$^{13}C/^{12}C$ exchange between calcite and graphite: a possible thermometer in Grenville marbles*

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Abstract—The fractionation of ^{13}C between calcite and graphite, $\Delta(Cc-Gr)$, is consistently small (2.6–4.8 permil) in 34 assemblages from upper amphibolite- and granulite-facies marbles of the Grenville Province. In 25 samples from the Adirondack Mountains, New York, it decreases regularly with increasing metamorphic temperature. The fractionations are independent of absolute $\delta^{13}C$ values of calcite (−2.9 to +5.0). For $T = 600$–800°C, the Adirondack data are described by $\Delta(Cc-Gr) = -0.00748T$ (°C) + 8.68. This good correlation between Δ and T suggests that carbon isotope equilibrium was attained in these high-grade marbles and that the theoretical calculations of this fractionation by Bottinga are approximately 2 permil too large in this temperature range. Because of the relatively high temperature sensitivity suggested by these results and by Bottinga's calculations. and the pressure independence of isotope fractionation, $\Delta(Cc-Gr)$ may provide a very good thermometer for high-grade marbles.

Comparison of this field calibration for $\Delta(Cc-Gr)$ vs temperature with results from other terranes supports the utility of $\Delta(Cc-Gr)$ for geothermometry and suggests that graphite is much more sluggish to exchange than calcite. that exchange between calcite and graphite occurs at temperatures as low as 300°C. and that equilibrium may normally be attained only when peak metamorphic temperatures are greater than 500–600°C.

Because ^{13}C exchange is an unavoidable metamorphic process at temperatures above 300°C. high values of $\delta^{13}C(Gr)$ in moderate- to high-grade carbonate-bearing rocks do not provide a sufficient criterion to infer an abiogenic origin for the graphite.

INTRODUCTION

GRAPHITE coexists with calcite in a wide variety of metamorphosed rocks of all ages. Several studies have shown that in comparison with organic carbonaceous matter the $\delta^{13}C$ values of graphite are often relatively high (> −10.0) and that the permil isotopic fractionations between calcite and graphite are relatively small (0.0–10.0) (HOERING and HART, 1964; HAHN-WEINHEIMER *et al.*, 1968; SHABO and MAMCHUR, 1973; ANDREAE, 1974; HOEFS and FREY, 1976; PINEAU *et al.*, 1976; KREULEN, 1977; PERRY and AHMAD, 1977; WADA, 1977; SCHLIDLOWSKI *et al.*, 1979). These high values of $\delta^{13}C(Gr)$ and small $\Delta(Cc-Gr)$ suggest an abiogenic mode of graphite formation during metamorphism because organically formed carbonaceous matter in sediments typically has very different values: $\delta^{13}C = -20$ to −30 and $\Delta(Cc-Gr) > 15$ (EICHMANN and SCHIDLOWSKI, 1975). Alternatively, high $\delta^{13}C$ (Gr) and small $\Delta(Cc-Gr)$ may result from

isotopic exchange during metamorphism (WADA, 1977). However, when the theoretically calculated fractionation between calcite and graphite (BOTTINGA, 1969a) is applied to these metamorphic pairs, temperatures are inferred that vary from less than 100 to over 1000°C, in contrast to other estimates, and no general agreement between natural data and theory has been obtained. Experimental results of CLAYTON *et al.* (1975) show that variable pressure cannot be the cause of this disagreement.

In this study, the isotopic composition of carbon in coexisting graphites and calcites has been determined in order to test equilibrium in amphibolite- and granulite-facies marbles and calc-silicates of the Grenville Province that were metamorphosed at 1 Byr. Most samples are from the Adirondack Mountains of New York where recent studies yield unusually consistent values of peak metamorphic temperature. Textural criteria have been applied in thin section examination to avoid retrograde samples.

Because there is often a complete gradation from organic carbonaceous matter in low temperature rocks to well ordered, crystalline graphite in high temperature rocks. we will, for simplicity, use the term graphite loosely to include all carbonaceous matter.

ADIRONDACK METAMORPHISM

Metamorphic grade in the Adirondacks increases from upper amphibolite facies in the N.W. Lowlands to garnet granulite facies in the Central Highlands (BUDDINGTON, 1939; DE WAARD, 1969). Peak metamorphic temperatures have been contoured across 20,000 km^2 of the Adirondacks from over 59 determinations (BOHLEN et al., 1980a). These temperatures were inferred at 57 localities from electron microprobe analysis of coexisting assemblages of K-feldspar-plagioclase (STORMER, 1975) and magnetite-ilmenite (BUDDINGTON and LINDSLEY, 1964). These two independent systems are in good agreement and for 6 pairs of samples where both assemblages were analyzed from localities within 5 km of each other, the mean difference in temperatures is less than ±15°C.

