Protolith carbon isotope ratios in cordierite from metamorphic and igneous rocks

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ABSTRACT

Cordierite commonly contains \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) 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 \( \text{CO}_2 \). Cordierite \( \text{CO}_2 \) from pelitic country rocks in the Etive aureole have \( \delta^{13}\text{C} \) values of \(-20.70 \pm 1.27\%o \) (\( n = 10 \)) that are unaffected by a ca. 150 °C thermal gradient and fluid-saturated and undersaturated regimes. These \( \delta^{13}\text{C} \) 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 \( \delta^{13}\text{C} \) 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 \( \delta^{13}\text{C}(\text{Crd}) = -12.51 \pm 2.45\%o \) (\( n = 17 \)). These isotope ratios are higher than those of cordierite in typical metasedimentary protoliths and are similar 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 \( \delta^{13}\text{C} = -23.61 \pm 2.08\%o \) (\( n = 13 \)), 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 \( \delta^{13}\text{C}(\text{Crd}) = -10.20 \pm 3.06\%o \) (\( n = 6 \)), which may indicate derivation from orthognerous 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 \( \delta^{13}\text{C} \) is preserved in granitoids is important for understanding the deep carbon cycle, and could serve as an important constraint in the search for low-\( \delta^{13}\text{C} \) 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 \([\text{Mg,Fe}_2][\text{Al}_5\text{Si}_3\text{O}_{10}(\text{OH})]\) 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 \( \text{H}_2\text{O} \) and \( \text{CO}_2 \), 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 \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) 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 \( \text{CO}_2 \) have been measured in several studies (Armburer 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 \( \text{CO}_2 \)-rich metamorphic fluid (Armburer et al. 1982; Santosh et al. 1993). At other localities \( \delta^{13}\text{C}(\text{Crd}) \) 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 \( \text{CO}_2 \) and coexisting graphite (Vry et al. 1990; Fitzsimons and Mattey 1995). Finally, variations in carbon isotopes of cordierite \( \text{CO}_2 \) from different localities in the Pikwitonei granulite domain (Superior Province, Canada) and Brattstrand Bluffs (East Antarctica) suggest preservation of pre-

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