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Protolith carbon isotope ratios in cordierite from metamorphic and igneous rocks

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ABSTRACT

Cordierite commonly contains H_2O and CO_2 in the channels formed by its ring structure. In many studies cordierite has been shown to have volatile contents and carbon isotope ratios consistent with high-temperature equilibrium, suggesting preservation of protolith carbon isotope ratios and motivating this survey of carbon isotopes in cordierite CO_2. Cordierite CO_2 from pelitic country rocks in the Etive aureole have $\delta^{13}C$ values of $-20.70 \pm 1.27‰$ (n = 10) that are unaffected by a ca. 150 °C thermal gradient and fluid-saturated and undersaturated regimes. These $\delta^{13}C$ values are consistent with expected carbon isotope ratios of organic carbon in protolith sediments. Similar lithologies from the Cooma and Huntly aureoles show more variable behavior in a more limited data set, with some rocks preserving organic carbon $\delta^{13}C$ values and others that may have been affected by externally derived fluids. In cordierite-gedrite gneisses, carbon isotopes of cordierite (Crd) are distinct from those of cordierite in pelites; when excluding one outlier new data plus those from the literature average $\delta^{13}C(Crd) = -12.51 \pm 2.45‰$ (n = 17). These isotope ratios are higher than those of cordierite in typical metasedimentary protoliths and are similar to published carbon isotope ratios of trace carbonate in altered submarine volcanic rocks, which are likely analogs for protoliths of many cordierite-gedrite rocks. Igneous cordierite from granitic plutons have $\delta^{13}C = -23.61 \pm 2.08‰$ (n = 13), which is interpreted as reflecting a magmatic carbon budget dominated by organic carbon from sedimentary source rocks. In contrast, small pegmatites reported in the literature have $\delta^{13}C(Crd) = -10.20 \pm 3.06‰$ (n = 6), which may indicate derivation from orthogneiss source materials. These new data show that carbon isotopes in cordierite can be used to help understand the protolith of even carbon-poor metamorphic rocks, and can also shed light on carbon in the sources of magmatic rocks. This latter approach has the potential for helping constrain the source rocks of peraluminous granitoids, which is controversial. Determining the extent to which organic carbon $\delta^{13}C$ is preserved in granitoids is important for understanding the deep carbon cycle, and could serve as an important constraint in the search for low-$\delta^{13}C$ graphite inclusions in Hadean detrital zircons, which have been reported as a potential biosignature for the early Earth.

Keywords: Stable isotopes, igneous petrology, metamorphic petrology, analysis, cordierite

INTRODUCTION

Cordierite $[(Mg,Fe)_2[Al_4Si_5O_{18}]\cdot(H_2O,CO_2)]$ is a common mineral in low- to medium-pressure pelitic metamorphic rocks and is an accessory mineral in some peraluminous granitoids (Fig. 1). In addition to being an important petrologic indicator mineral, the composition of cordierite is also used as an approach to understand igneous and metamorphic fluids. The structural channels in cordierite have long been known to contain measurable volatile species, predominately H_2O and CO_2, and this property has been used as a tool by many workers for constraining the fluid chemistry of metamorphic and igneous rocks (e.g., Vry et al. 1990; Harley et al. 2002; Della Ventura et al. 2009; Rigby and Droop 2008, 2011; Bebout et al. 2016). Cordierite from most of these studies have H_2O and CO_2 contents that are consistent with preservation of high-temperature fluid compositions, and cordierite from some localities show evidence for "leakage" or re-equilibration during cooling and uplift.

Carbon isotope ratios of cordierite channel CO_2 have been measured in several studies (Armbruster et al. 1982; Vry et al. 1988, 1990; Vry and Brown 1992; Santosh et al. 1993; Fitzsimons and Mattey 1995; Korja et al. 1996; Bebout et al. 2016), with the majority of the samples being from high-grade metamorphic rocks. For the most part these studies focused on fluid composition and constraining metamorphic fluid flow. In some cases evidence from carbon isotopes has been interpreted as indicating retrograde and channelized influx of a CO_2-rich metamorphic fluid (Armbruster et al. 1982; Santosh et al. 1993). At other localities $\delta^{13}C(Crd)$ values are interpreted as indicating the possibility of mixing between protolith carbon and carbon from externally derived fluid (Fitzsimons and Mattey 1995). Carbon isotope heterogeneity at many localities is suggestive of a lack of mixing via a melt or a pervasive metamorphic fluid (Vry et al. 1988, 1990; Vry and Brown 1992; Fitzsimons and Mattey 1995). High-temperature isotopic equilibrium is also preserved between cordierite CO_2 and coexisting graphite (Vry et al. 1990; Fitzsimons and Mattey 1995). Finally, variations in carbon isotopes of cordierite CO_2 from different localities in the Pikwitonei granulite domain (Superior Province, Canada) and Brattstrand Bluffs (East Antarctica) suggest preservation of pre-

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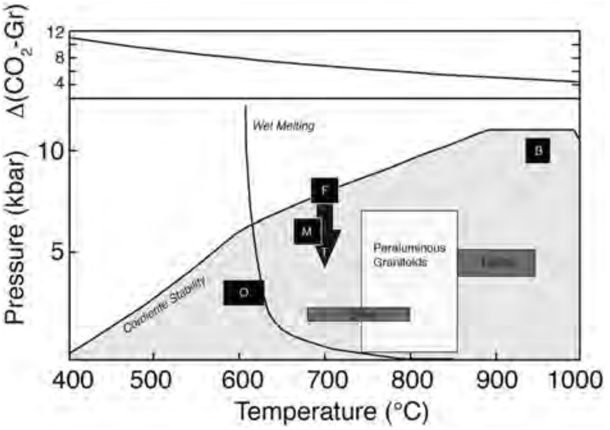

FIGURE 1. Schematic pressure-temperature diagram and equilibrium carbon isotope fractionation ($\Delta^{13}C$) between CO_2 and graphite as a function of temperature. Sources of the peak temperatures for metamorphic rocks in this study are found Tables 1 and 2 (and references therein). Cordierite-gedrite gneiss localities: B = Bondy Gneiss Complex, F = Fishtail Lake, M = Manitouwadge, O = Orijärvi, and T = Tobacco Root Mountains (showing decompression path). Typical conditions for generation and emplacement of peraluminous granitoids are from Phillips et al. (1981), and the cordierite stability field is from Schreyer (1999). Carbon isotope fractionation from Deines and Eggler (2009) and Chacko et al. (2001).

metamorphic protolith $^{13}C/^{12}C$ (Vry and Brown 1992; Fitzsimons and Mattey 1995), which in part motivated this study.

