Extraction and carbon isotope analysis of CO_2 from scapolite in deep crustal granulites and xenoliths

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Abstract—Carbon isotope compositions of scapolite from granulite facies gneisses and lower crustal xenoliths document the composition and constrain the source of carbon in scapolite from the lower crust. CO_2 is extracted from scapolite without fractionating carbon isotopes by reaction with phosphoric acid at 25 or 75°C. Thus, partial yields of CO_2 from scapolite are sufficient for accurate carbon isotopic analysis. Isotopic compositions of coexisting scapolite and calcite in high-grade calc-silicate gneisses and marbles, and consideration of the crystal chemical environment of CO_3 in the scapolite structure, indicate little fractionation of $^{13}C/^{12}C$ between scapolite and calcite (0.1 ± 1.2‰) at equilibrium conditions of 650–800°C.

The carbon isotope composition of CO_2 extracted from scapolite in twenty-nine samples of regional granulite facies gneisses, amphibolites, calc-silicate gneisses, and crustal xenoliths yield values of $\delta^{13}C$ that range from −10 to −1‰ (PDB). High-grade marbles and graphitic paragneisses are precluded as major sources of carbon for scapolite in the high grade rocks analyzed in this study, as the former are isotopically enriched, and the latter isotopically depleted in $^{13}C/^{12}C$ relative to the range of isotopic compositions determined here. The $\delta^{13}C$ values for mafic granulites and amphibolites in granulite terranes composed of supracrustal sequences (−10.1 to −4.0‰) may reflect the isotopic composition of diagenetic carbonate present in their basaltic protoliths. The values of $\delta^{13}C$ for scapolite in mafic xenoliths and some granulite facies orthogneisses (−8.2 to −1.2‰) are consistent with crystallization of the scapolite from a mafic melt or derivation of CO_2 from mafic melts emplaced in the lower crust or upper mantle. The values of $\delta^{13}C$ for scapolites from calc-silicate gneisses and calc-silicate xenoliths (−10.0 to −2.9‰) may result from depletion of $^{13}C/^{12}C$ as a result of decarbonation of calcite-bearing protoliths during prograde metamorphism.

INTRODUCTION

NUMEROUS PHASE EQUILIBRIA and geochemical techniques have been used to evaluate the role of a CO_2-rich fluid phase in the formation of granulite facies mineral assemblages. These techniques include calculation of water activities from biotite or amphibole dehydration equilibria (e.g., NEWTON, 1986; VALLEY et al., 1983; LAMB and VALLEY, 1988), limiting fluid composition based on estimates of f_{O_2} and graphite stability (e.g., LAMB and VALLEY, 1985), fluid inclusion analysis to evaluate the composition of the peak metamorphic fluid composition (e.g., TOURET, 1971; HANSEN et al., 1984; LAMB et al., 1991), gradients in oxygen isotope composition of marbles and orthogneisses to constrain scales of fluid-rock interaction (VALLEY and O'NEIL, 1984; CARTWRIGHT and VALLEY, 1991), and carbon isotope analysis of graphite and/or cordierite (VRY et al., 1988). Recent work on scapolite phase equilibria and carbon isotope analysis of scapolite has expanded the range of lithologies and crustal settings suitable for such studies (MOECHER and ESSENE, 1991; MOECHER et al., 1992).

The present study is a survey of the carbon isotopic composition of scapolite found in deep crustal mafic granulites, amphibolites, calc-silicates, and mafic xenoliths from a number of granulite terranes and xenolith localities. Scapolite (a solid solution of marialite, $Na_4Al_3Si_9O_{24}Cl$, meionite, $Ca_4Al_6Si_6O_{24}CO_3$, and sulfate meionite, $Ca_4Al_6Si_6O_{24}SO_4$)

in mafic granulites is invariably a CO_3-SO_4 solid solution (MOECHER and ESSENE, 1991). The pressures calculated from thermobarometric assemblages coexisting with scapolite and experimental evidence are consistent with these scapolite compositions having formed in the lower crust (9 to 15 kbar: MOECHER and ESSENE, 1991; GOLDSMITH and NEWTON, 1977). Therefore, carbon isotope analysis of scapolite provides a means of characterizing the isotopic composition of carbon in the lower crust.

MOECHER et al. (1992) illustrated the practicality of using the carbon isotopic composition of scapolite to ascertain fluid sources in high-grade metamorphic settings. This paper outlines the methods determined to be most accurate and efficient for extracting and analyzing CO_2. In addition the fractionation of $^{13}C/^{12}C$ between coexisting scapolite and calcite was measured in high-grade marbles and calc-silicates in order to estimate the fractionation between scapolite and CO_2. These methods were applied to high-grade scapolite-bearing assemblages from granulite terranes and mafic lower crustal xenoliths to assess the source of CO_2 that may have led to scapolite formation.

ANALYTICAL METHODS

Previous Work

HOEFS et al. (1981) carried out carbon and sulfur isotope analyses of scapolite in granulite facies gneisses of variable bulk composition
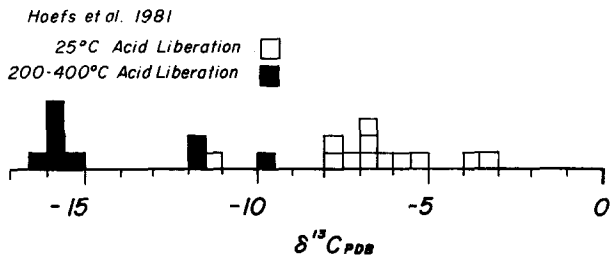
FIG. 1. Results of HOEFS et al. (1981) on measurement of $\delta^{13}C$ for CO_2 extracted from scapolite in granulite facies gneisses from the Furua Complex, Tanzania, by reaction with concentrated H_3PO_4 at 25°C and 200–400°C.

