

KECK GEOLOGY CONSORTIUM

**PROCEEDINGS OF THE TWENTY-FIFTH
ANNUAL KECK RESEARCH SYMPOSIUM IN
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Keck Geology Consortium: Projects 2011-2012
Short Contributions— Grenville Province, Ontario Project

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CARBON ISOTOPE THERMOMETRY IN THE CENTRAL METASEDIMENTARY BELT BOUNDARY THRUST ZONE GRENVILLE PROVINCE, ONTARIO

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Research Advisor: William H. Peck

INTRODUCTION

The Mesoproterozoic Grenville Province in Ontario consists of two major belts, the Central Gneiss Belt (CGB) in the west and the Central Metasedimentary Belt (CMB) in the east (Streepey et al. 1997). The CMB is a compilation of domains that range in age from 1.4 -1.16 Ga (Hanmer et al. 2000 and references therein), and have a key role in geologic history of the Laurentian margin. The CGB and CMB are separated in southern Ontario (Fig.1) by the Central Metasedimentary Belt boundary thrust zone (CMBbtz) (Hanmer et al. 2000). The CMBbtz borders (or includes, in some reconstructions) the westernmost Bancroft Terrane, which borders the Elzevir Terrane in the east. The CMBbtz, Bancroft Terrane, and the western Elzevir Terrane were all metamorphosed to the amphibolites facies.

This study reports the stable isotope composition of marbles from the westernmost edge of the Elzevir Terrane through the Bancroft Terrane and the CMBbtz. Ratios of $^{13}\text{C}/^{12}\text{C}$ of calcite (reported using standard $\delta^{13}\text{C}$ -notation relative to PDB) are used to derive the relationship between carbonate depositions of these three areas. Carbon isotope thermometry also is attempted using the Calcite-Graphite thermometer. The goal of these approaches is to attain a better understanding of the geologic history of these terranes and to fill in thermometry that has been sparse in the area.

Almost no calcite-graphite thermometry data has been published from the Bancroft Terrane with the exception of van der Pluijm and Carlson (1989) whose data range from temperatures between 650-765°C when the thermometer from Kitchen and Valley (1995) is applied. Streepey et al. (1997) compiled thermometry data for the CMB. These data include a significant portion of the Elzevir Terrane, however there

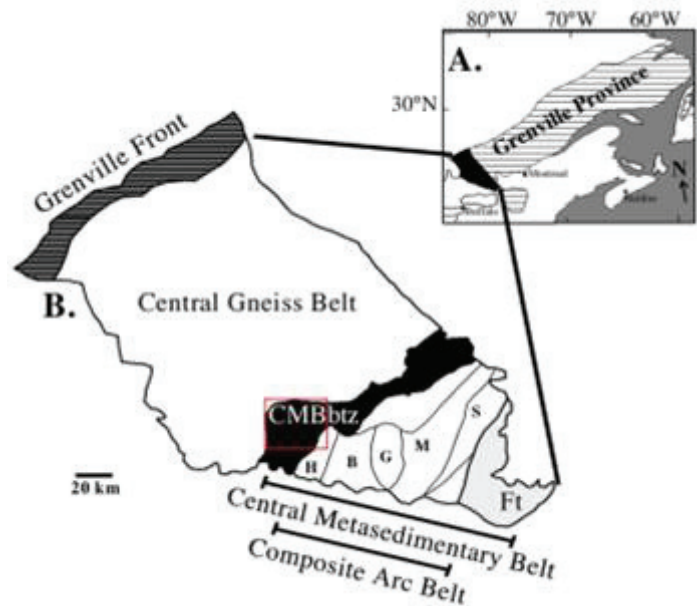


Figure. 1. A. Location map of the Grenville Province. B. The southern Grenville Province of Ontario, after Hanmer and McEachern (1992). The red box signifies the study area. CMBbtz, Central Metasedimentary Belt boundary thrust zone; Sub-divisions of the Elzevir terrane: the Harvey-Cardiff (H), Belmont (B), Grimsthorpe (G), Mazinaw (M), and Sharbot Lake (S) domains after Easton (1992). Ft= Frontenac terrane.

are very few data points west of the Bancroft Shear Zone (BSZ). What data is present west of the BSZ have a range of 650-750°C. The Elzevir Terrane has been shown by Dunn and Valley (1992), Rathmell et al. (1999), and Dunn (2005) to feature an increasing temperature trend towards the northwest (approaching the Bancroft Terrane) reaching temperatures of approximately 650°C approximately 20 km east/south-east of the data presented here. This study extends calcite-graphite thermometry further to the northwest and uses the stable isotopes of marbles to help constrain the relationship of marbles in the Bancroft and Elzevir Terranes.