This study focuses on testing the hypothesis of preservation of parent rock carbon isotope ratios in cordierite by examining several suites of well-constrained, genetically related cordierite-bearing igneous and metamorphic rocks. The results confirm that, even in the absence of carbonate or graphite, often times cordierite faithfully preserves the carbon isotope ratio of metamorphic protoliths and igneous source materials and thus gives us insights into the genesis of these rocks.

MATERIALS AND METHODS

Two sampling strategies were employed in this study. First, suites of igneous and metamorphic rocks were assembled that formed from parent rocks that typically have distinct carbon isotope ratios. These include S-type granitoids that are thought to originate from the melting of sediments (Chappell and White 1992) and cordierite-gedrite gneisses and related rocks that are thought to be metamorphosed hydrothermally altered volcanic rocks (Peck and Smith 2005). The metamorphic rocks analyzed for this study span a wide range of amphibolite to granulite facies temperatures (Fig. 1). Data from these samples are compared to carbon isotopes in cordierite from metamorphic rocks with clear sedimentary protoliths, which are well-represented in previous studies (Vry et al. 1990; Fitzsimons and Mattey 1995; Korja et al. 1996; Bebout et al. 2016). The second sampling strategy was to examine two low-pressure contact-metamorphosed suites that had already been studied for H_2O and CO_2 contents. Samples from the Etive aureole (Rigby et al. 2008) and the Huntly Complex (Droop et al. 2003; Rigby and Droop 2008) allow the carbon isotopes of cordierite to be examined in similar pelitic lithologies that experienced conditions spanning several 100 °C, and including partial melting (Fig. 1).

Samples were crushed, processed, and hand-picked using a binocular microscope to produce pure mineral separates. Cordierite was initially located using petrographic thin sections, followed by identification in matching rock billets. Because cordierite is visually so different in different rocks processing was tailored to individual samples. Some crushed samples were magnetically processed using a Frantz Isodynamic Separator and, for some rocks, identification of cordierite in mineral separates was achieved with energy-dispersive X-ray spectroscopy using a scanning electron microscope with an Oxford X-max silicon drift X-ray detector. Alteration- and inclusion-free cordierite was the goal of mineral picking, and was achieved in some samples by scraping and breaking individual crystals using tweezers and dental tools. In very fine-grained hornfels samples, inclusions could not be entirely avoided and, in some granitic samples, it was impossible to entirely separate cordierite from pinite alteration. Measured carbon contents thus may be minimum values due to the inclusion of non-cordierite material in the relatively large mineral separates needed for analysis. Several tests were done comparing inclusion-rich and altered mineral splits with pure mineral splits, which proved to have identical $\delta^{13}C$ values within analytical uncertainty. All analyzed samples contain no visible graphite. A representative group of cordierite mineral splits were also soaked in cold 15% HCl and showed visible evidence for dissolution after treatment. Partially dissolved samples have identical $\delta^{13}C$ values to untreated samples, indicating a minimal role of carbonate alteration.

Powdered cordierite splits were combusted in a Costech ECS 4010 elemental analyzer (EA) online with a Delta Plus Advantage mass spectrometer in continuous flow mode after Peck and Tumpane (2007). Data are standardized to USGS-24 and instrument conditions were monitored by multiple daily analyses of in-house standards, including a calcite that has been analyzed using phosphoric acid. Average cordierite sample size ranged from ca. 5–50 mg because of the variable and sometimes low carbon contents of cordierite, and the small analytical blank caused by trace carbon in the tin cups used for combustion (Peck and Tumpane 2007). Reproducibility of cordierite samples averaged ±0.12‰ (81% of samples were duplicated or triplicated), which compares well to the average daily reproducibility of standards (±0.05–0.20‰).

RESULTS

Contact-metamorphosed pelites

Cordierite from graphite-free pelitic metasediments was analyzed from the Etive contact aureole (Droop and Moazzen 2007) and the Huntly complex, Scotland (Droop et al. 2003). Results are shown in Table 1 and Figures 2 and 3. Samples of the Dalradian Leven Schist from Etive range from corundum to sillimanite metamorphic zones, and have very constrained $\delta^{13}C(Crd) = -22.18$ to -18.95‰ ($n = 10$). Carbon contents range from 0.18–0.33 wt% CO_2. This similar but slightly higher than the 0.07–0.25 wt% range in CO_2 concentrations measured using Fourier transform infrared spectroscopy (FTIR) spot analyses on these rocks by Rigby et al. (2008). These authors also documented systematic variability (~0.1 wt% CO_2 in the middle aureole and ~0.2 wt% CO_2 at the igneous contact) that is not seen in the new data, probably reflecting heterogeneity that is differently sampled while hand-picking tens of milligrams for isotope analysis vs. 15–20 μm spot analyses by FTIR. At the

TABLE 1. Carbon isotopes of cordierite from contact aureole pelitic rocks

Sample		$\delta^{13}C$ (‰ PDB)	CO_2(wt%)
	Etive aureole (Droop and Moazzen 2007; Rigby et al. 2008)		
MM193Y	Sillimanite zone hornfels (3m)	–21.09	0.31
MM197A	Sillimanite zone hornfels (15m)	–21.31	0.22
MM210A	Sillimanite zone hornfels (20m)	–20.79	0.29
MM166F	Sillimanite zone hornfels (90m)	–21.84	0.22
MM166A	Sillimanite zone hornfels (130 m)	–22.16	0.19
MM166H	Sillimanite zone hornfels (140m)	–19.15	0.19
MM169B	Sillimanite zone hornfels (140m)	–18.95	0.27
MM188B	Upper spinel zone hornfels (330 m)	–22.18	0.22
MM133	Lower spinel zone hornfels (450 m)	–19.02	0.33
MM185A	Lower spinel zone hornfels (490 m)	–20.76	0.24
	Huntly Complex (Droop et al. 2003; Rigby and Droop 2008)		
10035	Orthopyroxene-cordierite hornfels	–17.97	0.37
BQ41	Orthopyroxene-cordierite hornfels	–20.45	0.17
PIR1	Orthopyroxene-cordierite hornfels	–21.18	0.12
10038	Cordierite norite	–18.84	0.41
BQ38	Cordierite norite	–15.07	0.45
FOW1	Garnet-cordierite tonalite	–21.89	0.49

Notes: Distance to the Etive igneous complex given parentheses. The upper and lower spinel zones are separated by the melt-in isograd (Rigby et al. 2008).