from the Furua Complex, Tanzania. They used H_3PO_4 to extract CO_2 from scapolite, obtaining two generations of CO_2 at different temperatures (Fig. 1). Evolution of CO_2 at low temperature (25°C) was interpreted to result from reaction of H_3PO_4 with carbonate inclusions that were presumed to be present in the granulites, but *not* from of reaction of H_3PO_4 with the carbonate group in scapolite. A second generation of CO_2 was obtained by reaction at higher T (200–400°C) in H_3PO_4, with the CO_2 produced by this reaction being precipitated as $BaCO_3$ in $Ba(OH)_2$ solution. The $BaCO_3$ was then reacted in H_3PO_4 at 25°C to obtain CO_2 for isotopic analysis. At high temperature the CO_2 was inferred to have been liberated from the scapolite structure. The high temperature fraction of CO_2 was isotopically distinct and generally depleted in $^{13}C/^{12}C$ relative to the low temperature fraction (Fig. 1). HOEFS et al. (1981) did not report reaction times or yields for their isotope analyses.

CO_2 Extraction Experiments: This Study

In order to further evaluate methods of extraction and obtain better control on the reaction of scapolite with H_3PO_4, a series of reaction experiments were performed on well-characterized scapolite mineral separates. These experiments were intended to evaluate the extent of reaction of the carbonate group in scapolite with H_3PO_4 at 25 and 75°C, and test whether structural CO_2 is extractable at temperatures below 200°C. In addition, the variation (if any) of $\delta^{13}C$ with differing amounts of reaction of scapolite was evaluated at two temperatures for varying periods of time, and with different pretreatments of the sample in order to remove extraneous carbon sources such as secondary calcite.

Two scapolite mineral separates of similar composition were characterized by optical, backscattered electron imaging, cathodoluminescence, and electron microprobe methods in order to determine the composition and homogeneity of the scapolite, and to identify the presence of carbonate minerals that would contaminate the sample. The theoretical yield of CO_2 for calcite is ten times that of the scapolites used here (approximately 10 vs. 1 μmol CO_2/mg mineral). Therefore, small amounts of calcite contamination could seriously affect experimental yields and $\delta^{13}C_{scap}$.

The BOLT scapolite is from an occurrence near Bolton, Massachusetts. Microprobe analysis yields the formula $Na_{1.22}Ca_{2.79}K_{0.02}$ $Si_{7.11}Al_{4.89}O_{24.02}[Cl_{0.12}(CO_3)_{0.88}]$. The scapolite was found to contain 50–100 μm-sized inclusions of calcite, 10–100 μm-wide veins of calcite associated with secondary sericitization along fractures, and 500 μm to 1 mm inclusions of zoisite that in turn include calcite, quartz, and plagioclase. The total amount of calcite and zoisite was estimated to be on the order of 1 modal%. The GAT scapolite, from Gatineau, Quebec, yields the formula $Na_{0.96}Ca_{2.89}K_{0.03}Si_{7.10}Al_{4.90}O_{23.95}[Cl_{0.02}$ $(CO_3)_{0.98}]$. This scapolite contained traces of 50 μm inclusions of calcite concentrated along brittle fractures that amount to much less than 0.5 modal%, 30 μm to mm-sized flakes of graphite, and various silicate inclusions (intergrowths of zoisite and K-feldspar; approximately 2 modal percent).

Mineral separates of both samples were prepared for analysis by crushing and sieving coarse grains to a size range of 75–150 μm. The samples were then immersed in dilute (0.5 m) HCl solution at room

temperature for 10 minutes in order to dissolve any calcite contamination. Splits of BOLT were also analyzed without the dilute acid treatment in order to evaluate the effect of this pretreatment method on $\delta^{13}C$ of scapolite. No significant reaction of scapolite in the dilute HCl solution was detected for this short reaction time or grain size, as determined by weighing a calcite-free sample before and after reaction. However, leaching of very finely ground scapolite by dilute HCl may be facilitated by the increased surface area of the powder. The samples were leached in dilute HCl before any further grinding, in order to reduce the possibility of leaching CO_2 from the scapolite structure. After HCl treatment, samples were ground to a fine powder in order to increase surface area and facilitate reaction of scapolite with H_3PO_4. The finely ground scapolite powder was then reacted at 25°C and 75°C with H_3PO_4 in evacuated sidearm flasks. Samples were reacted with the acid for varying lengths of time. Experimental yields of CO_2 were measured manometrically for all runs. Isotopic analysis of CO_2 was performed on a Finnigan MAT 251 mass spectrometer. Values of $\delta^{13}C$ are reported in standard permil notation relative to PDB. Analytical precision for sample and standard CO_2 is typically less than 0.1‰ for carbon.

Results of the extraction experiments are summarized in Fig. 2 and Table 1. Reaction of scapolite in 25°C H_3PO_4 is sluggish compared to that at 75°C. In H_3PO_4 at 25°C, 60 hours reaction time was required to obtain approximately 10% of expected CO_2, whereas experimental yields greater than 80% of expected CO_2 were obtained at 75°C. At 75°C experimental yields are higher for longer reaction times (as much as 87% after 115 hrs).

Values of $\delta^{13}C$ for the acid extractions are constant as a function of experimental yield, indicating that the reaction of scapolite in H_3PO_4 does not fractionate the carbon isotopes (Fig. 2). SHARMA and CLAYTON (1965) reached a similar conclusion concerning $\delta^{13}C$ for various carbonates that are slow to react in H_3PO_4 at 25°C. Furthermore, values of $\delta^{13}C$ obtained for scapolite reacted in 25°C acid are virtually identical to those for samples reacted in 75°C acid. If $\delta^{13}C$ at 75°C is an accurate representation of the carbon isotopic composition of scapolite, then CO_2 is extractable from scapolite at 25°C, although yields are low.

