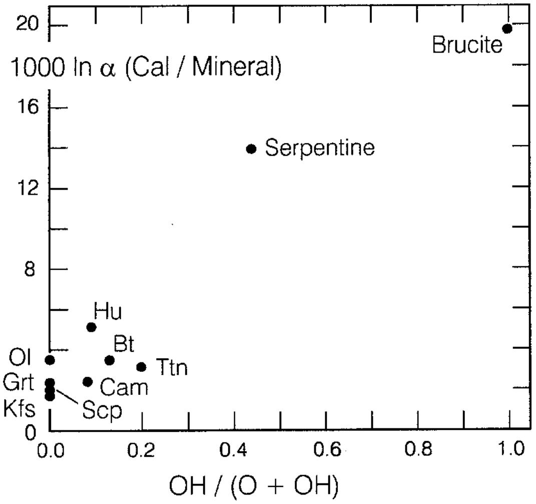

FIG. 12. Trend of increasing 1000 ln α ^{18}O (calcite/mineral) with increasing OH/(O + OH) in the designated mineral. Data from Table 8. Mineral symbols in Table 2; Hu here denotes clinohumite.

Where comparisons are possible, present results for $1000 \ln \alpha$ agree well with those from the Adirondacks (Valley & O'Neil 1984), as follows (Adirondack data in brackets): Cal/Cpx = 2.0 (1.7, $n = 6$), Cal/Cam = 2.4 (1.7, $n = 2$), Cal/Kfs = 1.8 (1.8, $n = 7$).

Only some of the fractionation factors have been calibrated, and temperature estimates for these are reported in Table 8. The α (calcite/olivine) and α (calcite/Ca amphibole) estimates give temperatures close to the peak of metamorphism. Others give somewhat higher or lower temperatures, but only one (calcite/clinohumite) differs by more than 110° from 700°C; this finding is consistent with the absence of large-magnitude departures for isotopic exchange equilibrium for the given mineral pairs.

DISCUSSION

Results presented here on *absolute* concentrations of isotopes in calcite of common Grenville marble (Fig. 4, open symbols) are the same as in Ontario and the Adirondacks, and all are comparable to those in unmetamorphosed Proterozoic limestone (Table 6). Thus a large volume of Grenville marble, with a surface area of approximately 18 000 km^2 and an estimated thickness of some 15 000 m (Baer 1976) has, for the most part, retained its original sedimentary or diagenetic isotopic composition. H_2O of any origin, coming in contact at elevated temperatures with calcite crystals of the specified composition would, by isotopic exchange, rapidly decrease the ^{18}O content of the crystals (Friedman *et al.* 1977, Fig. 13; Chacko *et al.* 1991). One must conclude, therefore, that during the entire metamorphic and post-metamorphic history of the marble, either a large-scale passage of H_2O through this significant volume of the Earth's crust did not occur, or if it did occur, the H_2O had equilibrated with high-^{18}O calcite or other crystals elsewhere, as described in general terms by Bowman *et al.* (1994). This inference applies even where some H_2O was obviously introduced to produce serpentine and brucite, and at these places it seems likely that only small amounts of H_2O were introduced, possibly by diffusion rather than by fluid flow. Similar conclusions for Grenville marble have been expressed by Sheppard & Schwarcz (1970) and Valley & O'Neil (1984), and for other regional metamorphic terranes by Sharma *et al.* (1965), Li *et al.* (1991) and Bol *et al.* (1995).

TABLE 9. OBSERVED VARIATION IN FRACTIONATION FACTORS (α)

		mean α	s	100 s / mean α	n
^{18}O	calcite/dolomite	1.000 295	0.000 642	0.064	11
^{13}C	calcite/dolomite	0.999 654	0.000 447	0.045	12
^{18}O	calcite/biotite	1.003 492	0.000 419	0.042	5
^{13}C	calcite/graphite	1.003 743	0.000 272	0.027	5

s estimate of standard deviation, n number of samples.

Concentrations of ^{18}O and ^{13}C in varieties of marble here referred to as Minor marble (Fig. 4, closed circles and triangles), are relatively low, and the history of these small bodies has been more complex, with possibly an introduction of oxygen and carbon that originated at a deeper level.

Results presented here on *relative* concentrations of isotopes in crystals, *i.e.*, on the distribution of isotopes among minerals of the marble, was considered in relation to exchange transformations and exchange equilibrium. At a constant temperature, the concept of isotopic exchange equilibrium requires, for a given isotope pair and mineral pair, a constant fractionation-factor; only minor perturbations may be expected, resulting from changes in phase composition. In the study area, particular fractionation-factors for calcite–dolomite were found to differ from place to place, but the differences are small and are, for the most part, consistent with a close approach to equilibrium.