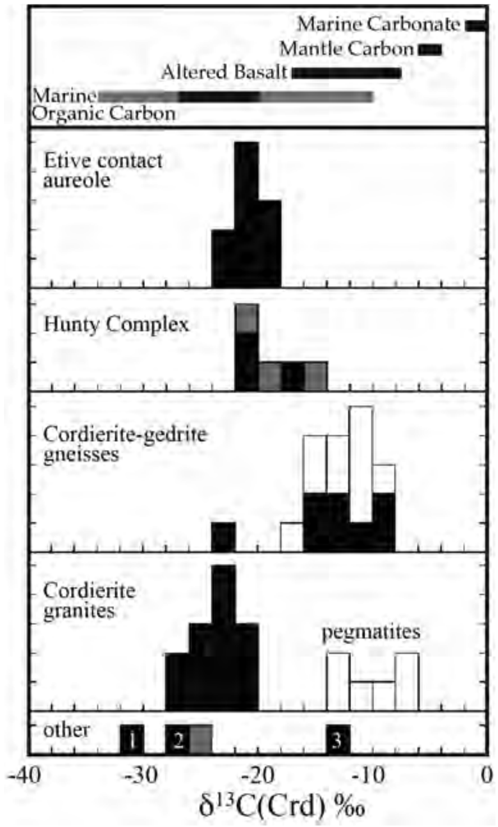

FIGURE 2. Carbon isotope analyses of cordierite (Crd) from analyzed samples (black and gray) and literature values (white; from Vry et al. 1990 and Bebout et al. 2016). Typical carbon isotopes of marine carbonate, mantle carbon, and organic carbon from recent marine sediments are from Deines (1980) and Schidlowski (2001), and altered basalt (Costa Rica Rift) is from Furnes et al. (1999). Gray range of marine organic carbon shows <10% of values; black shows >90% of values. Huntly Complex cordierite samples include hornfels (black) and igneous-textured metasediments (gray). "Other" samples from the Cooma contact aureole are (1) shale from outside of the aureole (whole-rock analysis), (2) cordierite + andalusite + K-feldspar gneiss, and (3) migmatitic cordierite + sillimanite + K-feldspar gneiss. Gray = mylonitic paragneiss, Bohemian Massif.

Huntly complex three orthopyroxene-bearing hornfels samples have δ^{13}C(Crd) = –21.18 to –17.97‰. Carbon contents range from 0.12 to 0.37 wt% CO_2. Three migmatitic rocks with igneous textures derived from Dalradian sediments have δ^{13}C(Crd) = –21.89 to –15.07‰. Carbon contents for igneous-textured rocks are higher, and range from 0.41–0.49 wt% CO_2. This difference was not seen in the narrower 0.08–0.17 wt% range in CO_2 concentrations measured from these rocks using FTIR by Rigby and Droop (2008).

Cordierite-gedrite gneisses

Carbon isotopes were measured for cordierite-gedrite gneisses in eight samples from five well-characterized localities, all of which have been documented as having hydrothermally altered volcanic protoliths (Table 2; Fig. 2). Carbon isotope ratios for seven samples (four localities) span from –15.76 to –9.25‰ (average δ^{13}C = –12.33‰). One cordierite sample from the Spuhler Peak Metamorphic Suite (Tobacco Root Mountains, Wyoming Province) is –23.05‰. Carbon contents range from 0.12–2.38 wt% CO_2. Vry et al. (1990) and Bebout et al. (2016) present data from cordierite-gedrite and related rocks that can be compared to new analyses. This includes analyses from two of the localities sampled in this study: the Manitouwadge and Orijärvi volcanogenic massive sulfide (VMS) camps, Superior Province and Svecofennian Orogen (Table 2). Literature values are very similar to the new analyses presented here: they have an average δ^{13}C(Crd) = –12.71‰ and range from –16.50 to –8.40‰ (n = 9).

Cordierite-bearing granitoids

Cordierite was analyzed for carbon isotope ratio from 13 samples representing 8 major intrusive complexes (Table 3). With the exception of the Cornucopia Stock (Johnson et al. 1997) these samples are all from bodies thought to have formed at least in part by melting of sedimentary rocks (Chappell and White 1992; Finger and Clemens 1995; Erdmann et al. 2004; Antunes et al. 2008). Carbon isotope ratios range from –27.05 to –20.07‰ [average δ^{13}C(Crd) = –23.61‰]. These carbon isotope ratios are distinctly different from the small cordierite-bearing pegmatites reported by Vry et al. (1990) and Bebout et al. (2016), which range from –14.0 to –6.9‰. Measured carbon contents of cordierite from granitoids range from 0.11–0.84 wt% CO_2. These are similar to the 0.03–0.62 wt% range in CO_2 concentrations of four samples of cordierite-bearing granitoids analyzed by ion microprobe by Harley et al. (2002). Three samples related to cordierite granitoids were also analyzed. A mylonitic metasedimentary rock from the South Bohemian Batholith (Austria) has δ^{13}C(Crd) = –24.08‰. Two metasedimentary samples from the contact aureole around the Cooma granodiorite (Australia) have δ^{13}C(Crd) = –26.05 and –12.41‰, while a sedimentary equivalent outside of the aureole has δ^{13}C(whole-rock) = –30.80‰ (Fig. 2).