For this study, it is assumed that these temperatures, which were measured primarily in orthogneisses, represent peak metamorphic temperatures for other rock types in the Adirondack terrane. Mineral assemblages in Adirondack marbles and calc-silicates are consistent with this assumption when independently determined pressures of 6 kbar in the Lowlands (BROWN et al., 1978) and 8 kbar in the Highlands (Jaffe et al., 1978; BOHLEN et al., 1980b; VALLEY and ESSENE, 1980b) are applied and the effects of mineral solid solutions and variable fluid fugacities are considered (VALLEY and ESSENE, 1980a). These temperature estimates are believed to be accurate to within ±30°C.

Peak metamorphic mineral equilibria are unusually well preserved in the Adirondacks, although some minor retrogradation is evident. In orthogneisses, the thermometry of BOHLEN et al. (1980a) required careful observation of textures and reintegration of unmixed iron-titanium oxides and of exsolved feldspars. VALLEY and ESSENE (1980a) also found limited evidence of retrogradation in marbles and calc-silicates but concluded that, with the exception of occasional coarse, secondary dolomites, it was generally recognizable and could thus be avoided. The close agreement of temperature and pressure estimates from such diverse rock types as charnockite, mangerite, pelitic metasediment, marble, and calc-silicate supports the conclusion that all rock types equilibrated under the same conditions at the peak of metamorphism. If this were not so, differences in H$_2$O fugacity and in mineralogy would be expected to cause variable blocking temperatures to be recorded along the retrograde P–T path.

angles at grain-boundary triple junctions. the absence of chemical zonation in silicate minerals as detected by electron microprobe. and the absence of retrograde textures such as exsolution and rimming. It is possible that other workers who have not taken similar precautions have obtained anomalous values of Δ(Cc-Gr) that can be explained as retrograde.

For this reason it is important to consider possible mechanisms of retrogradation. Experimental studies have shown the rates of graphite exchange are much more sluggish than those of calcite. Little or no exchange was observed in short-term dry graphite experiments up to 1000°C at 1 kbar (HOERING. personal communication. 1979) and in the presence of water at 700°C. 5 kbar (VALLEY et al., unpublished data). Calcite. on the other hand. exchanges with CO$_2$ in laboratory systems at temperatures as low as 350°C (NORTHROP and CLAYTON, 1966; O'NEIL and EPSTEIN, 1966). Thus it is likely that if a sample were to back react. only calcite would exchange. However, long periods of time, higher pressures, and retrograde fluids all enhance reaction rates and may facilitate retrograde exchange between graphite and calcite in nature.

VALLEY and ESSENE (1980a) considered the extent of retrogradation in Adirondack marbles. They found, on textural, chemical and petrologic grounds, that occasional rims of tremolite on diopside and talc on tremolite were secondary but that there was no evidence for wholesale silicate recrystallization after the peak of metamorphism. Among carbonates, however, when calcite coexists with dolomite, exsolution and recrystallization are common. Primary and secondary dolomite can be observed in thin sections that are stained with alizarin red in dilute aqueous HCl solution. In Adirondack marbles a complete gradation of secondary dolomite can be seen from: (1) small, 10- to 100-μm, symplectic blebs of exsolved dolomite in calcite; to (2) elongate grains of dolomite along calcite grain boundaries; to (3) coarse, equant grains of dolomite, now externally located with respect to the calcite host. that are texturally indistinguishable from primary dolomite. Electron microprobe analysis of calcite coexisting with such 'primary looking' dolomite shows low Mg in calcite rims and higher Mg in calcite cores. and this evidence suggests that Mg has migrated out of calcite to form dolomite. Although it is not known whether such unmixing occurs by Mg diffusion in a solid or by solution and recrystallization, it is likely that such unmixing is accompanied by carbon isotope exchange. Thus, carbonate unmixing may be a driving force for retrograde isotopic exchange. For this reason calcites that coexist with dolomite have not been analyzed in this study. Calcites that are free of dolomite exsolution and that do not coexist with dolomite are relatively low in Mg and have less tendency to unmix and exchange. The two dolomites that have been analyzed. GOV78-20 and GOV83. are from samples that are dominantly dolomite and thus they must be primary.

Graphites and calcites have been separated from the same 25 cm^3 volume of rock. Only marbles with less than 2% graphite have been selected. More graphite-rich samples may be found in the Adirondacks (ALLING. 1918). but these have been avoided because thick graphite layers may not have equilibrated with nearby calcite.

