This is a preprint, the final version is subject to change, of the American Mineralogist (MSA)
Cite as Authors (Year) Title. American Mineralogist, in press.
(DOI will not work until issue is live.) DOI: http://dx.doi.org/10.2138/am-2016-5767

Revision 1

Protolith carbon isotope ratios in cordierite from metamorphic and igneous rocks

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Abstract

Cordierite commonly contain 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±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 dataset, 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±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±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±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.

Introduction

Cordierite ($(Mg,Fe)_2[Al_4Si_5O_{18}]\bullet(H_2O,CO_2)$) 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 commonly used as an approach to constrain 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 co-existing 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) are suggestive preservation of pre-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 which typically have distinct carbon isotope ratios. These include S-type granitoids which are thought to originate from the melting of sediments (Chappell and White, 1992) and cordierite-gedrite gneisses and related rocks which 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 $\delta^{13}C$(cordierite)= -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 10s of milligrams for isotope analysis versus 15-20 μm spot analyses by FTIR. At the Huntly complex three orthopyroxene-bearing hornfels samples have $\delta^{13}C$(cordierite)= -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 $\delta^{13}C$(cordierite)= -21.89 to -15.07‰. Carbon contents for igneous-textured rocks are higher, and range from 0.41 to 0.49 wt% CO_2. This difference was not seen in the narrower 0.08 to 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 $\delta^{13}C$= -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 $\delta^{13}C$(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 eight 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 $\delta^{13}C$(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 $\delta^{13}C$(cordierite)= -24.08‰. Two metasedimentary samples from the contact aureole around the Cooma granodiorite (Australia) have $\delta^{13}C$(cordierite)= -26.05 and -12.41‰, while an sedimentary equivalent outside of the aureole has $\delta^{13}C$(whole-rock)= -30.80‰ (Fig. 2).

Discussion

Cordierite channel volatiles during metamorphism

A number of 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 aH_2O and aCO_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 $aH_2O \approx 1$ far from the contact to fluid-undersaturated with $aH_2O \approx 0.5$ 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 (grey). Petrologic evidence points towards 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 which 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 hornfelses 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 co-existing 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 unchanged. 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

276 exotic fluids (which would be consistent with other geochemical evidence), or perhaps
277 merely sedimentary variability in original $\delta^{13}C$. An inherent complication here is the
278 large range in organic carbon $\delta^{13}C$ in modern marine sediments: ca. -30 to -10‰,
279 although most are in the range -27 to -20‰ (Deines, 1980). However, preservation of
280 'typical' organic carbon $\delta^{13}C$ values in cordierite appears to be common in high-grade
281 pelitic metasedimentary rocks, and has been documented in several studies (Vry et al.,
282 1990; Santosh et al., 1993; Fitzsimons and Mattey, 1995; Korja et al., 1996; Bebout et al.,
283 2016). Especially telling of the preservation of protolith $\delta^{13}C$ are the very low $\delta^{13}C$
284 values of cordierite (and graphite) from Pikwitonei granulite domain (ca. -38 to -30‰),
285 which likely is a reflection of the anomalously low $\delta^{13}C$ carbon cycle excursion at ca. 2.7
286 Ga known from lower-grade Archean rocks (Vry et al., 1988; 1990).
287
288 **Protoliths of cordierite-gedrite gneisses**
289 Although many cordierite-bearing gneisses have $\delta^{13}C$(Crd) consistent with
290 sedimentary organic carbon, others have higher $\delta^{13}C$ values in the range -16.5 to -8.4‰
291 (n= 9; Vry et al., 1990; Bebout et al., 2016). These samples are from cordierite-
292 orthoamphibole (gedrite or anthophyllite) and related rocks, a group of schists or gneisses
293 similar to metapelites but with unusually Ca-poor and Mg and Al-rich bulk compositions
294 and typically lacking graphite. Some cordierite-gedrite localities have been ascribed to
295 Mg-rich sedimentary rocks (e.g. Reinhardt, 1987) or metasediments that have been
296 modified by melt extraction (e.g. Grant 1968), but the localities considered here have
297 been shown to have hydrothermally altered volcanic protoliths (e.g. chlorite-sericite-
298 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 ten 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 (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 ≤ ca. 250°C before high-grade metamorphism, while cordierite-gedrite rocks associated with the Manitouwadge VMS deposit have oxygen isotopes consistent with high temperature (≤ ca. 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 ($\delta^{13}C\approx0$) 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