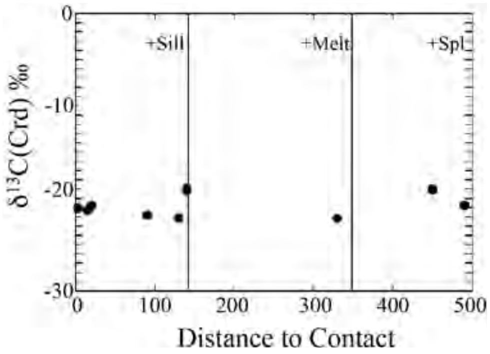

FIGURE 3. Carbon isotope ratios of cordierite in the pelitic Leven Schist from the high-temperature portion of the Etive thermal aureole. Metamorphic conditions of metasediments range from fluid saturated below the ~680 °C melt-in isograd to strongly fluid-undersaturated above the ~705 °C sillimanite-in isograd, and possibly affected by magmatic fluids at the ~800 °C contact (Rigby et al. 2008). Carbon isotopes in cordierite are not influenced by variable metamorphic temperature or fluid regime. The spinel-in isograd is off of the diagram ca. 40 m to the right.

TABLE 2. Carbon isotopes of cordierite from cordierite-gedrite gneisses

Sample	Lithology	Locality	$\delta^{13}C$ (‰ PDB)	CO_2(wt%)	Reference
96FL6	Cordierite-gedrite gneiss	Fishtail Lake	–9.25	1.32	Peck and Valley 2000
96FL7	Cordierite-gedrite gneiss	Fishtail Lake	–9.37	0.29	Peck and Valley 2000
96FL11	Cordierite-biotite gneiss	Fishtail Lake	–13.45	2.38	Peck and Valley 2000
96FL29	Cordierite-gedrite gneiss	Fishtail Lake	–12.61	0.40	Peck and Valley 2000
97MW7	Cordierite-gedrite gneiss	Manitouwadge	–15.49	0.23	Peck 2000
O-5B	Cordierite-gedrite gneiss	Orijärvi	–15.76	0.16	Smith et al. 1992
POD	Cordierite-kornerupine segregation	Bondy Gneiss Complex	–10.40	2.16	Peck 2000
WP6B93	Cordierite-gedrite gneiss	Tobacco Root Mtns	–23.05	0.12	Burger et al. 2004

TABLE 3. Carbon isotopes of cordierite from cordierite-bearing granitoids

Sample	Lithology and locality	$\delta^{13}C$ (‰ PDB)	CO_2 (wt%)	Reference
SMBCRD1	Aplite in Sandy Lake Monzogranite, SMB	–25.30	0.12	MacDonald 2001
SMBCRD2	Harrietsfield Leucomonzogranite, SMB	–23.19	0.12	MacDonald 2001
SMBCRD3	Aplite in Sandy Lake Monzogranite, SMB	–22.62	0.84	MacDonald 2001
SMBCRD4	Harrietsfield Leucomonzogranite, SMB	–20.07	0.25	MacDonald 2001
SMBCRD5	Harrietsfield Leucomonzogranite, SMB	–23.71	0.34	MacDonald 2001
MBD15–438	Musquodoboit Batholith	–25.26	0.18	MacDonald and Clark 1985
07AU14	Numbla Vale Monzogranite, Berridale Batholith	–21.74	0.11	Chappell and White 1992
07AU15	Minnegans Monzogranite, Kosciusko Batholith	–25.00	0.40	Chappell and White 1992
07AU27	Cooma Granodiorite, Murrumbidgee Batholith	–27.05	0.63	Chappell and White 1992
G4	Granite, Castelo Branco Pluton, Iberian Variscan Belt	–26.49	0.59	Antunes et al. 2008
CS104	Trondhjemite, Cornucopia Stock	–22.38	0.66	Johnson et al. 1997
CS101	Trondhjemite, Cornucopia Stock	–22.75	0.76	Johnson et al. 1997
FI 77/85	Cordierite+garnet cumulate, Weinsberg granite, south Bohemian batholith	–21.37	0.41	Finger et al. 1997
FI 3/92	Mylonitic paragneiss, south Bohemian batholith	–24.08	0.49	Finger et al. 1997
07AU23	Andalusite+Kspar gneiss Cooma aureole	–26.05	0.81	Chappell and White 1976
07AU26	Migmatite, Cooma aureole	–12.41	0.37	Chappell and White 1976
07AU19	Shale, outside of Cooma aureole	–30.76[a]	–	Chappell and White 1976

Note: SMB = South Mountain Batholith. [a] Whole-rock analysis.

DISCUSSION

Cordierite channel volatiles during metamorphism

Several studies have examined cordierite channel H_2O and CO_2 in contact and regionally metamorphosed rocks. In some metamorphic rocks H_2O and CO_2 contents are found to be consistent with fluid-saturation during peak metamorphic conditions, and in others low calculated a_{H_2O} and a_{CO_2} is taken as indicating fluid absence (e.g., Vry et al. 1988; Harley et al. 2002; Rigby and Droop 2008). In most rocks $H_2O >> CO_2$ contents, but in some localities $CO_2 > H_2O$ contents (including $CO_2 > 1$ wt%), in both fluid-saturated and fluid-undersaturated rocks (Rigby and Droop 2011). It has also been found that in some cases cordierites lose and/or re-equilibrate H_2O (Harley et al. 2002; Rigby and Droop 2008) or more rarely CO_2 (e.g., Rigby et al. 2008) after the peak of metamorphism, consistent with slower CO_2 diffusion rates than H_2O in cordierite channels (Radica et al. 2016). The processes that regulate this "selective leakage" are not well understood (Harley et al. 2002; Rigby and Droop 2008).