GEOLOGIC HISTORY

The Southern Grenville Province in Ontario is divided into the CGB and the CMB. The CGB is a domain of pre-1400 Ma rocks that are attributed to the Laurentian craton (Timmerman et al. 1997, Hanmer et al. 2000). The CGB is composed primarily of orthogneiss (Peck and Smith 2005) and other high grade metamorphic rocks. It is debated as to how the CGB and CMB relate to one another. The literature shows two prevailing thoughts on this relationship. Carr et al. (2000) believe that the CMB consists of a group of island arcs and associated basins accreted onto the continent. In contrast, Hanmer et al. (2000) see the CMB as representing back arc and rift basins that were always part of the Laurentian margin. Even the premise of a large thrust fault separating the two is debated (Timmerman et al. 1997).

The CMBbtz is composed of annealed marble tectonites surrounding plutonic thrust sheets along with mylonites and syenites (Peck and Smith 2005, Hanmer et al. 2000). The Bancroft Terrane similarly contains a sequence of marbles, calc-silicate rocks, and breccias but has a notable lack of the plutonic rocks closer to the CMBbtz (Hanmer et al. 2000). It borders the Elzevir Terrane to the east by means of the Bancroft Shear Zone (BSZ). The BSZ is suggested by Streepey et al. (1997) to separate rocks of the Bancroft Terrane with ^{40}Ar - ^{39}Ar hornblende cooling ages

of ~1021-1026 Ma from those of the Elzevir Terrane with cooling ages of 959-989 Ma. The Elzevir Terrane contains other metasedimentary rocks in addition to many intrusive bodies such as the Cheddar Dome granitic gneiss (Sendek, this volume).

Samples from all terranes are dominated by calcite, pyroxene, feldspar, and phlogopite. The outcrops from the Bancroft and Elzevir Terranes are very similar, with the most notable difference being the lack of marble breccias in the Elzevir Terrane. Marbles in outcrop often are found near other calc-silicates and sometimes have a weathered rind.

CMBbtz and Bancroft Terrane

In the westernmost CMBbtz/Bancroft Terrane, marbles surround dismembered igneous thrust sheets, such as the Allsaw anorthosite (Marshall, this volume) and the Dysart and Redstone thrust sheets (Agustsson, this volume). Marble in this area is mainly a tectonic breccia (Fig. 2) that frequently contains large amounts of dolomite, diopside and, rarely, fine-grained graphite in thin bands. Some samples adjacent to the thrust sheets contain apatite and retrograde talc. The marble breccias are evidence of the large amounts of deformation in the area.

Progressing east, the marbles become predominately present in large outcrops with less breccias present.



Fig. 2. An outcrop from the Bancroft Terrane. This outcrop shows a marble breccia that was sampled. Rock hammer for scale.



Fig.3. This sample (11BM31) is a typical hand sample of marble collected. Note the white calcite and presence of graphite and silicates. Weathered rinds were removed and not analyzed. Field notebook for scale.

These contain primarily calcite with many calc-silicates present. Pyroxenes, especially diopside, and large flakes of graphite are also present in these samples.

Peck and Smith (2005) have used REE analysis and Neodymium isotopes of cordierite-gedrite rocks from the Bancroft Terrane and found them similar to the Tudor volcanics of the Belmont Domain (Elzevir Terrane). This argues for a grouping of the Bancroft Terrane with the Elzevir Terrane. However, a major argument against this grouping is the general lack of volcanic rocks in the Bancroft Terrane compared to the Elzevir except for in the westernmost CMBbtz near the tonalitic thrust sheets, where they are only in tectonic contact with the local marble (Carr et al. 2000).