SAMPLE SELECTION

Special care was taken in this study to choose mineral pairs that were in equilibrium at the peak of metamorphism and to avoid samples that may have back-reacted or exchanged after the peak of metamorphism. All Adirondack samples were examined in thin section and are described petrographically (VALLEY and ESSENE, 1980a). Chemical equilibrium is indicated in thin section by the annealed texture of calcite grains with approximately 120°

ANALYTICAL METHODS

Graphite separates were hand-picked from coarsely crushed samples. Picking was facilitated by dissolution of carbonate in dilute HCl. All graphite separates were greater than 99% pure. Individual graphite flakes vary in size but are generally larger than 1 mm and occasionally larger than 10 mm. weighing up to 5 mg.

Graphite was combusted to CO$_2$ for isotopic analysis. Samples of 3 to 5 mg were combusted with 350 mg of CuO

Table 1. Isotopic compositions of calcite. dolomite and coexisting graphite

Sample	Calcites $\delta^{18}O$	Calcites $\delta^{13}C$	Graphites $\delta^{13}C$	$\Delta Cc–Gr$ *$\Delta Dol–Gr$	Temperature °C
Adirondack Mountains. New York. amphibolite facies					
GOV78-10	23.3 (2)	2.2 (2)	−1.4	3.6	670
GOV78-17	27.2 (2)	2.3 (2)	−1.1	3.4	660
GOV78-20 (dolomite)	23.4	2.7	−0.6	3.3*	650
GOV78-22	27.0 (2)	3.2 (2)	−0.5	3.7	660
GOV83 (dolomite)	21.1	2.4	−2.3	4.7*	640
GOV104	22.5 (2)	1.7 (2)	−3.1	4.8	610
V3-11-514	18.1	−2.7	−6.5	3.8	670
Adirondack Mountains. New York. granulite facies					
AUS78-10	22.6	1.6	−1.5	3.0	660
BL2-2	21.9	1.4	−1.8	3.2	670
IL2-6	13.5	0.4	−2.9	3.3	730
IL2-7	13.8	0.4	−2.7 (2)	3.1	730
IL11	17.0	0.2	−3.3	3.5	730
IL20	12.8 (2)	1.6 (2)	−1.7	3.3	730
IL25	20.9	1.1	−2.4	3.5	740
IL27	22.7 (2)	2.2 (2)	−1.1 (2)	3.3	720
LP8-2	18.3	−2.9	−5.8	2.9	730
LP77-216-1	19.8	−2.9	−5.7 (2)	2.8	760
LP200	23.2	1.4	−1.2	2.6	760
NC7-76	22.7	0.0	−3.7	3.7	710
NC12	22.7	2.4	−1.2	3.6	730
NC18-5	23.3 (2)	1.8 (2)	−1.5 (2)	3.3	710
NC78-6	22.2	−0.3	−3.8 (2)	3.5	710
OF203-1	13.9	0.8	−3.1	3.9	700
SL9-1	17.8	1.8	−1.6	3.4	720
TP10-1	24.3	2.2	−0.7	2.9	760
TP16	14.3	1.1	−2.5	3.6	720
W78-3	23.7	1.5	−1.9	3.4	660
Grenville Province. outside of the Adirondack Mountains					
FN2	22.4	0.8	−2.4	3.2	
HBU79-1-1	16.8	0.6	−2.5	3.1	
HBU79-1-2	16.6	0.5	−2.5	3.0	
MR7	24.8	1.4	−1.6	3.0	
PS79-1-1	16.6	−1.5	−5.2	3.7	
Q100	23.6	5.0	+1.8	3.2	
Q120	20.3	2.1	−1.5	3.6	

Numbers in parentheses refer to replicate analyses.

at 1000°C for 15 min. Yields, measured manometrically, were typically 95–105%. Blanks of 1000 mg CuO showed no carbon contamination.

Calcites were reacted with 100% H_3PO_4 at 25°C (McCREA, 1950; SHARMA and CLAYTON, 1965). Carbon and oxygen isotope analyses were made with standard, double-collecting, isotope ratio mass-spectrometers. Isotopic compositions are given in permil relative to PDB and are reproducible to better than ±0.1. Isotopic fractionation is defined as $\Delta(Cc–Gr) = 10^3 \ln(1000 + \delta Cc/1000 + \delta Gr)$ which is approximately $\delta Cc–\delta Gr$.

RESULTS

Isotopic compositions of graphite and calcite are given in Table 1. All samples have relatively high $\delta^{13}C(Gr)$ values ranging from −6.5 to 1.8 and small $\Delta(Cc–Gr)$, ranging from 2.6 to 4.8. Figure 1 shows these fractionations plotted on a map of the Adirondacks with the isotherms of BOHLEN et al. (1980a) shown for comparison. The sample localities are described by VALLEY and ESSENE (1980a). It is significant that all values of $\Delta(Cc–Gr) < 3.0$ fall inside or near the 750°C isotherm, whereas values of $\Delta(Cc–Gr) > 4.0$ fall at the perimeter of the map area.