Carbon isotope data from previous studies support the common retention of cordierite channel CO_2 after the peak of metamorphism (e.g., Vry et al. 1990; Santosh et al. 1993; Fitzsimons and Mattey 1995), and also some cases where post-peak fluids have been recorded by cordierite channel $\delta^{13}C$ values (Armbruster et al. 1982; Santosh et al. 1993). However, these studies did not focus on rocks where protolith $\delta^{13}C$ was well constrained, or examine samples across a metamorphic gradient with a variable temperature and fluid regime. New data from the Etive aureole hornfelses shows incredibly consistent cordierite channel CO_2 $\delta^{13}C$ values (–20.72 ± 1.27‰, Fig. 3), spanning from metamorphic temperatures of ~ 660 °C near the spinel-in isograd to ~800 °C at the igneous contact (Droop and Moazzen 2007). Over this temperature gradient metamorphic fluid compositions recorded by cordierite range from fluid saturated with $a_{H_2O} \approx 1$ far from the contact to fluid undersaturated with $a_{H_2O} \approx 0.5$ to 0.8 at temperatures above the melt-in isograd (Rigby et al. 2008). Proximal (≤30 m) to the igneous contact cordierite H_2O and CO_2 contents are higher, perhaps due to magmatic fluid influx (Rigby et al. 2008). The one sample examined here that was shown by Rigby et al. (2008) to have these higher CO_2 contents is sample MM193Y, which has $\delta^{13}C = 21.09$ and 0.3 wt% CO_2, indistinguishable from other samples in the aureole. These data would suggest that there is negligible isotope fractionation of CO_2 in cordierite over these temperatures.

Measured $\delta^{13}C$ values (–20.72 ± 1.27‰) are consistent with likely organic carbon in shale protoliths to the Leven Schist (e.g., Deines 1980; Schidlowski 2001). The Leven Schist does not contain graphite (Droop and Moazzen 2007), but Neoproterozoic sediments correlative to the Dalradian Leven Schist elsewhere contain reduced carbon that has similarly low $\delta^{13}C$ values, typically in the range of –28 to –20‰ (see Hayes et al. 1999). The initial carbon isotope ratio of reduced carbon would be expected to be fractionated during diagenesis and metamorphism, and bacterial processes and thermal decarboxylation typically shift $\delta^{13}C$ values of the remaining carbon to higher values. These processes, in addition to variability in initial carbon isotope ratios, causes the variety of $\delta^{13}C$ values found in sedimentary reduced carbon (Deines 1980; Fig. 2). Determining which processes operated at lower temperatures and to what extent is not always possible in high-grade metamorphic rocks, but the distribution of $\delta^{13}C$ of kerogen and graphite in ancient rocks shows that the typical shift of reduced carbon during metamorphism of metasediments is on the order of a few per mil (Schidlowski 2001), and a similar result is seen here and in other studies of cordierite $\delta^{13}C$. Note that cordierite CO_2 originally from marine carbonate protoliths would have $\delta^{13}C \approx 0‰$, which is not observed in any cordierite analyzed in this study. If sample MM193Y was affected by CO_2-rich late magmatic fluids then the $\delta^{13}C$ of the fluid was likely initially acquired by the magma from country rock metasediments, but with no detectable isotopic fractionation during metamorphic devolatilization or magmatic degassing, so the $\delta^{13}C$ of this sample has not changed. It is notable that these samples have identical $\delta^{13}C$(Crd) in fluid-undersaturated and fluid-saturated portions of the contact aureole, consistent with robust retention of protolith organic carbon $\delta^{13}C$ values in cordierite channel CO_2.

The six samples examined from the Huntly complex (Fig. 2) are also cordierite-bearing and derived from Dalradian sediments; some are orthopyroxene-bearing hornfelses (black in Fig. 2) and others are igneous-textured diatexites (gray). Petrologic evidence points toward peak conditions of ca. 900 °C and all samples having experienced ~55–60% melt extraction (Droop et al. 2003). Water contents of cordierite from these samples are interpreted as reflecting re-equilibration with melt during cooling after the peak of metamorphism and more extensive exchange in diatexites that may have remained in contact with melt to lower temperatures than the hornfelses (Rigby and Droop 2008). If this is the case, then more exchange with melt for diatexites than for hornfelses may explain the slightly higher CO_2 contents measured in diatexite cordierite than measured in hornfels cordierite (Table 1). The cause of carbon isotope variability (~3‰ in hornfels and ~7‰ in diatexites) is less clear. Both lithologies have low $\delta^{13}C$ samples ca. –21 to –22‰, similar to the Etive samples and consistent with CO_2 derivation from sedimentary organic carbon (e.g., Deines 1980; Schidlowski 2001). The measured range in values could be interpreted as representing protolith rocks with a range in $\delta^{13}C$ values, or the variable effects of diagenesis, or mixtures of a sedimentary carbon signature with isotopically heavier CO_2 from late magmatic fluids of the Huntly Gabbro. Mantle-derived carbon typically has $\delta^{13}C$ values of –7 to –5‰ (Deines 1980), and although carbon isotope fractionations between mafic melts (where carbon is mostly carbonate species) and CO_2 are not well constrained for late magmatic temperatures, CO_2 1–4‰ heavier than a coexisting magma is consistent with experiments (Deines 2004), meaning that gabbro-derived CO_2 may explain a component of the carbon isotope variability in the Huntly samples. This kind of effect was not seen in the one Etive sample that may have experienced magmatic fluid alteration.

The other locality where multiple metamorphic samples were analyzed is the Cooma metamorphic complex, where Ordovician metasediments show progressive metamorphism up to melting in the aureole of the Cooma granodiorite (Chappell and White 1976). Cordierite + andalusite + K-feldspar gneiss has $\delta^{13}C$(Crd) = –26.05‰, similar to sedimentary organic carbon (e.g., Deines 1980; Schidlowski 2001) as does the whole-rock $\delta^{13}C$ = –30.76‰ for a shale sample from outside of the contact aureole (Table 1). A lower $\delta^{13}C$ of whole-rock reduced carbon than of cordierite channel CO_2 is consistent with the expected carbon isotope fractionation at metamorphic temperatures (Fig. 1). A migmatitic cordierite + sillimanite + K-feldspar gneiss from closer to the contact has $\delta^{13}C$(Crd) = –12.41‰. This anomalously high $\delta^{13}C$(Crd) is accompanied by a higher $\delta^{15}N$(whole-rock) compared to other aureole rocks, which Jia (2006) proposed could be caused by a magmatic fluid originating from the Cooma granodiorite. However, the Cooma granodiorite has $\delta^{13}C$(Crd) = –27.05‰, so the source of the high $\delta^{13}C$ (and likely $\delta^{15}N$ as well) that affected the Cooma migmatite zone is likely not the Cooma granodiorite and is still unclear.