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

357 Cordierite is a common accessory mineral in strongly peraluminous (mol Al_2O_3/
358 $Na_2O+K_2O+CaO > \sim 1.1$) granitoids (Miller, 1985; Chappell and White, 1992). In some
359 granites cordierite has been interpreted as being inherited from metasedimentary source
360 rocks of the granites or entrained as xenocrysts from country rocks, but for the most part
361 cordierite textures and mineral chemistry are consistent with being the result of formation
362 from melt (Chappell et al., 1987; Clarke, 1995; Erdmann et al., 2005). The samples
363 analyzed here (Table 3) range from small satellite plutons of larger batholiths (Cooma
364 and Cornucopia) through major phases of batholiths occupying thousands of square
365 kilometers (Kosciusko, South Mountain, South Bohemian Batholiths). Detailed
366 petrologic studies of these plutons document a magmatic origin for cordierite in a variety
367 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; Erdman et al., 2005; 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; Dienes, 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 versus 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

391 metasedimentary rock as carbon source materials for the granites (e.g. shales or
392 greywackes). Other metasedimentary rock-types have also been considered as possibly
393 being important parental source materials to peraluminous granitoids, for example marls
394 because of some similarities between the high CaO and Na_2O of these rocks and
395 Australian S-type granites (see Collins, 1996). The marine carbonate $\delta^{13}C \approx 0‰$ of marls
396 make them an unlikely source of carbon for cordierite granites.

397 The $\delta^{13}C$ measured from cordierite can not easily be compared to the intermediate
398 to felsic igneous source materials proposed as being parental to some peraluminous
399 granitoids (e.g. Miller, 1985), as the bulk $\delta^{13}C$ of this reservoir is not well constrained.
400 Wedepohl (1995) estimates that the average carbon content of continental metamorphic
401 rocks is ~800 ppm with $\delta^{13}C$= ca. -13‰, which does not does not match well the
402 cordierite granitoids $\delta^{13}C(Crd)$= -23.61±2.08‰, but is a closer match to the $\delta^{13}C(Crd)$= -
403 10.20±3.06‰ (n=6) measured by Vry et al. (1990) and Bebout et al. (2016) for cordierite
404 from small granite pegmatites. No cordierite-bearing pegmatites were sampled in this
405 study, but this distinctive lithology appears to be commonly derived from melting of
406 igneous source materials (Heinrich, 1950). At least some of these cordierite pegmatites
407 are associated with cordierite-gedrite gneisses (e.g. Schumacher, 1990), which (as shown
408 above) have a very similar $\delta^{13}C(Crd)$= -12.51±2.45‰.

409 The most straightforward interpretation of the bimodal distribution of igneous
410 cordierite carbon isotope ratios is that that the $\delta^{13}C(Crd)$= -10.20±3.06‰ measured from
411 cordierite pegmatites in other studies is indicative of orthogneiss or other igneous source
412 materials, while the $\delta^{13}C(Crd)$= -23.61±2.08‰ measured from the localities in Table 3
413 represent organic carbon from pelitic paragneiss or other clastic metasediments. For