The general consistency between the concentric temperature pattern and the isotopic fractionations suggests that carbon isotope equilibrium was attained during metamorphism. Temperatures for the peak of metamorphism have been inferred for each Adirondack sample from the isotherms (Table 1) and $\Delta(Cc–Gr)$ is plotted against temperature in Fig. 2. Temperatures are assumed to vary gradually between isotherms without regard to rock type and without small-scale, local variations. A simple least-squares regression of the Adirondack data over the temperature interval of 610 to 760°C is shown in Fig. 2 and expressed by the following equation:
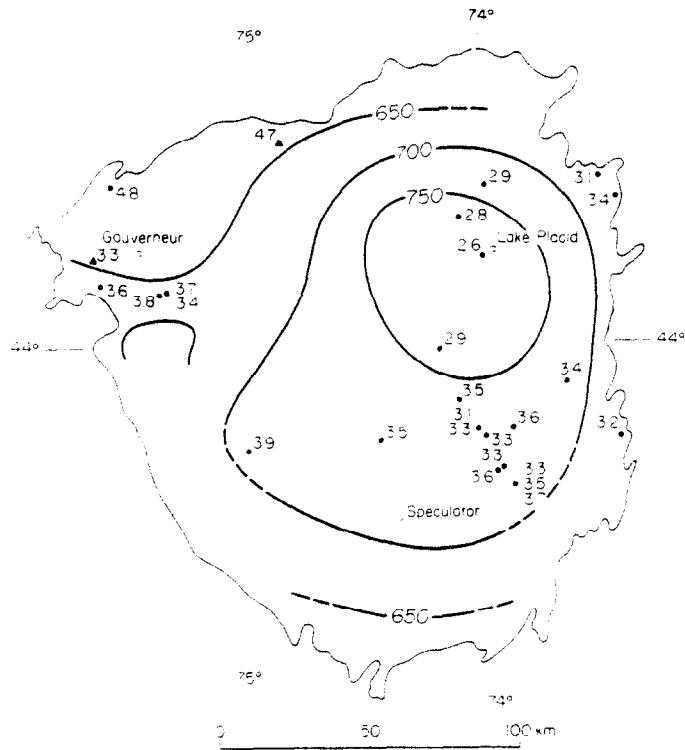
$$\Delta(Cc–Gr) = -0.00748T + 8.68 \quad (T \text{ in } °C)$$

Fig. 1. Fractionation of ^{13}C between coexisting calcite and graphite Δ(Cc–Gr) for samples from the Adirondack Mountains. New York. Isotherms, representing peak metamorphic temperature, are from BOHLEN et al. (1980a). Two assemblages of dolomite–graphite are shown by triangles.

The two dolomite–graphite assemblages shown in Table 1 and Fig. 2 were not used in this calculation although they are consistent with the other data.

The Adirondack data show a good correlation between fractionations and temperature, but until more measurements are made for temperatures above 730 or below 650°C. the possibility of a somewhat different temperature coefficient must be considered. In particular, the slope of this line is heavily influenced by the point at 610°C. As will be discussed later, values of Δ(Cc–Gr) measured in rocks formed at 500–600°C are either equal to or slightly larger than
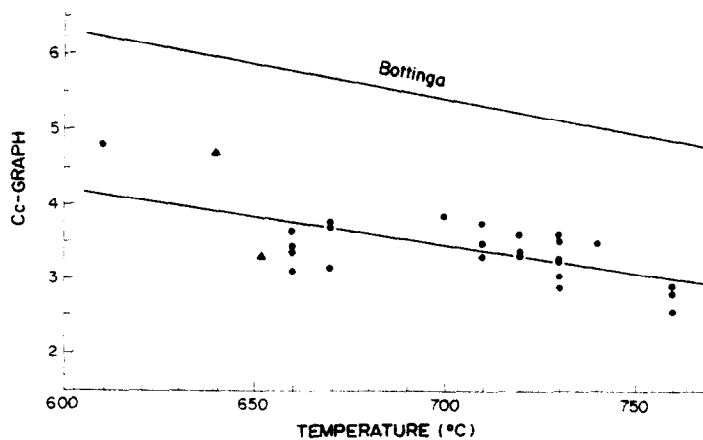