Of the three contact aureole case studies the Etieve aureole has the most clear results: across variable temperature and fluid conditions during metamorphism $\delta^{13}C$(Crd) is the same. This may be in part because $\delta^{13}C$ initially had a small range in the Leven Schist protolith sediments. The Huntly and Cooma complexes preserve protolith sedimentary $\delta^{13}C$(Crd) values, but also higher $\delta^{13}C$ values that may show the influence of exotic fluids (which would be consistent with other geochemical evidence), or perhaps merely sedimentary variability in original $\delta^{13}C$. An inherent complication here is the large range in organic carbon $\delta^{13}C$ in modern marine sediments: ca. –30 to –10‰, although most are in the range –27 to –20‰ (Deines 1980). However, preservation of "typical" organic carbon $\delta^{13}C$ values in cordierite appears to be common in high-grade pelitic metasedimentary rocks, and has been documented in several studies (Vry et al. 1990; Santosh et al. 1993; Fitzsimons and Mattey 1995; Korja et al. 1996; Bebout et al. 2016). Especially telling of the preservation of protolith $\delta^{13}C$ are the very low $\delta^{13}C$ values of cordierite (and graphite) from Pikwitonei granulite domain (ca. –38 to –30‰), which likely is a reflection of the anomalously low $\delta^{13}C$ carbon cycle excursion at ca. 2.7 Ga known from lower-grade Archean rocks (Vry et al. 1988, 1990).

Protoliths of cordierite-gedrite gneisses

Although many cordierite-bearing gneisses have $\delta^{13}C$(Crd) consistent with sedimentary organic carbon, others have higher $\delta^{13}C$ values in the range –16.5 to –8.4‰ (n = 9; Vry et al. 1990; Bebout et al. 2016). These samples are from cordierite-orthoamphibole (gedrite or anthophyllite) and related rocks, a group of schists or gneisses similar to metapelites but with unusually Ca-poor and Mg- and Al-rich bulk compositions and typically lacking graphite. Some cordierite-gedrite localities have been ascribed to Mg-rich sedimentary rocks (e.g., Reinhardt 1987) or metasediments that have been modified by melt extraction (e.g., Grant 1968), but the localities considered here have been shown to have hydrothermally altered volcanic protoliths (e.g., chlorite-sericite-quartz rocks). This is based on major and trace element geochemistry of these rocks (Smith et al. 1992; Peck and Smith 2005), their oxygen isotope ratios (Araujo et al. 1996; Peck and Valley 2000; Burger et al. 2004), and their common association with VMS ore deposits (Araujo et al. 1996).

In addition to the 10 published carbon isotope analyses of cordierite from cordierite-gedrite rocks in the literature, eight other rocks from well-characterized cordierite-gedrite gneiss localities were analyzed, including two from localities associated with VMS deposits that had already been sampled (Manitouwadge and Orijärvi; Table 2). These rocks are from localities where major element geochemistry points to volcanic protoliths ranging from basalt to rhyolite in composition that have been variably leached of alkalis and calcium by seawater (Smith et al. 1992; Pan and Fleet 1995; Blein et al. 2004; Burger et al. 2004; Peck and Smith 2005). Oxygen isotopes from the Fishtail Lake and Bondy Gneiss Complex Grenville Province localities (Peck

2000; Peck and Valley 2000) and the Tobacco Root Mountains cordierite-gedrite rocks (Burger et al. 2004) indicate moderate to low-temperature hydrothermal alteration ≤ ~250 °C before high-grade metamorphism, while cordierite-gedrite rocks associated with the Manitouwadge VMS deposit have oxygen isotopes consistent with high-temperature (≥ ~250°C) alteration (Araujo et al. 1996; Peck 2000). These new samples all have $\delta^{13}C$(Crd) values similar to those reported by Vry et al. (1990) and Bebout et al. (2016), except for one sample from the Tobacco Root Mountains with $\delta^{13}C$(Crd) = –23.05‰. In this sample cordierite is a texturally late replacement of garnet related to decompression (Fig. 1), where in the other samples cordierite more consistently shows textural equilibrium with other phases. Excluding this sample cordierite-gedrite gneisses have $\delta^{13}C$(Crd) = –12.51 ± 2.45‰ (n = 17), considerably higher than the organic carbon signature in pelitic metasediments (Fig. 2).

A likely explanation for the measured $\delta^{13}C$(Crd) values from cordierite-gedrite gneisses is that they record the carbon isotope ratio of the protolith, even though these rocks would normally be thought of as essentially carbon-free because of their general lack of carbonate or graphite. The departure from marine organic carbon $\delta^{13}C$ values (Fig. 2) makes a clear distinction between cordierite-gedrite rocks and typical pelites. A possible modern analog for the protolith carbon source of cordierite-gedrite rocks is trace (<1%) carbonate found in altered seafloor basalts (Furnes et al. 2006). This trace carbonate is found in the bioaltered rims of pillow basalt from ocean crust with intermediate spreading rates, and typically has $\delta^{13}C$ values between –15 and –5‰, which is attributed to derivation from CO_2 generated by oxidation of organic material (Furnes et al. 2006). The average $\delta^{13}C$(Crd) of cordierite-gedrite rocks (–12.51 ± 2.45‰) is essentially identical to the –12.08 ± 2.90‰ (n = 12) measured from trace carbon in basalts from the Costa Rica Rift (Furnes et al. 1999), and (with other geochemical data) fits well with a hydrothermally altered volcanic protolith. The carbon isotope ratios of cordierite-gedrite gneisses also help exclude some sources of protolith carbon. High $\delta^{13}C$ values (>0‰) caused by methanogenesis are found in altered volcanics from slow-spreading ocean crust (Furnes et al. 2006), which are inconsistent with carbon isotopes from cordierite-gedrite rocks. Likewise marine carbonate ($\delta^{13}C \approx 0$) and mantle-derived carbon ($\delta^{13}C \approx$ –7 to –5‰) are also excluded as a major contributors of carbon for these rocks.