Elzevir Terrane

The Elzevir Terrane is composed of three smaller domains (Rathmell et al. 1999, Hanmer et al. 2000)

however this study focuses on the Harvey-Cardiff Domain. The area is thought to be a back arc basin by Hanmer et al. (2000) having accreted 1.34 billion years ago onto Laurentia. The study area is dominated nearby by the plutonic Harvey-Cardiff domain (lying just east of most sample sites). The marbles here frequently are calcite dominated with graphite which is finer-grained than in the Bancroft Terrane, but still visible via hand lens.

CALCITE-GRAPHITE THERMOMETRY

The calcite-graphite carbon isotope thermometer is ideal for use in the CMB because graphite-bearing marble occurs widely throughout the region. The thermometer calculates the temperature using the ratio of ^{12}C to ^{13}C in both the calcite and graphite, where $\Delta_{\text{cal-gr}}$ is a function of temperature. The graphite is resistant to retrograde exchange as its self-diffusion is extremely slow (Dunn 2005), making it an ideal candidate for a thermometer. The thermometer has been carefully calibrated by Kitchen and Valley (1995) by compari-

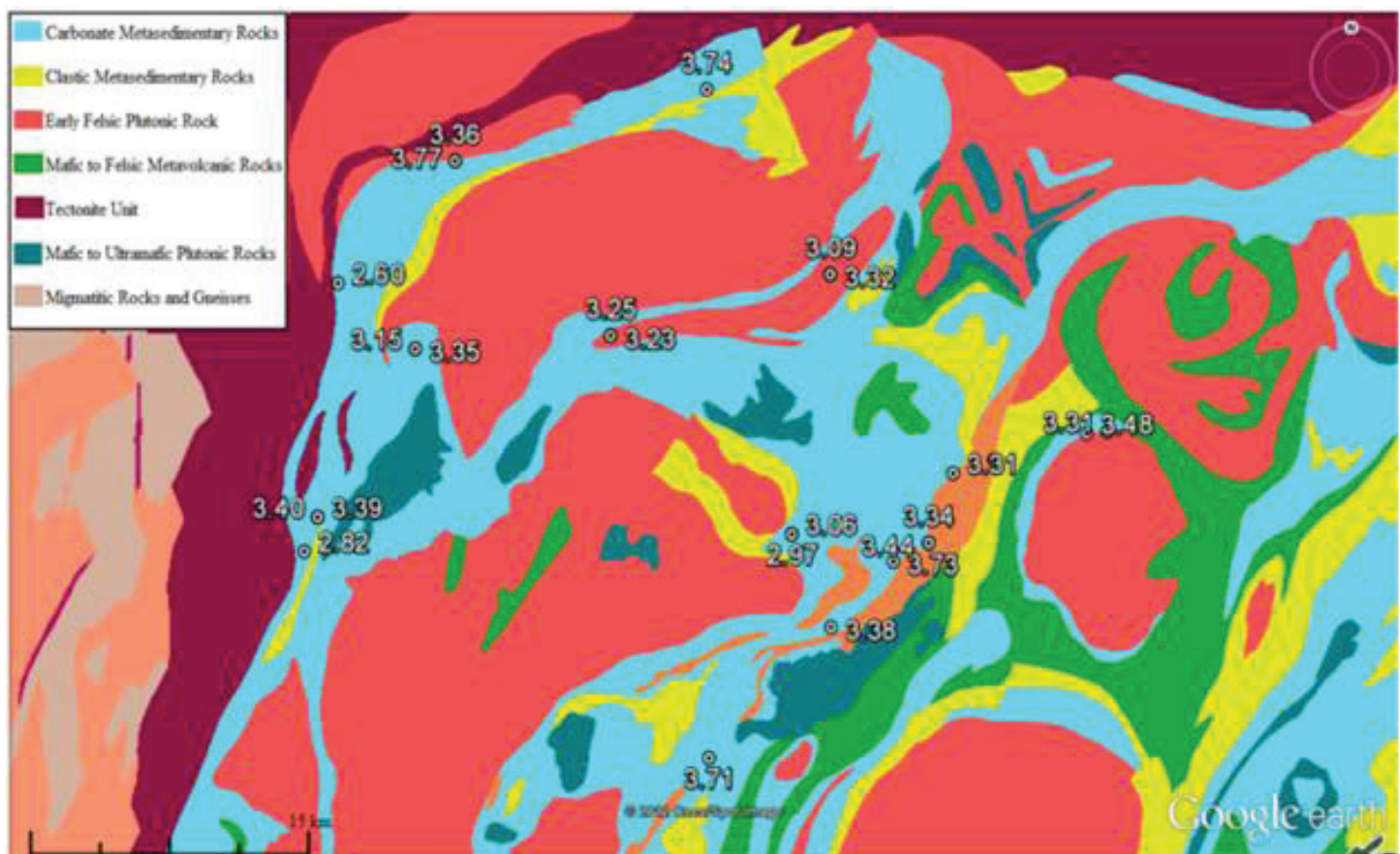


Fig. 4. The $\Delta^{13}\text{C}(\text{cal-gr})$ across the study area plotted on Google Earth with an Ontario Geologic Survey map overlay. The tectonite unit on the left represents the CGB border. The $\Delta^{13}\text{C}(\text{cal-gr})$ of the terranes are extremely similar with no trends in any potential transects.

son to cation thermometers in the Adirondack region of the Grenville Province. Rathmell et al. (1999) and Dunn (2005) found that the calcite-graphite thermometer records temperature variations concurrent with these other thermometers and estimate its reproducibility to $\pm 25^\circ\text{C}$. The calibration of Kitchen and Valley (1995) ($\Delta^{13}\text{C}(\text{cal-gr}) = 3.56 \times 10^{-6} T^2 (\text{K})$) is applied for samples in this study.