Fig. 2. Fractionation of ^{13}C between coexisting calcite and graphite Δ(Cc–Gr) from Adirondack samples plotted versus temperature as inferred from the isotherms of BOHLEN et al. (1980a). The lower line is a least-squares regression of the data. The upper line was calculated by BOTTINGA (1969a). Two assemblages of dolomite–graphite are shown by triangles and were not used in the least-squares calculation.
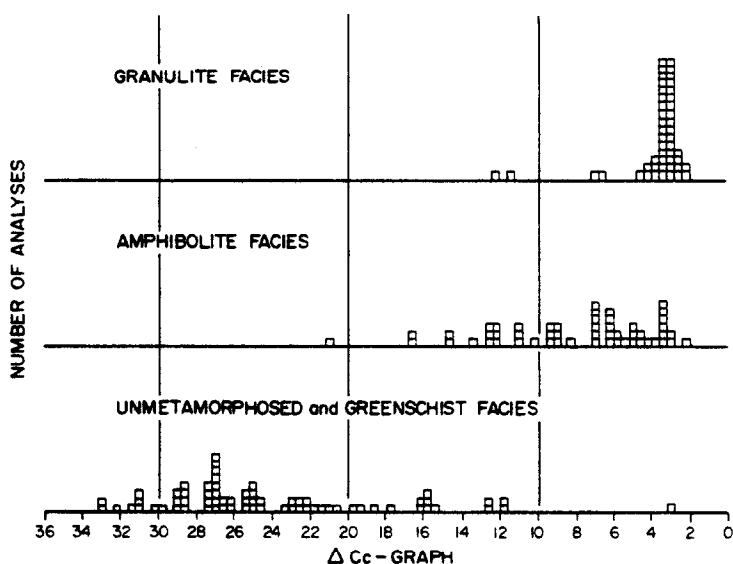
Fig. 3. Fractionation of ^{13}C between coexisting carbonate and graphite (or carbonaceous matter) from different metamorphic facies. Equilibrium is normally attained only in the granulite facies. Only Pre-Cambrian samples are included under unmetamorphosed carbonaceous matter. Analyses are from: HOERING and HART (1964), HAHN-WEINHEIMER et al. (1968), SHABO and MANCHUR (1973), ANDREAE (1974), EICHMANN and SCHIDLOWSKI (1975), HOEFS and FREY (1976), PINEAU et al. (1976), KREULEN (1977), PERRY and AHMAD (1977), SCHIDLOWSKI et al. (1979), this study.

the equilibrium values. An equilibrium fractionation at 610°C that is smaller than that measured would result in a more shallow slope and a geothermometer that is less sensitive.

A theoretically calculated expression for $\Delta(Cc-Gr)$ (BOTTINGA, 1969a) is also shown in Fig. 2. The slopes of the two lines are similar, but the Adirondack fractionations are approximately 2 permil less than those predicted by the calculated expression. The calculated expression is undoubtedly in error because unreasonably high temperatures of 1000 to 1500°C would be inferred for the smaller fractionations observed in nature. Because such calculations involve factors that cannot now be fully evaluated, an error in the magnitude of fractionation is not surprising, but the slope is more likely to be correct.

The calculations of Bottinga further support the assumption made here that calcite and graphite have not exchanged after the peak of metamorphism. If the Adirondack data reflect such exchange then the equilibrium fractionation must be smaller than that shown by natural assemblages rather than larger as indicated by the calculations.

CALCULATED VERSUS EMPIRICAL
$\Delta(Cc-Gr)$

The significance of the 2 permil difference between the Adirondack data and the theoretical calculation can be better understood after a consideration of the relative errors associated with each curve.

The Adirondack results are subject to uncertainties in the temperature estimates and effects arising from possible disequilibrium or compositional heterogeneity of the samples. The uncertainty of the BOHLEN et al. (1980a) isotherms is believed to be generally less than $\pm30°C$ on the basis of: (1) the estimated error of feldspar thermometry in the appropriate composition and temperature range ($\pm30°C$, STORMER, 1975); (2) the estimated error of oxide thermometry ($\pm50°C$, BUDDINGTON and LINDSLEY, 1964); (3) the statistics of electron microprobe reintegration, and (4) the statistics of averaging the large number of independent measurements that were contoured. This uncertainty of $\pm30°C$ corresponds to ±0.3 in $\Delta(Cc-Gr)$ (Fig. 2) and is thus of secondary importance relative to the 2 permil discrepancy under discussion.