Cordierite CO_2 in Granitoids

In general, the carbon isotope systematics of magmatic carbon are not as well constrained as isotope systems that are hosted in refractory rock-forming igneous minerals (e.g., U-Pb and O isotopes in zircon, Sm-Nd and O isotopes in garnet). In contrast, the carbon isotope budgets of magmas are mainly known from studies of magmatic volatiles (e.g., Blank and Brooker 1994) and analysis of trace carbonate and reduced carbon in igneous rocks (Fuex and Baker 1973; Hoefs 1973). The magmatic volatile literature focuses on oceanic and subduction zone volcanism, so does not bear directly on the cordierite granites analyzed here. The interpretation of carbon isotopes of trace carbonate and reduced carbon in igneous rocks is problematic and controversial (Deines 2004), and are likely prone to easy resetting by various magmatic and late-stage hydrothermal processes, making this component of the deep carbon cycle difficult to constrain. In cordierite granites there is the unusual case of being able to sample CO_2 trapped in cordierite, a relatively refractory mineral, and to thus constrain carbon signatures in the igneous source materials.

Cordierite is a common accessory mineral in strongly peraluminous (mol $Al_2O_3/Na_2O+K_2O+CaO > \sim 1.1$) granitoids (Miller 1985; Chappell and White 1992). In some granites cordierite has been interpreted as being inherited from metasedimentary source rocks of the granites or entrained as xenocrysts from country rocks, but for the most part cordierite textures and mineral chemistry are consistent with being the result of formation from melt (Chappell et al. 1987; Clarke 1995; Erdmann et al. 2004). The samples analyzed here (Table 3) range from small satellite plutons of larger batholiths (Cooma and Cornucopia) through major phases of batholiths occupying thousands of square kilometers (Kosciusko, South Mountain, South Bohemian Batholiths). Detailed petrologic studies of these plutons document a magmatic origin for cordierite in a variety of rock types, ranging from trondhjemite to granite in composition and including cumulate and aplitic phases (Chappell and White 1992; Finger and Clemens 1995; Johnson et al. 1997; Erdmann et al. 2004; Antunes et al. 2008).

Given the variety of magmatic cordierite analyzed it is surprising that carbon isotopes are so consistent: $\delta^{13}C$(Crd) = –23.61 ± 2.08‰ (n = 13; Fig. 2). These values are exactly what would be expected for CO_2 derived from organic carbon in sedimentary rocks (e.g., Deines 1980; Schidlowski 2001), but are distinct from other reservoirs such as mantle carbon and marine carbonate in limestones or marls. The $\delta^{13}C$(Crd) is interpreted as reflecting the carbon isotope ratio of magmatic CO_2 of the peraluminous granitic magmas, and a general similarity between carbon source materials among the studied plutons. In mafic magmas carbon is dissolved primarily as carbonate, so degassing of CO_2 will fractionate $\delta^{13}C$ (Blank and Brooker 1994). Carbon in granitic magmas primarily exists as CO_2, so degassing will not appreciably fractionate $\delta^{13}C$ (Blank and Brooker 1994; Deines 2004), and $\delta^{13}C$(Crd) should closely reflect the isotope ratio of magmatic source materials.

Many peraluminous granitoids are interpreted to have formed from melting of sedimentary rocks at depth (e.g., S-type granites), but this interpretation is contested in some cases, and peraluminous compositions are also observed in rocks consistent with derivation from melting of igneous sources (Miller 1985; Chappell and White 1992). A review of the petrologic evidence for derivation from pelitic sediments vs. psammic compositions or a mixture of sedimentary and igneous source rocks for strongly peraluminous granitoids is beyond the scope of this paper, but the magmatic carbon isotope ratios presented here help constrain some of these models. As a first-order interpretation the $\delta^{13}C$(Crd) = –23.61 ± 2.08‰ is consistent with organic carbon in clastic metasedimentary rock as carbon source materials for the granites (e.g., shales or graywackes). Other metasedimentary rock-types have also been considered as possibly being important parental source materials to peraluminous granitoids, for example marls because of some similarities between the high CaO and Na_2O of these rocks and Australian S-type granites (see Collins 1996). The marine carbonate $\delta^{13}C \approx 0$‰ of marls make them an unlikely source of carbon for cordierite granites.

The $\delta^{13}C$ measured from cordierite cannot easily be compared to the intermediate to felsic igneous source materials proposed as being parental to some peraluminous granitoids (e.g., Miller 1985), as the bulk $\delta^{13}C$ of this reservoir is not well constrained. Wedepohl (1995) estimates that the average carbon content of continental metamorphic rocks is ~800 ppm with $\delta^{13}C$ = ca. –13‰, which does not does not match well the cordierite granitoids $\delta^{13}C$(Crd) = –23.61 ± 2.08‰, but is a closer match to the $\delta^{13}C$(Crd) = –10.20 ± 3.06‰ (n = 6) measured by Vry et al. (1990) and Bebout et al. (2016) for cordierite from small granite pegmatites. No cordierite-bearing pegmatites were sampled in this study, but this distinctive lithology appears to be commonly derived from melting of igneous source materials (Heinrich 1950). At least some of these cordierite pegmatites are associated with cordierite-gedrite gneisses (e.g., Schumacher 1990), which (as shown above) have a very similar $\delta^{13}C$(Crd) = –12.51 ± 2.45‰.