METHODS

Sixty-one samples of marble were collected from 30 sites in the CMBbtz, Bancroft Terrane, and Elzevir Terrane containing calcite and visible flakes of graphite. Twenty-four samples were chosen for isotopic analysis based upon mineral composition and location (Fig. 3). Twenty samples were chosen for petrographic analysis. For isotope analysis, 1cm^3 pieces were gently ground in a steel mortar and pestle, and examined using a binocular microscope. Clear calcite and shiny euhedral graphite flakes that showed no secondary overgrowth were hand-picked. For Elemental Analyzer analysis, $\sim 0.2\text{ mg}$ graphite (usually

two or three flakes) was loaded into tin capsules with 10x their weight in CuO . Colgate Standard Graphite (CSG-1) was used to standardize each analysis session.

Calcite samples (5-10 mg) including CCA-1 (Colgate University's calcite standard) were loaded into Y-shaped glass vacuum vessels with phosphoric acid. These were evacuated and heated to 50°C in a bath of antifreeze and water, and then reacted. The CO_2 was isolated and purified on the vacuum line and analyzed using a Delta Plus Advantage Stable Isotope Mass Spectrometer. CCA-1 ties the two methods isotope scales.

CCA-1 analyzed using phosphoric acid had an average $\delta^{13}\text{C}$ value of $-18.36 \pm 0.03\text{‰}$ ($n=5$) on five different days. CCA-1 analyzed using the EA had a $\delta^{13}\text{C}$ value of $-18.36 \pm 0.05\text{‰}$ ($n=4$). NBS-19 analyzed using phosphoric acid had an average $\delta^{13}\text{C}$ of $2.00 \pm 0.02\text{‰}$ ($n=3$). NBS-19 analyzed using the EA had a $\delta^{13}\text{C}$ $2.02 \pm 0.06\text{‰}$ ($n=4$), which compares well with the known value of this standard (1.95‰).