Calcite-bearing, scapolite-free rock samples prepared as blanks (samples ground to 100 μm, reacted in 0.5 m HCl at 23°C for 10 min, and reground to 10–25 μm before reaction) yielded either no measurable amounts of CO_2 when reacted in H_3PO_4 at 25 or 75°C, or only small quantities of gas ($\leq$1 μmole CO_2 for three grams of powdered whole rock sample; the yield of CO_2 for 1% calcite is 300 μmole). The samples provide a test of the efficacy of the HCl leaching process, as the blanks initially contained 1 modal% secondary calcite before leaching.

Thus, an alternative interpretation of the data of HOEFS et al. (1981) regarding the extraction of CO_2 from scapolite can be made. The low temperature generation of CO_2 that HOEFS et al. (1981)
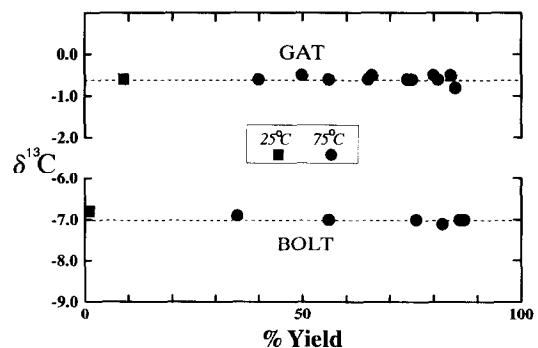
FIG. 2. Values of $\delta^{13}C$ for scapolite mineral separates from Bolton, Massachusetts (BOLT), and Gatineau, Quebec (GAT), as a function of experimental yield of CO_2 liberated by reaction in concentrated H_3PO_4 (specific gravity = 1.92). $\delta^{13}C$ remains constant for both samples at 25 and 75°C, and is independent of yield, indicating that carbon isotopes are not fractionated during the reaction of scapolite in H_3PO_4.

TABLE 1. Experimental data for **BOLT** scapolite mineral separate; scapolite leached in 0.5 m HCl and reacted at specified T in H_3PO_4

T°C	Yield %	Time hrs	$\delta^{13}C$
25	1	12	-6.8
75	35	4	-6.9
75	56	12	-7.0
75	76	34	-7.0
75	82	59	-7.1
75	86	83	-7.0
75	87	115	-7.0
Ave. at 75°C			-7.0(0.1)

Scapolite treated same as above but without leaching in 0.5 m HCl.

75	41	13	-7.3
75	65	34	-7.4
75	76	59	-7.4
75	84	83	-7.3
75	82	116	-7.3
Ave.			-7.3(0.1)

Yield is % of theoretical maximum. Numbers in parentheses are 2σ

Experimental data for **GAT** scapolite mineral separate; scapolite leached in 0.5 m HCl and reacted at specified T in H_3PO_4.

T°C	Yield	Time hrs	$\delta^{13}C$
25	9	60	-0.6
75	50	11	-0.5
75	66	18	-0.5
75	40	22	-0.6
75	56	36	-0.6
75	74	41	-0.6
75	84	58	-0.5
75	65	60	-0.6
75	75	82	-0.6
75	81	82	-0.6
75	80	154	-0.5
75	85	203	-0.8
Ave. at 75°C			-0.6(0.1)

Number in parentheses is 2σ

inferred was derived from carbonate inclusions in the Furua granulites could alternatively be obtained from partial reaction of scapolite at 25°C. It could also be a mixture of gas derived from carbonate inclusions (or other extraneous carbonate not in isotopic equilibrium

with scapolite) with a $\delta^{13}C$ near 0‰ and the much lighter carbon derived from the scapolite structure. The scatter in the data would reflect a range in abundance of such inclusions. In contrast, the distinct difference in $\delta^{13}C$ between the low and high temperature generations of CO_2 indicate that the high temperature generation may reflect the true $\delta^{13}C$ of scapolite in the Furua granulites.

Acid extraction of CO_3/SO_4 scapolites yields SO_2 in addition to CO_2. Gases collected from reaction of SO_4-bearing scapolites in H_3PO_4 at 75°C were scrubbed of SO_2 by distillation in an n-pentane slush. Mass spectrometer scans indicated that SO_2 is removed in this manner, yielding clean CO_2 for accurate analysis. Similar treatment (as a blank) of a calcite lab standard whose carbon isotopic composition is well constrained indicated no fractionation of ^{13}C by the CO_2/SO_2 distillation. Isotopic analysis of chlorine-rich scapolite using H_3PO_4 extraction requires an additional step to remove HCl but is not discussed here (MOECHER, 1988).

Summary of Extraction Techniques

The preferred method of CO_2 extraction for this study is reaction in H_3PO_4 at 75°C as it provides consistent and precise values of $\delta^{13}C$ along with relatively large yields of CO_2 for a reasonable reaction time. In order to extract CO_2 from scapolite in high-grade gneisses, whole rock powders of two different size fractions (106–150 μm and 150–300 μm, with mafic phases removed magnetically) were first treated with dilute HCl at 23°C to remove extraneous carbonate. These coarse powders were then ground in air to a finer grain size and reacted at 75°C in concentrated H_3PO_4 (specific gravity = 1.92) for 48–120 hours. Depending on the modal abundance of scapolite, up to 5 grams of sample were run in this manner. All samples were examined optically to ascertain approximate modal abundances of scapolite and the presence of secondary calcite. High-grade gneisses may contain significant secondary calcite along grain boundaries and fractures. This carbonate may not be visible under the polarizing microscope but is evident under cathodoluminescence, as the calcite luminesces bright orange (MORRISON and VALLEY, 1988). Inspection of the samples analyzed for this study indicated scattered occurrences of what are interpreted to be secondary calcite. Some samples contained no visible calcite, whereas others contained pervasive grain boundary calcite. Garnet, clinopyroxene, and hornblende typically contain the most calcite, which is concentrated along fractures, in contrast to plagioclase and quartz which contain few fractures with calcite. The effect of secondary calcite was minimized by magnetic separation of mafic phases from all samples before leaching with dilute HCl.