Recently, in a study of the distribution of trace elements among silicate minerals, Kretz *et al.* (1999) introduced an index (e) as a measure of departure from exchange equilibrium, and the same index can be applied to isotopes. Where several samples are available from a terrane of uniform metamorphic grade, the variation found in the magnitude of a particular distribution-coefficient or fractionation-factor, expressed as $e = 100$ s / mean α, forms a measure of the tendency toward or away from equilibrium in the group of samples and, by extension, in the terrane studied. Thus a very small value of e corresponds to a condition of near-perfect equilibrium, and increasing e, to an increasing tendency toward non-equilibrium. Because of analytical imprecision, a value of e equal to 0.000 would be improbable and unexpected, and a lower limit can be found by referring to Figure 7, where all of samples F5, B2, F12a, H6, and H3 have indistinguishable $\alpha^{18}O$ values, to yield e approximately equal to 0.005. Thus in a range that extends from $e = 0.005$ to 0.40 or more (a random scatter of data points in Figs. 7, 8, 10, 11), results from the present study ($e \sim 0.05$, Table 9) are indicative of very small departures from equilibrium within the study area.

In the above analysis, a *mean* value of α was chosen as the best estimate of α at the peak temperature or a temperature on the cooling path. Another interpretation, applied for example to the ^{18}O data of Figure 7, is to view samples F3 and H8, in which α is a *maximum* (Fig. 9), as representative of equilibrium at 700°C, and to view all other samples (barring S6) as having approached equilibrium more or less closely, beginning possibly with an α value close to that expressed by the dotted line in Figure 7. If so, then the finding that for both ^{18}O and ^{13}C (Figs. 7, 8), half the samples have α values that are nearly identical (*i.e.*, they fall almost exactly on the line representing mean α) must be viewed as being improbable, and this interpretation was therefore not adopted.

With regard to ^{18}O and ^{13}C (calcite/dolomite; Figs. 7, 8), one can try to understand the small-magnitude variations that exist, in relation to the silicate minerals that are present. Notice that in D2, both $\alpha^{18}O$ and $\alpha^{13}C$ are relatively low (Fig. 9), and this could possibly be related to the crystallization of 17% of Ca amphibole in D2, but H1 and C33, which also record relatively low α values, contain only 5 and 1% of silicates, respectively. Also, in F3 an H8, both $\alpha^{18}O$ and $\alpha^{13}C$ are relatively high (Fig. 9), and in F3, this condition could possibly be related to the presence of 23% of serpentine in F3, but H8 is devoid of serpentine. Similarly, the anomalous $\alpha^{18}O$ in S6 ($\alpha^{13}C$ is normal) cannot be understood at present.

By use of equation (6), one can obtain an estimate of the change in Gibbs energy (the driving force) of isotopic exchange reactions. These estimates, which amount to only a few J mol^{-1}, are much smaller than corresponding values for trace-element exchange (several thousand J mol^{-1}; Kretz *et al.* 1999) and other kinds of mineral transformations. It is therefore surprising that, in general, a close approach to equilibrium was realized with regard to the distribution of isotopes among the various minerals in the marble study area. The explanation possibly lies in widespread synmetamorphic deformation and dynamic recrystallization, which, as noted by Mueller (1966) and Yund & Tullis (1991), facilitate the rearrangement of atoms needed to achieve a condition of equilibrium. From this viewpoint, the absence of deformation and recrystallization permits some systems, originally at equilibrium, to persist largely unchanged during uplift and cooling.

CONCLUSIONS

The principal conclusions are as follows:

1) The $^{18}O/^{16}O$ and $^{13}C/^{12}C$ values of calcite in major marble units of the Otter Lake of Quebec area are similar to those elsewhere in the Grenville Province and in unmetamorphosed Proterozoic limestone, thus strengthening the earlier conclusion that the isotopic composition of these units was largely preserved during their entire metamorphic and post-metamorphic history. Only minor shifts of approximately 1 δ unit have occurred while metamorphic reactions were in progress.

2) Near-constant fractionation-factors for the distribution of oxygen and carbon isotopes between calcite and dolomite and of carbon between calcite and graphite are viewed as evidence for a close approach to exchange equilibrium in the samples selected for study and in the study area. An apparent equilibrium involving calcite and biotite was possibly determined at some point on the cooling path.

3) Exploratory data on the distribution of oxygen isotopes between calcite and various associated silicates agree moderately well with experimental results produced at or extrapolated to approximately 700°C, which is the independent estimate of the peak temperature of metamorphism.

4) Data are now needed on microvariations in isotopic composition within the samples selected for study, especially in samples with biotite, and on the possible role of dynamic recrystallization in promoting isotopic exchange. New experimental results on the distribution of isotopes between calcite and dolomite in the range of 500 to 800°C would also be helpful in future studies of marble-bearing metamorphic terranes.

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