The tight clustering of data in Fig. 2 suggests that the effects of sample heterogeneity and disequilibrium can not be greater than the total scatter (±0.4 permil). This scatter includes any possible analytical and extraction errors as well as the temperature uncertainty of ±0.3 permil. However, sample heterogeneity could introduce a serious bias in $\delta^{13}C$ (graphite) when graphites are either so coarse that one analysis may represent a single 5-mg crystal or in banded rocks. PINEAU et al. (1976) found isotopic heterogeneity in graphite at the scale of 10 cm in granulite facies marbles from Gour Oumelalen, Algeria, and Limecrest Quarry, near Franklin Furnace, New Jersey, and suggested that this might be the cause of variations of ±1.0 permil in $\Delta(Cc-Gr)$ that they found in a few samples. However, both of these areas (unlike the

Adirondacks) may have been complicated by poly-metamorphism after the peak granulite-facies event.

Mechanisms have been proposed for the abiogenic formation of graphite that would account for small values of Δ(Cc–Gr) in the absence of equilibrium exchange between calcite and graphite (PINEAU et al., 1976; WADA, 1977). In such processes, Δ(Cc–Gr) would be controlled by the rate of reaction for various solid–fluid and fluid–fluid reactions, the ratio of CO_2/CH_4 and the size of the domain of exchange. These processes may be important in nature but they were not operative in the Adirondacks as evidenced by the consistent isotopic relations there over a wide range of calcite compositions ($\delta^{13}C = -2.9$ to 5.0). The large variability in modal percentage of minerals in Adirondack marble combined with variations in reaction rates would have made $\delta^{13}C$ (graphite) nearly independent of $\delta^{13}C$ (calcite) unless equilibrium exchange was also attained.

The importance of variations due to factors other than errors in temperature calibration was evaluated by analyzing samples from different lithologic units in coarsely layered marbles from single outcrops. At one outcrop, the fractionations measured in three samples agreed to within ± 0.2 [NC7-76, NC78-5, NC78-6, Δ(Cc–Gr) = 3.5 $\pm$ 0.2], and at another outcrop the fractionations measured in two samples were the same within ± 0.1 [IL2-6, IL2-7, Δ(Cc–Gr) = 3.2 $\pm$ 0.1]. There cannot have been appreciable temperature variation within either of these outcrops during regional metamorphism, and thus the maximum variation of ± 0.2, which may be largely due to heterogeneity, is probably characteristic of the reproducibility of Δ(Cc–Gr) from rocks metamorphosed at the same temperature. These small variations indicate that temperature calibration is probably the largest single source of error, but also that careful thermometry will require analysis of several assemblages from each outcrop.

The theoretically calculated fractionation of Δ(Cc–Gr) (BOTTINGA, 1969a) is derived by combination of calculations of Δ(CO_2–Gr) (BOTTINGA, 1969b) and of Δ(CO_2–Cc) (BOTTINGA, 1968). In calculating Δ(CO_2–Gr), Bottinga showed that two different phonon spectra for graphite yield differences in Δ of 1.5 at 700°C and 3.3 at 300°C. Each of these spectra produces good estimates of the specific heat of graphite, in agreement with measured values, but BOTTINGA (1969b, p. 304) prefers the Yoshimori–Kitano spectrum because it is 'based on a more rigorous theory.' When the other spectrum, that of Egelstaff, is used at 700°C, a value of Δ(Cc–Gr) results that is only slightly larger than that inferred from the Adirondack data (3.9 vs 3.4). This agreement does not necessarily verify one spectrum over the other, but it does serve to point out the sort of uncertainty involved. In addition, this calculation involves an inherent assumption that atomic vibrations are harmonic. BOTTINGA (1969b) notes that anharmonic terms may become important at high temperatures, but it is not possible to

estimate their magnitude with our present knowledge.

For calcite, the calculations of Δ(CO_2–Cc) are consistent with experimental results above 300° (NORTHROP and CLAYTON, 1966; O'NEIL and EPSTEIN, 1966). The experiments of O'Neil and Epstein were designed to determine ^{18}O fractionation, and unusual ^{13}C compositions were employed to trace the extent of exchange. This method resulted in an uncertainty of 2.4 permil in Δ(CO_2–Cc) for ^{13}C. Northrop and Clayton attempted to measure ^{13}C fractionations in this system but were able to achieve only 20 and 43% exchange at 300 and 400°C and thus could have introduced significant error through the necessary interpolation. The uncertainty in these experiments permits the possibility that Δ(CO_2–Cc) may be in error by 1–2 permil at 700°C.

We suggest that the Adirondack data represent equilibrium with an uncertainty at ± 0.4 permil. A 2-permil increase in the calculated values of Δ(Cc–Gr) at a temperature of 700°C might have been caused by errors in analyses of the phonon spectra or failure to incorporate anharmonicity terms. Perhaps the natural data can serve as a guide to evaluate these possibilities. The apparent agreement in the temperature coefficient of the empirical and calculated expressions (Fig. 2) is encouraging and suggests that we are close to an understanding of this isotopic system.