Fractionation of $^{13}C/^{13}C$ between Scapolite and Calcite

The equilibrium fractionation of $^{13}C/^{12}C$ between scapolite and calcite ($\Delta^{13}C_{Sc-Cc}$) at temperatures between 650 and 800°C was determined by analyzing the isotopic composition of coexisting scapolite-calcite pairs from high-grade marbles, calc-silicates, and skarns collected in the southwestern Grenville Province, Ontario, (MOECHER, 1988). Knowledge of $\Delta^{13}C_{Sc-Cc}$ allows calculation of the fractionation of $^{13}C/^{12}C$ between scapolite and CO_2 ($\Delta^{13}C_{Sc-CO_2}$), which can be used to constrain the isotopic composition of the fluid phase coexisting with scapolite.

Based on crystal chemical parameters and fractionations among simple carbonates, one can estimate the expected fractionation between scapolite and calcite. Table 2 lists coordination numbers (CN), densities, and average M-O bond distances between oxygen atoms in the carbonate group (O) and the cations (M) to which oxygen is coordinated for calcite and aragonite (M = Ca), dolomite (M = Ca and Mg), and a scapolite with the composition Me$_{84}$ (M = 84% Ca, 16% Na; AITKEN et al., 1984). The average M-O bond distance for dolomite is less than that for calcite, and the $\Delta^{13}C_{Do-Cc}$ is 2.1‰ at 25°C but less than 0.5‰ at $T > 600$°C (SHEPPARD and SCHWARCZ, 1970). The average M-O bond distance in aragonite is greater than calcite, but the coordination number and density are higher. The fractionation between aragonite and calcite is less than that of dolomite-calcite at 25°C. Estimates of the former range from 0.8‰ (SOMMER and RYE, 1978) to 1.8‰ (RUBINSON and CLAYTON, 1969). The crystal chemical environment of CO_3 in scapolite is more similar

TABLE 2. Crystal chemical parameters and $^{13}C/^{12}C$ fractionations between calcite and aragonite, dolomite, and scapolite.

	Mean M-O A	CN	ref	$\Delta^{13}C_{Min-Cc}$ 25°C	$\Delta^{13}C_{Min-Cc}$ 700°C	ref	Density g/cm3	ref
Calcite	2.36	6	1	0	0	-	2.712	7
Aragonite	2.53	9	2	0.8-1.8	na	4	2.930	7
Dolomite	Ca Mg 2.38 2.08	6	1	2.1	0.4	5	2.866	7
Scapolite+	2.47	8	3	-	0.1	6	2.740	3

CN: coordination number; na: not available; 1: MARKGRAF and REEDER (1985); 2: DE VILLIERS (1971); 3: AITKEN et al. (1984); 4: SOMMER and RYE (1978); RUBINSON and CLAYTON (1969); 5: SHEPPARD and SCHWARCZ (1970); 6: this study; 7: ROBIE et al. (1966); mean M-O is mean cation-oxygen bond distance; *: $\Delta^{13}C_{Min-Cc}$ between mineral and calcite at quoted T; +: Ca/(Ca+Na+K) = 0.84

to aragonite than calcite, and one might predict that the fractionation of $^{13}C/^{12}C$ between scapolite and calcite would be similar to that for aragonite-calcite.

The average measured $\Delta^{13}C_{Sc-Cc}$ for eleven scapolite-calcite pairs (Table 3) is $0.1 \pm 1.2‰$ (2σ). For practical purposes this value is essentially 0, and within the analytical precision of many of the analyses performed on scapolite gneisses. Based on the above fractionation and $\Delta^{13}C_{Cc-CO_2} = -3.3‰$ (CHACKO et al., 1991), $\Delta^{13}C_{Sc-CO_2}$ is approximately $-3.3‰$ in the temperature range 700-900°C. Although the equilibrium fractionation of $^{13}C/^{12}C$ between calcite and scapolite is essentially zero, the secondary carbonate common in many rocks may be isotopically distinct from primary scapolite. The experimental data on unleached samples of BOLT are consistent with this interpretation, as they yield slightly lighter values than leached samples (Table 1).

ISOTOPIC ANALYSIS OF SCAPOLITE GNEISSES

Samples of scapolite-bearing gneisses were collected for the present study from the Central Gneiss Belt of the southwestern Grenville Province, Ontario. In addition, samples of scapolite-bearing gneisses and granulites were obtained from a number of other granulite terranes, and from a number of volcanic provinces where scapolite-bearing mafic xenoliths occur. All scapolites were analyzed by electron microprobe, in particular to determine the anion site composition. Experimental yields of CO_2 were recorded for all phosphoric acid extractions. Data are listed in Table 4 and illustrated in Fig. 3.

Grenville Province, Ontario

Carbonate scapolite and carbonate-sulfate scapolite solid solutions occur in calc-silicate gneisses, amphibolites, and mafic granulites at a number of localities in the southwestern Grenville Province (MOECHER, 1988; MOECHER and ESSENE, 1991). Geobarometric studies indicate that a large part of the Central Gneiss Belt of Ontario experienced metamorphic pressures of at least 10 kbar (MOECHER et al., 1988; ANOVITZ and ESSENE, 1990) over an area of ca. 15,000 km² making it an extensive tract of exposed deep crust. The samples for this study are widely separated and from distinct lithotectonic domains that did not reach peak metamorphic conditions contemporaneously (MEZGER et al., 1993). Sample localities are compiled in MOECHER (1988). Mafic granulites (garnet-clinopyroxene-orthopyroxene-hornblende-plagioclase-scapolite) and amphibolites (hornblende-plagioclase-garnet-scapolite ± clinopyroxene) yield $\delta^{13}C$ of -10.1 to $-4.0‰$ (Fig. 3a). Calc-silicate gneisses with garnet-clinopyroxene-plagioclase-scapolite-sphene ± wollastonite yield $\delta^{13}C$ of -10.0 to $-8.4‰$ (Fig. 3b).