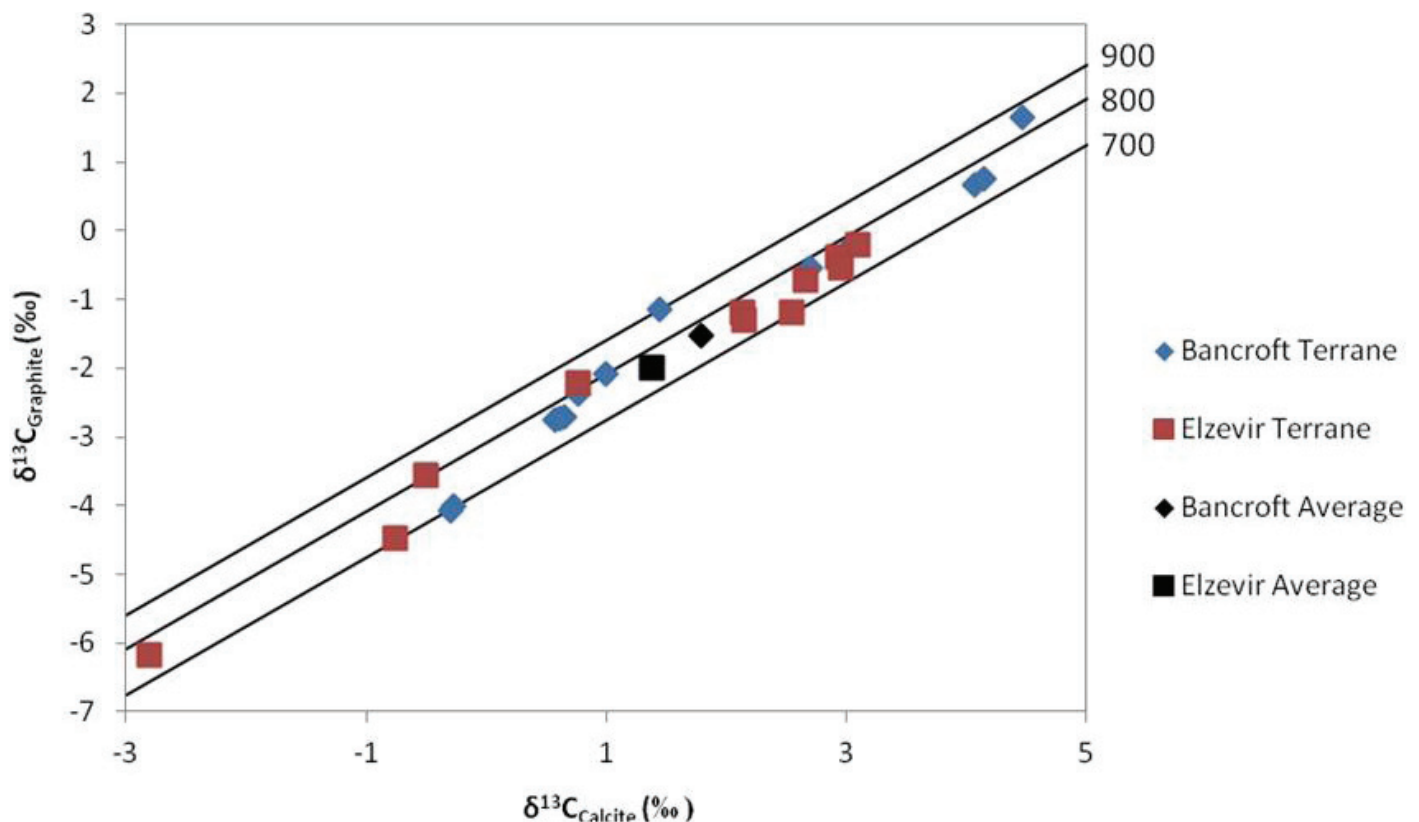


Fig. 5. A plot comparing the $\delta^{13}\text{C}$ of calcite and graphite of the 24 samples in this study. The averages for each terrane are in solid black. Note the close proximity of the average $\delta^{13}\text{C}$ Calcite- $\delta^{13}\text{C}$ Graphite of the Bancroft and Elzevir Terranes.

USGS-24 analyzed using the EA had a $\delta^{13}\text{C}$ value of $-15.86 \pm 0.11\text{‰}$ ($n=4$), which also compares well with the known value of this standard (-16.05‰). Five calcite samples were analyzed using both phosphoric acid and EA to check the cross-calibration of these methods. The $\delta^{13}\text{C}$ of these samples ranges from -0.48‰ to 4.04‰ , and reproducibility between these methods ranged from $\pm 0.04\text{‰}$ to $\pm 0.18\text{‰}$.