LOCALITIES OUTSIDE THE ADIRONDACKS

A comparison of calcite-graphite carbon isotope fractionation from other terranes further supports the Adirondack data as representing a close approach to isotopic equilibrium. Analyses of seven calcite-graphite assemblages from Grenville marbles outside of the Adirondacks are given in Table 1. The sample localities of these specimens are given in Appendix I. Sample FN2, from Franklin Furnace, New Jersey, and samples HBU, from the Honey Brook Uplands, Pennsylvania, show small fractionations (3.0–3.2) similar to the highest grade samples in the Adirondacks (750°C). This similarity is consistent with estimates of granulite-facies metamorphism for these terranes (CRAWFORD and HUNTSMAN, 1976; KEARNS, 1978). Likewise, sample MR7, from south of the Morin Anorthosite Massif, Quebec, has a small fractionation (3.0) and was metamorphosed at estimated conditions of 7 kbar and 700° to 820°C (NANTEL, 1977). The two Q samples from the Otter Lake area, Quebec, have fractionations (3.2 and 3.6) similar to samples from intermediate Adirondack temperatures (700°C). These results are consistent with temperature estimates of 650°C (KRETZ, 1977) and 660°C (MARCOTTY, personal communication, 1979) from calcite-dolomite solvus thermometry and 675°C (PERKINS, 1979) from K-feldspar-plagioclase and magnetite-ilmenite thermometry. Sample PS79-1-1, from Parry Sound, Ontario, has a larger fractionation (3.7), con-

sistent with estimates of upper amphibolite facies metamorphism.

PINEAU et al. (1976) analyzed calcite–graphite assemblages from Algeria. Namibia. and New Jersey. Ten assemblages from marbles of Gour Oumelalen (Ahaggar, Algeria) have average fractionations ranging from 2.5 to 4.0. The close similarity of this spread in values to that found in the Adirondacks supports the conclusions of PINEAU et al. (1976) that the highest grade of metamorphism was granulite facies. It is significant that there is no evidence of back reaction among the Algerian calcites and graphites. even though later amphibolite- and greenschist-facies events are proposed. Four of the six analyzed samples from amphibolite-facies marbles of the Damara Belt, Namibia. have fractionations from 3.6 to 4.7. If these values are averaged. the result (4.2) agrees very well with the line fit to the Adirondack data (4.0, Fig. 2). assuming PUHAN's (1976) calcite–dolomite temperature (620°C). This temperature was determined by optical and microprobe reintegration of coarsely exsolved dolomite in calcite. a technique that should give a result equal to or slightly less than the peak metamorphic value. The possibility that this 1.1 permil scatter in the Namibia data of Pineau et al. represents variable temperatures of metamorphism has not been evaluated: all samples are from within 15 km of each other. Two other samples from the Damara Belt show heterogeneity in graphite compositions and/or Δ(Cc–Gr) of 4 permil. This variation could be due to sample heterogeneity or to incomplete exchange of an originally organic graphite.

One sample from the Limecrest Quarry, from near Franklin Furnace. New Jersey. gave consistent fractionations of 3.8 (PINEAU et al., 1976). However, two other samples show heterogeneity in the isotopic compositions of graphites. but not in calcites, and have fractionations that range from 1.0 to 7.1. The 0.6 permil difference in fractionation between this one apparently homogeneous sample (3.8) and FN2 (3.2) which is also from near Franklin Furnace, may represent differences in metamorphic temperature. It is also important to state that although the terrane around Franklin Furnace was involved in the Grenville orogeny (1 Byr), it is not part of the Adirondack Mountains (as was mistakenly stated by PINNEAU et al., 1976) and is more than 200 km south of the nearest Adirondack exposures.

WADA (1977) analyzed calcite–graphite assemblages from several contact and regional metamorphic terranes in Japan. The general consistency of the results led Wada to conclude that equilibrium was generally attained and temperature estimates were made using Bottinga's calibration. Independent temperatures are not available for many of these samples, but in four regions where Wada reports that temperatures have been determined from other mineral systems. the carbon isotope temperatures are 100–200°C too high. Better temperature concordance is found if the empirical calibration of this study is used.

In terranes where organic carbonaceous matter can be traced from low to high grade. a progressive increase in $\delta^{13}C$ is commonly reported (BARKER and FRIEDMAN. 1969: HOEFS and FREY, 1976: RUMBLE et al., 1977). This increase may be due in part to progressive loss of CH_4 which would be depleted in ^{13}C, but exchange with isotopically heavy carbonates must also become important at high temperatures in marbles. Such exchange probably is kinetically controlled by the more sluggish graphite at intermediate temperatures below 600°C. Over this range. the fractionation between calcite and graphite may decrease with increasing temperature and yet not reach equilibrium. Thus other factors such as time. pressure, fluids, and stress will be important in controlling the amount of exchange and quantitative application of calcite-graphite thermometry will be impossible. It is important to evaluate the range of temperatures where carbonates and graphites begin to exchange and where equilibrium may finally be reached.