Bergen Arcs, Norway

Scapolite is reported in meta-anorthosite and meta-gabbro from the Holsnoy area in the Western Gneiss Region of Norway (AUSTRHEIM and GRIFFIN, 1985). Meta-anorthosite and meta-gabbro (plagioclase-clinopyroxene-orthopyroxene-garnet-scapolite) occur as 100 m- to 1000 m-thick layers in what was originally a layered mafic intrusion. The samples analyzed for this study contain granulite facies mineral assemblages equilibrated at 12-14 kbar at 800-900°C (AUSTRHEIM and GRIFFIN, 1985; MOECHER and ESSENE, 1991), although the terrane was subsequently subjected to eclogite facies conditions. Four samples of the meta-anorthosite yield $\delta^{13}C = -6.8$ to $-2.7‰$ (Fig. 3c).

Sargur Belt, Southern India

Scapolite-bearing, mafic granulite facies gneisses (assemblages same as Grenville samples) are reported from the Sargur Belt, near Mysore, southern Karnataka State, India (DEVARAJU and COOLEN, 1983; SRIKANTAPPA et al., 1985). The Sargur Belt consists of linear, km-scale enclaves of pelitic schists, and calc-silicate, mafic, and ultramafic gneisses within the Peninsular Gneiss of southern India (VISWANATHA and RAMAKRISHNAN, 1981). Scapolite-bearing calc-silicate assemblages (garnet-clinopyroxene-plagioclase-scapolite-sphene) have been reported from the Satnur area of southeastern Karnataka (DEVARAJU and SADASHIVAIAH, 1964). Paleopressures in this area approached 9 kbar at 800°C (SRIKANTAPPA et al., 1985; DEVARAJU and COOLEN, 1983; MOECHER and ESSENE, 1991). Three mafic granulites from the Mysore area yield $\delta^{13}C$ of -5.0 to $-4.4‰$ (Fig. 3a). Three samples of calc-silicate gneiss from the Satnur area yield $\delta^{13}C$ of -4.9 to $-2.9‰$ (Fig. 3b).

Furua Complex, Tanzania

HOEFS et al. (1981) examined the carbon and sulfur isotope composition of scapolite in granulites from the Furua Complex, Tanzania. The results of that study are reviewed here because they are relevant to the discussion of carbon reservoirs in the deep crust. Carbonate-sulfate scapolite solid solutions are reported in granitic, intermediate, and mafic garnet granulites, amphibolites, and calc-silicate gneisses of the Furua Complex (COOLEN, 1980). In contrast to the more widely

TABLE 3. Data relevant to calculation of $^{13}C/^{12}C$ fractionation between scapolite and calcite in calc-silicate gneisses and marbles

SAMPLE	Lith	X^{Sc}_{Ca} Sc	X_{CO_3} Sc	$\delta^{13}C$ Sc	$\delta^{13}C$ Cc	$\Delta^{13}C_{Sc-Cc}$
A85A-3c	CS	0.79	0.98	-8.7	-8.2	-0.5
A86B3-5	CS	na	na	-9.5	-9.9	0.4
H40d	CS	0.76	0.94	-3.7	-3.1	-0.6
O8e	CS	0.74	0.91	-2.6	-2.2	-0.4
PSO85A-5	MA	0.73	0.90	-0.2	-1.3	1.1
PS85A-7	M	0.78	0.96	0.7	-0.7	1.4
S86E-8c	M	0.69	0.90	0.9	-0.6	1.5
S86E-27B	M	0.76	0.93	0.1	-0.1	0.2
UK-1	M	0.78	0.98	-1.1	-1.4	0.3
X27	M	0.76	0.95	-1.5	-1.4	-0.1
82DMT114a	CS	0.79	0.98	-7.9	-8.1	0.2
Ave. (2σ)						0.1 (1.2)

M: marble; CS: calc-silicate; MA: meta-anorthosite
$X^{Sc}_{Ca} = Ca/(Ca+Na+K)$; $X_{CO_3} = CO_3/(CO_3+SO_4+Cl)$.

Table 4. Carbon isotopic and chemical composition of scapolite from granulite facies gneisses, amphibolites, calc-silicates, and xenoliths.

Sample	$\delta^{13}C$	Yield*	EqAn	X_{CO_3}	X_{SO_4}	%Scap	Sample	$\delta^{13}C$	Yield*	EqAn	X_{CO_3}	X_{SO_4}	%Scap
EXPOSED GRANULITE TERRANES							**XENOLITHS**						
Ontario, Canada							**Queensland, Australia**						
Mafic granulites and amphibolites							Garnet-clinopyroxene granulite						
A86E3-3a	-8.6	64	60	0.38	0.60	5	82-80	-2.5	39	54	0.59	0.41	10
A86E3-3c	-7.0	175	na			20	82-90	-2.1	77	67	0.51	0.48	15
S86E-53	-10.1	107	60	0.51	0.49	15	New S. Wales, Australia						
80DMA348d	-8.8	26	61	0.39	0.60	1	Garnet-clinopyroxene granulite						
80DMA351f	-9.3	17	na			1	R32041	-3.6	33	51	0.52	0.48	5
80DMA614p	-4.1	58	64	0.45	0.53	10	Lashaine, Tanzania						
85DMP174	-5.4	14	56	0.52	0.46	1	Garnetiferous meta-anorthosite						
85DMP272	-4.0	100	62	0.45	0.54	15	533	-4.5	279	56	0.89	0.11	15
Calc-silicate gneiss							Garnetiferous meta-gabbro						
A85A-3d	-10.0	142	74	0.98	0.00	20	BD98	-5.7	36	57	0.98	0.01	5
H85A-1d	-9.0	54	71	0.98	0.01	10	Montana, USA						
82DMT114d	-8.4	190	na			20	Clinopyroxene-scapolite-hornblende metagabbro						
Bergen, Norway							KC-1	-1.2	179	71	0.70	0.29	40
Mafic granulite facies meta-anorthosite							Chain des Puys, France						
HA54/83	-6.8	30	63	0.37	0.60	1	Scapolite megacryst						
HA46/85	-4.7	33	53	0.38	0.49	1	CDP-1	-8.2	74	56	0.62	0.33	100
HA10/83	-2.7	18	63	0.55	0.38	1	Chihuahua, Mexico						
HA53/80	-5.4	279	56	0.31	0.66	20	Calc-silicate gneiss						
Sargur, India							MN49	-5.0	48	60	0.27	0.69	15
Granulites							MN100	-3.9	131	66	0.62	0.38	30
TCD33	-5.0	46	58	0.43	0.57	5							
TCD39	-4.4	62	61	0.41	0.58	5							
Calc-silicates													
TCD4	-4.9	380	76	0.99	0.01	20							
TCD5	-4.4	380	74	0.99	0.00	20							
TCD25	-2.9	172	76	0.98	0.00	10							