The most straightforward interpretation of the bimodal distribution of igneous cordierite carbon isotope ratios is that that the $\delta^{13}C$(Crd) = –10.20 ± 3.06‰ measured from cordierite pegmatites in other studies is indicative of orthogneiss or other igneous source materials, while the $\delta^{13}C$(Crd) = –23.61 ± 2.08‰ measured from the localities in Table 3 represent organic carbon from pelitic paragneiss or other clastic metasediments. For some plutons, such as Australian S-type granites, sedimentary rocks are generally agreed to be either dominant (Chappell and White 1992) or an important part of a multi-component source (Kemp and Hawkesworth 2004). In the latter model metasediment-derived melts would dominate the carbon budget of resulting magmas when mixing with mantle-derived melts, explaining the sedimentary $\delta^{13}C$ of the cordierite granites. Substantial sediments in the source materials and in some cases assimilation of metasedimentary wall rocks are consistent with the petrologic characteristics of the other granitoid plutons sampled in this study (Finger and Clemens 1995; Erdmann et al. 2004; Lackey et al. 2011; Antunes et al. 2008), save one body. Johnson et al. (1997) propose that the composition of the Cornucopia Stock is best explained by melting of mafic igneous lithologies in the lower crust. Excepting carbonatites, detailed carbon isotope studies of continental igneous rocks are few and far between (e.g., Duke and Rumble 1986; Barnes et al. 2005), so there are clear open questions of the importance of source materials vs. later processes such as assimilation or deuteric alteration on $\delta^{13}C$ in granites. It may be in that in this case small amounts of metasedimentary rock in the source region dominate the carbon budget of the Cornucopia Stock magma but did not make a large impact on major or trace element geochemistry, or that low $\delta^{13}C$(Crd) reflects late addition carbon from metasedimentary country rocks.

Carbon isotopes in evolved igneous rocks are in general poorly understood, partly because the low solubility of CO_2 makes measurement of $\delta^{13}C$ in magmatic volatiles from evolved rocks difficult (Blank and Brooker 1994). This question is especially important because of the recent report of graphite with $\delta^{13}C \approx -24‰$ included within a single 4.1 Ga Jack Hills detrital zircon (Bell et al. 2015), which is interpreted by the authors as possibly being evidence for life on the earliest Earth. These Hadean detrital zircons are thought to derive from granitoids that had supracrustal lithologies as part of their source rocks (Peck et al. 2001; Bell et al. 2015), and the possibility that ≥4.1 Ga precursor rocks contained organic carbon has exciting implications for the evolution of life. Graphitized organic carbon inherited from clastic metasediments should on average have $\delta^{13}C \approx -25‰$, but graphite precipitated from magmatic CO_2 could be measurably lower. The fractionation at 900–700 °C between CO_2 and graphite should be in the range of 5–8‰ (Deines and Eggler 2009; Fig. 1), meaning that the cordierite granite $\delta^{13}C$(Crd) ≈ –24‰ would be in equilibrium with $\delta^{13}C$(graphite) ≈ –32 to –29‰. More work remains to be done on the carbon isotope systematics of granitic magmas and the origin of reduced carbon in granitoids to better understand the graphite $\delta^{13}C$ reported by Bell et al. (2015) and potential future reports of graphite in Hadean zircons.

IMPLICATIONS

Carbon isotope studies have a clear role in understanding the deep carbon cycle, and isotope data are as often employed as a tool for recognizing igneous and metamorphic source materials and subsequent rock alteration. Untangling these different isotopic signatures relies in part on identifying phases that preserve the part of the rock's history that is of interest and are resistant to subsequent processes. One approach is to focus on refractory minerals that have very high closure temperatures to diffusion as a way to "see through" postmagmatic and metamorphic alteration, such as garnet and zircon (e.g., Peck et al. 2003; Lackey et al. 2011). This approach is difficult for carbon isotopes in common igneous and meta-igneous rocks. Carbon dioxide is a minor component in magmas, and carbon is typically present in igneous rocks only as trace carbonate and reduced carbon (Fuex and Baker 1973; Hoefs 1973). High-temperature graphite would meet the criteria of a refractory carbon-bearing phase, but is very rare in igneous rocks (Duke and Rumble 1986).

Cordierite has been shown to be able to retain peak metamorphic or magmatic volatiles (Vry et al. 1990; Harley et al. 2002; Rigby and Droop 2008), and thus allows carbon isotope analysis of trapped CO_2 even in rocks that do not contain another carbon-bearing mineral. Atmospheric pressure experiments of CO_2 diffusion rates in cordierite indicate relatively fast diffusion along channels, but the extent to which these experiments model geologic pressures and temperatures is unclear (Radica et al. 2016). Zoning in CO_2 concentrations in natural cordierite has not been observed using FTIR (e.g., Rigby et al. 2008; Della Ventura et al. 2009), and the bulk cordierite $\delta^{13}C$ data presented here and in previous studies point to relatively slow CO_2 diffusion. It has been proposed that alkali cations and CO_2 itself may occlude cordierite channels and retard volatile exchange (e.g., Vry et al. 1988), which might make alkali-rich igneous cordierites especially retentive of H_2O and CO_2. Zoning studies of CO_2 and $\delta^{13}C$ in cordierite-bearing rocks with different peak temperatures and cooling rates would be a welcome contribution to resolving some of these open questions and determining the effective closure temperature of carbon isotopes in cordierite. More work on the carbon isotope systematics of cordierite-bearing rocks would help better understand processes such as the carbon budgets of peraluminous granitic plutons and the bimodal distribution of $\delta^{13}C$(Crd) from igneous rocks documented in this study. It will also serve as an important benchmark in the search for further carbon isotope biomarkers in Hadean zircons (Bell et al. 2015).

High-temperature, refractory carbon-bearing phases are not common, but there has been success in analysis of carbonate in apatite (Peck and Tumpane 2007) and scapolite (Moecher et al. 1994). This general approach might yield interesting information when applied to uncommon C-bearing minerals, for example silicate-carbonate minerals such as harkerite, spurrite, or tilleyite in high-temperature contact metamorphic rocks, or cancrinite in silica-undersaturated granitoids. The feldspathoids in general may be fruitful to investigate, as they have been shown to trap measurable CO_2 in channel and cage-like structures of their crystal lattices (Della Ventura et al. 2008). Reconnaissance analysis of beryl showed that the $\delta^{13}C$ of channel CO_2 ranges from –25.8 to 2.3‰ (n = 22), but does not clearly correlate with rock type or gemstone classification (Peck and Dawson 2015). This kind of variability may reflect an obstacle in interpreting carbon isotope data from minerals with trace carbon, where there are not other phases present with which to assess isotope fractionation and the carbon budget of source rocks are not well constrained. A better understanding of how carbon isotopes are fractionated in metamorphic and especially igneous settings will allow better constraints on carbon budget of the crust and mantle.

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