HOEFS and FREY (1976) show a progressive increase in $\delta^{13}C$(graphite) from about -26 to -11 in a traverse of 44 samples in the Swiss Alps. δ-values of -25 to -29 were found in unmetamorphosed sediments in the north. and δ-values of -14 to -11 were found in the south where metamorphic temperatures of 550°C are inferred. In the range 350–450°C. $\delta^{13}C$ increases sharply for graphites that coexist with more than 5 percent carbonate minerals: at the same time, $\delta^{13}C$ decreases for these carbonate phases. At 550°C the two graphite samples that coexist with more than 4% carbonate minerals have fractionations of 6.2 and 7.3. which the Adirondack data would suggest are still slightly larger than the equilibrium values. Samples with less than 2% calcite show a much greater scatter, consistent with the presence of small amounts of secondary calcite. Thus 350–550°C may be the range in which kinetics of exchange are important. It is significant that this is the same range of metamorphic conditions over which graphite generally coalesces from disseminated submicroscopic particles that commonly produce a gray marble to coarser crystals within white marble. Volatilization and increased degree of crystallinity have also been observed as a function of increasing metamorphic temperature and are described by LANDIS (1971). These processes are probably concomitant with isotopic exchange, although isotopic equilibrium may not be attained until temperatures of 600°C and above are reached.

The onset of exchange equilibrium at about 600°C is seen in Fig. 3 where fractionations are shown in relation to metamorphic facies. In unmetamorphosed or low grade samples large fractionations are found due to the preservation of low values of $\delta^{13}C$ in organic carbonaceous matter. In the amphibolite facies there is a general decrease in fractionation as graphite forms and exchanges with carbonate. Some samples may attain exchange equilibrium. but many do not. In the granulite facies nearly every sample has attained or closely approached isotopic equilibrium.

At high metamorphic temperatures, the low values of $\delta^{13}C$ that are characteristic of sedimentary organic matter should not be preserved in the presence of high $\delta^{13}C$ carbonates. Thus, high $\delta^{13}C$ in graphite is not a sufficient criterion to infer an abiogenic origin in high-grade marbles. In the absence of a second carbon-bearing phase, graphite should preserve its premetamorphic $\delta^{13}C$ value. This explains a low $\delta^{13}C$ value of -30.3 measured for a graphite from an Adirondack quartz–graphite schist (HOERING and HART, 1964).

Note added in proof

Recent SEM photographs of Adirondack graphites (WEIS, 1980) give evidence of more than one generation of graphite growth. Graphites may be 'lustrous, dense and well-crystallized' as are nearly all of the graphites in this study, or they may be 'skeleton forms'. Skeleton graphite may appear alone or as overgrowths on well-crystallized graphite. We have also observed these skeleton graphites with a light microscope in HCl insoluble residues from marbles and have avoided them with the exception of NC 12. In sample NC 12 a thin overgrowth of skeleton graphite surrounds well-crystallized graphite such that the overgrowth represents less than one percent of the mass of the crystal.

We interpret skeleton graphite as having crystallized after the peak of Grenville metamorphism. This is supported by textures and stable isotopic compositions. WEIS (1980) reports analyses of a marble from Eagle Lake, New York where Δ(calcite–well-crystallized graphite) = 2.6 per mil and Δ(calcite–skeleton graphite) = 4.9 per mil. This suggests crystallization of skeleton graphite at lower temperatures than well-crystallized graphite, demonstrating the importance of careful optical examination for any attempted thermometric study.

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APPENDIX

Sample localities outside the Adirondacks

FN2	Franklin Station, New Jersey, Franklin limestone from north side of Furnace Pond.
HBU79-1-1,-2	Pottstown, Pennsylvania. 7 1/2' Quadrangle, 2.4 km S.W. of Anauertown, 0.1 km W. of road intersection 522 on Horsehoe Trail.
MR7	Quebec, near southern margin of the Morin anorthosite massif.
PS79-1-1	South of Parry Sound, Ontario, along Rt 69, 17 km N. of Port Severn, 0.8 km N. of the MacDonald River.
Q100	Kazabazua, Quebec Sheet, 3.5 km N.E. of Lac Sinclair, 1.2 km S. of road junction
Q120	Kazabazua, Quebec Sheet, 5 km N.E. of the east end of Mecham Lake.