*: yields in μmoles CO_2. EqAn = (Al-3)/3 based on Si+Al = 12 in scapolite formula. Anion site composition in terms of X_{CO_3} and X_{SO_4} where $CO_3+SO_4+Cl = 1$

spaced scapolite granulites from the Grenville Province, samples from the Furua complex are from an area on the order of 75 km². Paleopressures for the peak metamorphism in this terrane were 10 kbar at 800°C (COOLEN, 1980; MOECHER et al., 1988; MOECHER and ESSENE, 1991). If the high temperature data of HOEFS et al. (1981) (−15.8 to −9.7 for seven samples of mafic granulite, −15.6 and −15.1 for two samples of calc-silicate granulite) are accepted as the most accurate values of $\delta^{13}C$ in the Furua scapolite (Fig. 1), then the values are markedly more depleted in ^{13}C than those for granulites from the Grenville Province and Sargur Belt.
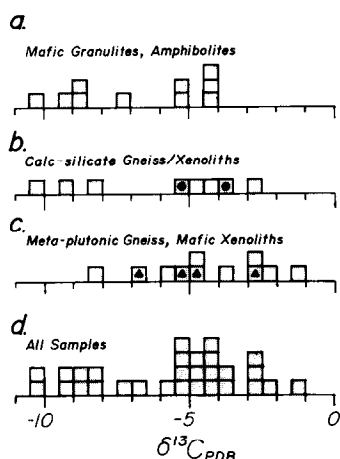

FIG. 3. Summary of carbon isotopic compositions of scapolite from this study. Triangles denote meta-anorthosite and meta-gabbro from Norway, to distinguish them from xenoliths. Circles denote calc-silicate xenoliths from Mexico, to distinguish them from Grenville or Indian calc-silicates.

Sulfur isotope analysis of the same samples yields a limited range in $\delta^{34}S$ of 0.3 to 3.6‰ relative to Canyon Diablo Troilite. This range reflects an ultimate mantle or magmatic derivation. Pyrrhotite and pyrite are ubiquitous in the Furua granulites (COOLEN, 1980). The sulfate in scapolite is most likely derived from oxidation of sulfides during metamorphism of a sulfide-bearing igneous protolith. The sulfur isotopes may reflect a different source for anion site constituents than the carbon, and different processes for its isotopic evolution.

Scapolite-Bearing Mafic Xenoliths

Australia

Scapolite has been found in mafic xenoliths from a number of volcanic provinces in eastern Australia (LOVERING and WHITE 1964, 1969; RUDNICK and TAYLOR, 1987). STOLZ (1987) described sulfate-rich scapolite in four of twenty mafic granulite xenoliths examined from Cone 32, McBride Province, Queensland. Two xenoliths with clinopyroxene-garnet-scapolite-spinel ± plagioclase assemblages yield $\delta^{13}C = -2.1$ and −2.5‰ (Fig. 3c). WILKINSON (1974) reported scapolite in a mafic garnet-clinopyroxene-plagioclase-scapolite-rutile granulite xenolith from New South Wales. This sample yields $\delta^{13}C$ of −3.6‰ (Fig. 3c).

Chain de Puys, Massif Central, France

BOIVIN and CAMUS (1981) reported xenocrysts of sulfate-carbonate scapolite in basanites from the Chain de Puys volcanic province, Massif Central, France. The scapolite is associated with a megacryst assemblage of plagioclase, ilmenite, apatite, hornblende, and clinopyroxene. The minerals are

interpreted to be igneous phenocrysts. A 1 cm scapolite xenocryst yields $\delta^{13}C$ of $-8.2\%_0$ (Fig. 3c).

Lashaine, Tanzania

Scapolite occurs in xenoliths of varying bulk composition in alkalic basalts and carbonatites from the Lashaine volcano, Tanzania (JONES et al., 1983). Two samples analyzed here, a garnet meta-anorthosite (533) and a garnet-orthopyroxene granulite (BD98) yield $\delta^{13}C$ of -4.5 and $-5.7\%_0$, respectively (Fig. 3c).

Mexico

Sulfate scapolite occurs in clinopyroxene-scapolite-sphene $\pm$ plagioclase xenoliths from Chihuahua, Mexico (NIMZ et al., 1986). Except for the absence of garnet, these samples are similar to the Grenville calc-silicate gneisses and skarns. The major difference between scapolite in the calc-silicate xenoliths and that in calc-silicate gneisses from the Grenville or S. India is that the scapolite is sulfate-rich in the former, and sulfate-poor in the latter (Table 4). The composition of scapolite at this occurrence is consistent with derivation of the xenoliths from the deep crust. Two xenoliths yield $\delta^{13}C$ of -3.9 and $-5.0\%_0$ (Fig. 3b).

Bearpaw Mts., Montana

A clinopyroxene-scapolite-hornblende xenolith of uncertain protolith occurs in the alkalic magmas of the Bearpaw Mts., Montana (K. D. Collerson, pers. commun., 1989). This sample yields the highest value of $\delta^{13}C$ of this study ($-1.2\%_0$) (Fig. 3c).