RESULTS

The average precision of the 24 samples run in triplicate was 0.12‰ (1σ) for graphite run in the EA. Only one sample had an uncertainty greater than 0.40‰ (11BM7: 0.42‰) and without this sample the average uncertainty was $\pm 0.10\text{‰}$. The samples had an average $\Delta^{13}\text{C}(\text{Cal-Gr})$ of $3.35\text{‰} \pm 0.24\text{‰}$ ($n=24$), ranging from 2.6‰ to 3.77‰ (Fig. 4). The $\delta^{13}\text{C}_{\text{Calcite}}$ ranged from -2.8‰ to 4.46‰ while the $\delta^{13}\text{C}_{\text{Graphite}}$ ranged from -6.18‰ to 1.64‰ . The Bancroft Terrane had $\delta^{13}\text{C}_{\text{Calcite}}$ values ranging from -0.03‰ to 4.46‰ (average: 1.79‰) while the $\delta^{13}\text{C}_{\text{Graphite}}$ ranged from -4.07‰ to 1.64‰ (average: -1.53‰). The Elzevir had similar values with $\delta^{13}\text{C}_{\text{Calcite}}$ ranging from -2.8‰ to 2.95‰ (average: 1.38‰) while the $\delta^{13}\text{C}_{\text{Graphite}}$ ranged from -6.18‰ to -0.21‰ (average: -1.99‰) (Fig. 5).

Using the calibration of Kitchen and Valley, $\Delta^{13}\text{C}(\text{Cal-Gr})$ values measured in this study produce temperatures that are slightly high, given the upper amphibolite facies mineral assemblages reported and observed in this area. The average temperature is $760 \pm 37^\circ\text{C}$ ($n=24$) for all the samples. The Bancroft Terrane (and CMBbtz) has an average of $765 \pm 40^\circ\text{C}$ ($n=13$) and the Elzevir Terrane has an average of $755 \pm 35^\circ\text{C}$ ($n=11$).

DISCUSSION

In most of the rocks examined, calcite is the dominant carbon-bearing mineral, with graphite in trace amounts ($<3\%$). Thus, $\delta^{13}\text{C}$ of calcite approximates whole-rock $\delta^{13}\text{C}$ in these rocks, which is inherited from primary deposition. Similar $\delta^{13}\text{C}$ of the calcites in both the Bancroft and Elzevir Terranes suggest a similar depositional history. The $\delta^{13}\text{C}$ values found in this study are very similar to $\delta^{13}\text{C}$ values found in both Rathmell et al. (1999) of -3.60 to 5.97‰ and

Dunn (2005) of -2.24 to 6.17‰ , studies focused on other parts of the Elzevir Terrane.

These studies found an increasing temperature trend to the northwest, approaching this study area. However, those temperatures, and the temperatures found in Streepey et al. (1997) suggest that the temperatures found in this study are approximately $50\text{--}75^\circ\text{C}$ higher than expected, and similarly higher than temperatures found by Nesbit (this volume) in the southern portion of the Bancroft Terrane.

The consistency in the multiple analyses suggests that regional trends in $\Delta^{13}\text{C}(\text{Cal-Gr})$ are correct. Such a strong similarity in $\delta^{13}\text{C}$ values for calcite for both terranes, and sharing unusually high $\delta^{13}\text{C}$ values compared to other Grenville marbles, suggest that these two terranes are very similar geologically and underwent similar metamorphic histories, even though the Bancroft Terrane lacks the volcanic rocks of the Elzevir Terrane (Fig. 5). Based on this data, this study suggests that the Bancroft Terrane should be grouped with the Elzevir Terrane in geologic interpretations (Hanmer et al. 2000, Peck and Smith 2005) in contrast to it representing a different depositional environment associated with the Central Gneiss Belt (Carr et al. 2000). This interpretation adds credence to geologic history presented in studies where the Bancroft Terrane and CMBbtz represent a back arc basin on the Laurentian Craton (Hanmer et al. 2000).

CONCLUSIONS

In summary, the average $\Delta^{13}\text{C}(\text{Cal-Gr})$ recorded in the Bancroft and Elzevir Terranes is $3.35 \pm 0.24\text{‰}$. Using the calibration of Kitchen and Valley (1995) this indicates an average temperature of $760 \pm 37^\circ\text{C}$. While this is higher than expected from extrapolating regional thermometry reported previously in the literature (Streepey et al. 1997, Rathmell et al. 1999, Dunn 2005), consistency in $\Delta^{13}\text{C}(\text{Cal-Gr})$ across a range of $\delta^{13}\text{C}_{\text{Calcite}}$ suggest that isotopic data is reflective of regional temperature variation. Measured $\delta^{13}\text{C}_{\text{Calcite}}$ values show a similarity between the Bancroft and Elzevir Terranes consistent with similar depositional environments of marble protoliths. The common values allow a similar geologic history between the two terranes. More work is required in

the region with both calcite-graphite thermometry and other thermometers to confirm these results.

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