414 some plutons, such as Australian S-type granites, sedimentary rocks are generally agreed
415 to be either the dominant (Chappell and White, 1992) or an important component in a
416 mixture of the granite source materials (Kemp and Hawkesworth, 2004). In the latter
417 model metasediment-derived melts would dominate the carbon budget of resulting
418 magmas when mixing with mantle-derived melts, explaining the sedimentary $\delta^{13}C$ of the
419 cordierite granites. Substantial sediments in the source materials and in some cases
420 assimilation of metasedimentary wall rocks are consistent with the petrologic
421 characteristics of the other granitoid plutons sampled in this study (Finger and Clemens,
422 1995; Erdman et al., 2005; Lackey et al., 2007; Antunes et al., 2008), save one body.
423 Johnson et al. (1997) propose that the composition of the Cornucopia Stock is best
424 explained by melting of mafic igneous lithologies in the lower crust. Excepting
425 carbonatites, detailed carbon isotope studies of continental igneous rocks are few and far
426 between (e.g. Duke and Rumble, 1986; Barnes et al., 2005), so there are clear open
427 questions of the importance of source materials versus later processes such as
428 assimilation or deuteric alteration on $\delta^{13}C$ in granites. It may be in that in this case small
429 amounts of metasedimentary rock in the source region dominate the carbon budget of the
430 Cornucopia Stock magma but did not make a large impact on major or trace element
431 geochemistry, or that low $\delta^{13}C$(Crd) reflects late addition carbon from metasedimentary
432 country rocks.

433 Carbon isotopes in evolved igneous rocks are in general poorly understood, partly
434 because the low solubility of CO_2 makes measurement of $\delta^{13}C$ in magmatic volatiles
435 from evolved rocks difficult (Blank and Brooker, 1994). This question is especially
436 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 $\delta^{13}C(Crd) \approx$ -24‰ would be in equilibrium with $\delta^{13}C(graphite) \approx$ -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 graphite in Hadean zircons.

Implications

Carbon isotope studies have a clear role for understanding the deep carbon cycle, and isotope data is as often employed as a tool for understanding 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 is present only in igneous rocks 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 models geologic pressures and temperatures is unclear (Radica et al., 2016). Zoning in CO_2 concentrations in natural cordierite it 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 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

483 important benchmark in the search for further carbon isotope biomarkers in Hadean
484 zircons (Bell et al., 2015).

485 High-temperature, refractory carbon-bearing phases are not common, but there
486 has been success in analysis of carbonate in apatite (Peck and Tumpane, 2007) and
487 scapolite (Moecher et al., 1994). This general approach might yield interesting
488 information when applied to uncommon C-bearing minerals, for example silicate-
489 carbonate minerals such as harkerite, spurrite, or tilleyite in high-temperature contact
490 metamorphic rocks, or cancrinite in silica-undersaturated granitoids. The feldspathoids in
491 general may be fruitful to investigate, as they have been shown to trap measurable CO_2 in
492 channel and cage-like structures of their crystal lattices (Della Ventura et al., 2008).
493 Reconnaissance analysis of beryl showed that the $\delta^{13}C$ of channel CO_2 ranges from -25.8
494 to 2.3‰ (n= 22), but does not clearly correlate with rock type or gemstone classification
495 scheme (Peck and Dawson, 2015). This kind of variability may reflect an obstacle in
496 interpreting the carbon isotope data from minerals with trace carbon, where there are not
497 other phases present with which to assess isotope fractionation and the carbon budget of
498 source rocks are not well constrained. A better understanding of how carbon isotopes are
499 fractionated in metamorphic and especially igneous settings will allow a better
500 understanding of the carbon budget of the crust and mantle.
501

502 **Acknowledgements**

503 In the early days of this project the late Bruce Chappell and Ian Williams very
504 generously took me on a field trip to collect S-type granites in the Lachlan Fold Belt,
505 which I gratefully acknowledge. I also thank Margarida Antunes, D. Barrie Clarke, Giles

Droop, Brent Elliott, Friedrich Finger, Kenneth Johnson, and Michael MacDonald for providing cordierite-bearing rocks for this study, as well as colleagues who donated samples that were not ultimately used. The use of samples that were analyzed for CO_2 and H_2O contents using FTIR by Giles Droop and Martin Rigby is especially recognized. Simon Harley and John Valley are thanked for their thoughtful reviews, which improved the manuscript. Acquisition of the mass spectrometer at Colgate University was supported by NSF (EAR-0216179).

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Figure Captions

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 (2001).

Figure 2. Carbon isotope analyses of cordierite (Crd) from analyzed samples (black and grey) 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). Grey 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 (grey). '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. Grey= mylonitic paragneiss, Bohemian Massif.