DISCUSSION

Overall, carbon in high-grade scapolite-bearing gneisses and xenoliths is depleted in ^{13}C relative to PDB. Before attempting to interpret the observed isotopic compositions, it is important to consider the nature of the protoliths of these samples, which represent a wide range of rocks with highly variable geological histories. Amphibolites and granulites from the Grenville Province, Furua, and S. India have mafic bulk compositions and are interlayered with marble, pelitic gneiss, and metavolcanics having supracrustal protoliths. Potential protoliths for the scapolite-bearing granulite and amphibolites are mafic lava flows or plutonic rocks that intrude a supracrustal sequence. Calc-silicate gneisses likely represent carbonate- and/or graphite-bearing siliceous protoliths. The above samples must have had an extensive upper crustal history, possibly involving weathering and interaction with meteoric water or seawater. In contrast, the metaplutonic rocks from Norway were emplaced into an orthogneiss terrane at relatively high pressure and may have been isolated from supracrustal sources of carbon.

Some xenoliths may represent supracrustal material derived by plucking from conduit walls during ascent of the host magma. For example, scapolite-bearing calc-silicate xenoliths like those described above occur with high-grade paragneiss and mafic xenoliths throughout northern Mexico (NIMZ et al., 1986). In contrast, mafic xenoliths have been

shown to represent mafic cumulates or the recrystallized equivalents of magmas emplaced deep in the crust or in the uppermost mantle (WILKINSON, 1974; RUDNICK and TAYLOR, 1987; STOLZ, 1987). They are less likely to have had a prior upper crustal history than rocks in exposed granulite terranes.

Thus, the lowermost crust may be viewed as consisting of high pressure granulites of supracrustal origin underlain by high pressure mafic granulites of mantle origin. Carbonate-bearing lithologies such as marbles are noticeably absent from compilations of xenolith lithologies (e.g., RUDNICK and TAYLOR, 1987; GRIFFIN and O'REILLY, 1987). Therefore, aside from graphite in paragneiss which occurs locally (e.g., PADOVANI and CARTER, 1977; HAYOB et al., 1989), scapolite is locally the dominant carbon reservoir in the lower crust *as represented by rock-forming minerals in xenoliths*. Based on modal abundance of scapolite, scapolite composition, and relative number of scapolite-bearing samples in a xenolith suite, the carbon content of the lower crust (as contained in scapolite) is on the order of 10–100 ppm.

The isotopic data may be interpreted in terms of the relative influences of source isotopic signatures vs. those resulting from processes such as decarbonation. Supracrustal rocks are potentially open to introduction of carbon from a number of sources (marble, graphitic paragneisses, calcite precipitation during diagenesis), each with a distinctive isotopic composition. Furthermore, during prograde metamorphism carbon isotopic compositions may become mixed or be strongly depleted, especially in protoliths with low modal amounts of carbonate (e.g., VALLEY, 1986). In contrast, if mafic xenoliths are recrystallized subcrustal mafic magmas they are more likely to reflect mantle source compositions with a clustering of values at $\delta^{13}C = -8$ to $-4\%_0$, and they are less likely to be modified by the processes affecting supracrustal granulites.

Several scenarios may account for the formation of scapolite in the mafic rocks examined here. These scenarios assume that carbon was not present in the protolith but was introduced during metamorphism. The first scenario would involve introduction of CO_2 into a mafic gneiss and formation of scapolite, without fractionation of carbon during the process of scapolite formation (all CO_2 consumed in scapolite formation). The isotopic composition of carbon in scapolite should reflect the isotopic composition of the infiltrating fluid (e.g., MOECHER et al., 1992). One possible reservoir for carbon that might serve as a source of CO_2-rich fluid is marble. A compilation for this study of published isotopic data for marbles from greenschist to granulite facies settings yields an average $\delta^{13}C$ of $0.4 \pm 3.9\%_0$ (2σ). Because the $\Delta^{13}C_{Sc-Cc}$ is essentially zero, scapolites should exhibit the range of values that marbles exhibit if (1) on average, carbon in scapolite-bearing silicates were derived from marble by devolatilization, or (2) if scapolite had exchanged with calcite in marble. The data presented here indicate that, for the most part, neither is the case and decarbonation of marble and interaction of CO_2 with mafic silicate lithologies is not a general mechanism for forming scapolite in the deep crust.

The above process was documented by MOECHER et al. (1992); CO_2 that had equilibrated with marble infiltrated the margins of a meta-anorthosite pluton in the Grenville Province. Values $\delta^{13}C$ of scapolite in the meta-anorthosite increase

from less than $-3‰$ in the core of the body to $-0.5‰$ at the margin where the meta-anorthosite is in contact with marble. The latter value is essentially the same as the average value for marble at the meta-anorthosite contact ($-0.4 \pm 0.6‰$ 2σ). This example illustrates the expected isotopic effects of infiltration of a mafic rock by CO_2-bearing fluid.

A second carbon reservoir in the crust is graphite in metamorphosed sediments. Graphite in metamorphic rocks is strongly depleted in $^{13}C/^{12}C$ in the absence of calcite, with values typically less than $-20‰$ (DEINES, 1980; STRAUSS, 1986). Based on the empirically derived fractionation of ^{13}C between calcite and graphite (DUNN and VALLEY, 1992) and the experimentally determined fractionation between CO_2 and calcite (CHACKO et al., 1991), the value of $\Delta^{13}C_{CO_2\text{-graphite}}$ at $700-900°C$ is $7.1 - 6.0‰$ so that CO_2 equilibrated with graphite would have a maximum value of $-12.9‰$. None of the samples analyzed for the present study overlap this lower limit for graphite equilibrated with CO_2. However, the high temperature generation of CO_2 extracted from scapolite in Furua Complex granulites overlaps this range (Fig. 1).

A third possible source of carbon is CO_2 from the mantle and melts derived by partial melting of the mantle. The solubility of CO_2 in basalt liquids is pressure dependent, on the order of 0.1 to 1.0 wt% at 15 kbar (MYSEN et al., 1975; SPERA and BERGMAN, 1980). This is sufficient CO_2 to form the small modal abundances of sulfate-carbonate scapolite in many mafic granulites and xenoliths (see Table 4 for composition and estimates of modal abundance of scapolite in each sample). As melts rise through the upper mantle and stabilize at the base of the crust, the CO_2 may exsolve and infiltrate overlying rocks, forming scapolite, or igneous scapolite may crystallize from the melt. If, in the former case, exsolved CO_2 completely reacts to form scapolite in infiltrated rocks, scapolite should record the carbon isotopic composition of the exsolved CO_2.

The isotopic composition of carbon dissolved in mid-ocean ridge and oceanic island basalt glasses varies widely (-19 to $-6‰$; TAYLOR, 1986). The lower values probably reflect varying degrees of degassing of magmas (TAYLOR, 1986), whereas the higher values likely represent the average carbon isotopic composition of the mantle. The fractionation $\Delta^{13}C_{CO_2\text{-melt}}$ determined empirically and experimentally, is in the range 2 to 3‰ (see compilation in TAYLOR, 1986; also, MATTEY et al., 1989, 1990). Thus, CO_2 exsolved from mantle-derived mafic melts should vary from -17 to $-3‰$. In fact, the carbon isotopic composition of CO_2 in volcanic gases and fluid inclusions in volcanic glass exhibits a much more limited range (-8 to $-1‰$; TAYLOR, 1986). The carbon isotopic composition of the dissolved carbon fraction would thus range from approximately -11 to $-3‰$.

Assuming all CO_2 dissolved in the magma is incorporated into scapolite, scapolite crystallizing from mafic magmas should have values ranging from -11 to $-3‰$. Alternatively, if CO_2 exsolved from a mafic magma, infiltrated surrounding rocks, and then quantitatively reacted to form scapolite, scapolite should have values ranging from -8 to $-1‰$. All carbon isotopic values for scapolite in xenoliths and the scapolite xenocryst from the present study overlap this range of values expected for the above mantle processes. Thus, these

samples may have incorporated mantle-derived CO_2 or have crystallized directly from a CO_2-bearing mantle derived melt. The xenoliths analyzed for this study equilibrated at pressures approaching the crust-mantle boundary, where shifts in $\delta^{13}C$ due to degassing effects would have been smaller relative to MORB. Although the samples from Queensland are relatively enriched in $^{13}C/^{12}C$, they overlap the upper range of values typical of mantle carbon.

In contrast to scenarios that involve derivation of carbon from external sources during metamorphism, several mechanisms may account for the presence of carbon in a primary or secondary carbonate phase in granulite protoliths. Subgreenschist to amphibolite facies metabasites commonly contain calcite, the carbonate being introduced during hydrothermal alteration or subaerial exposure. Calcite in mafic volcanics and volcaniclastic sediments from the Abitibi and Wawa Archean greenstone belts in Canada exhibit $\delta^{13}C$ of -9.5 to $-0.1‰$ (KERRICH, 1990). Calcite in prehnite/pumpellyrite facies metabasalts from the Proterozoic Keweenawan volcanic system, northern Michigan, exhibit an average $\delta^{13}C$ of $-3.6 \pm 3.2‰$ (2σ) (LIVNAT, 1983). If basalts that have experienced an early carbonate forming event undergo a subsequent high-grade metamorphism, carbonate may react with plagioclase to form scapolite. The latter would record the isotopic composition of the carbonate phase stable at lower grade, possibly modified to varying degrees by prograde decarbonation reactions. The carbon isotopic composition of scapolite in the mafic granuiltes and amphibolites from supracrustal granulite terranes (Fig. 3a) overlap the range of carbon isotope values for carbonate in altered basalts.

Calc-silicate gneisses would contain calcite at low to intermediate metamorphic grades, the carbon isotopic composition of which depends on that of the original calcite and degree of decarbonation during prograde metamorphism. In calc-silicates at granulite facies, where decarbonation reactions have proceeded to high degrees, carbon may be strongly depleted in ^{13}C relative to pure marbles (VALLEY, 1986). During prograde metamorphism, calcite would be consumed in silicate-forming reactions with CO_2 evolved in a fluid phase. Because of the positive fractionation of ^{13}C between CO_2 and calcite, the remaining calcite would exhibit progressively lower $\delta^{13}C$ with continued decarbonation. If plagioclase is present at higher grades, calcite may cease decarbonation and react instead with plagioclase to form scapolite. Scapolite would then record the isotopic composition of carbon remaining in the rock. This value would tend to be less than ca. 0‰, as shown by scapolite in the calc-silicates of this study (Table 4).

SUMMARY

Carbon isotope analysis of CO_2 extracted from scapolite may be used to exclude reservoirs such as marble and graphitic meta-sediments as principal sources of C in the lower crustal silicate lithologies. In addition, the range of $\delta^{13}C$ values in mafic xenoliths and orthogneisses overlaps the range of values characteristic of the mantle. This consistency, and the fact that we can rule out other potential sources of carbon, supports the conclusion that the carbon in scapolite from high-grade, lower crustal silicate lithologies is dominantly derived

from mafic magmas. This conclusion is only strictly applicable to the lower crust sampled by xenoliths, *i.e.*, that below most exposed granulite terranes, and granulite facies orthogneisses that have not had an upper crustal history. In contrast, granulites from supracrustal sequences are more likely to have had carbon introduced as diagenctic carbonate before high grade metamorphism. In the case of xenoliths and deep crustal orthogneisses, the amounts of CO_2 involved are small. Based on scapolite abundance and composition in a variety of mafic scapolite-bearing granulites, MOECHER (1993) calculated minimum volumetric CO_2-rock ratios ≤ 0.01 for CO_2-bearing magmas that crystallize scapolite or rocks infiltrated by a CO_2-rich fluid.

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