724

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

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734 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

735 Note: Distance to the Etive igneous complex given parentheses. The upper and lower

736 spinel zones are separated by the melt-in isograd (Rigby et al., 2008).

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743 Table 2. Carbon isotopes of cordierite from cordierite-gedrite gneisses.
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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

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747 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	*	Chappell and White, 1976

748 Note: SMB= South Mountain Batholith. * Whole-rock analysis

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Cite as Authors (Year) Title. American Mineralogist, in press.
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Figure 1

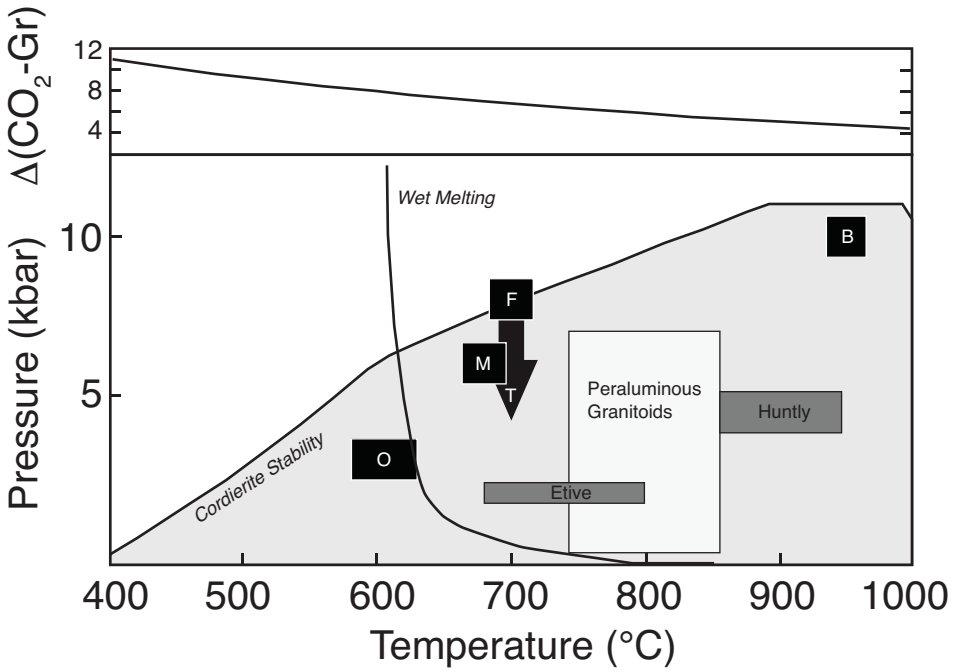

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Figure 2

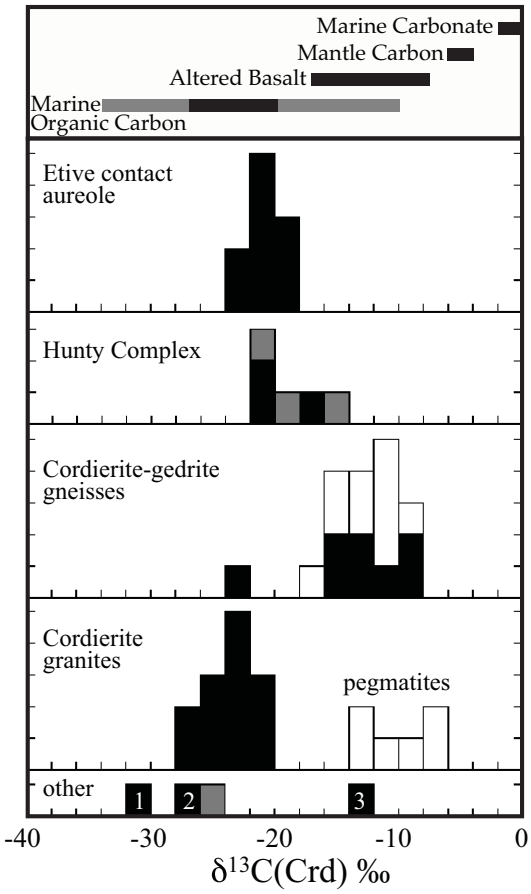

Figure 3