U–TH–PB MONAZITE CONSTRAINTS ON THE TIMING OF PALEOPROTEROZOIC METAMORPHISM IN BIG THOMPSON CANYON, COLORADO FRONT RANGE

by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirement for the degree of Master of Science (Geology).

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ABSTRACT

Paleoproterozoic supracrustal rocks in Big Thompson Canyon (BTC), Colorado Front Range, are some of the oldest known regionally metamorphosed rocks that record a coherent isograd sequence (Mahan et al., 2013). Regionally metamorphosed rocks are able to keep a usable record of island and continental arc accretion, crustal thickening, and burial metamorphism (Mahan et al., 2013). Metapelites from Big Thompson Canyon allow for a rare opportunity to constrain the pressure–temperature–time (P–T–t) evolution in this region of the Colorado Front Range.

Petrographic characterization was performed on twenty-seven metapelites collected from the biotite/garnet-, staurolite-, andalusite-, sillimanite-, and K-feldspar-zones in Big Thompson Canyon. Bright-phase element mapping using automated mineralogy of ten key samples confirmed the presence of monazite in four of the five isograd zones in this study. Bulk-rock geochemical data in combination with high-precision, phase diagram-based thermobarometry for all five isograd zones was used to determine the conditions of peak metamorphism and the relative stability of mineral assemblages as functions of P and T conditions for each zone.

To better understand monazite intra-grain compositions, and their relationships to calculated ages, detailed element mapping of U, Th, Pb, Ce, and Y using an electron probe microanalyzer (EPMA) was performed. Using the element maps of monazites, specific data point locations were chosen from each monazite to perform geochronology. U–Th–Pb_{total} in–situ monazite geochronology results using the EPMA show that there are two distinct compositional age groupings. One of these age groupings is within the Mazatzal Orogeny (~1.7–1.6 Ga) and the second is within the Granit-Rhyolite Province or Picuris Orogeny (~1.4–1.3 Ga).

Phase-diagram based thermobarometry yielded an upward progression of P–T conditions from east to west through Big Thompson Canyon. Metamorphic conditions are estimated to be ~420–550 °C and >2–4.5 kbar for lower grade isograd zones (biotite/garnet) and increase up to ~560–735 °C and ~2.8–8.8 kbar for the highest grade isograd zone (K-feldspar). Therefore, there is an estimated upward P–T progression from east to west in BTC of ~420–735 °C and >2–8.8 kbar.
Based on the progression of isograd zones through P–T space and all isograd zones yielding ages within the Mazatzal Orogeny, it can be concluded that this metamorphic event was regional style metamorphism. On the other hand, two of the five isograd zones yielded compositional ages that align with the Picuris Orogeny. These ages that fall into the much further south Picuris Orogeny may be the result of proximal magmatism that caused intrusions, crustal underplating and melting in the same region as Big Thompson Canyon.
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CHAPTER ONE

INTRODUCTION

1.1 Implications of regional style metamorphism

Metamorphic rocks can be used to examine plate tectonic processes, including the rates, durations and styles of mountain building (orogenesis) at convergent plate margins. Phanerozoic orogens, such as the Andes and Himalaya, have been studied in detail owing to their ongoing deformation and good exposure. However, older examples from the Proterozoic and Archean are classically more difficult to interpret because of later deformation and/or metamorphism. Having multiple metamorphic events in a single region may overprint and obscure the primary structures and metamorphic assemblages of the rocks. Colorado and its surrounding states preserve evidence of several orogenic episodes since c. 2 Ga, many of which are related to arc–continent and continent–continent accretion to the southern margin of the Archean Wyoming craton. Big Thompson Canyon (BTC), located in northern Colorado, exposes a wide variety of sedimentary and volcanic rocks that were metamorphosed during arc–continent collision associated with Yavapai (~1.8–1.7 Ga) and/or Mazatzal (~1.7–1.6 Ga) orogenic events (e.g. Mahan et al., 2013 and references therein). The suture zone between these two orogenic events is not well defined, leaving a large ~300 km transition zone between both provinces. To further skew the deformation history of this region, some past studies have reported monazite with c. 1.4 Ga ages (Shah and Bell, 2012). The significance of these studies is uncertain, but may be related to the recently discovered, cryptic Picuris Orogeny (~1.4 Ga) of the same age. The Picuris Orogeny may be the cause of overprinting in the Yavapai and/or Mazatzal metamorphic rocks as far north in Colorado as BTC.

1.2 Role of monazite within metamorphic rocks

Monazite is a common accessory mineral in metapelites and metapsammites and is invaluable in constraining the timing and rates of tectonometamorphic processes such as regional metamorphism (Štípská et al., 2015). Monazite grains often contain overgrowths that correspond
to a variety of potential processes, such as prograde or retrograde metamorphic reactions, or deformation events (Štípská et al., 2015). In addition, monazite composition is sensitive to the coexisting major-mineral assemblage at the time of growth during metamorphism (Rocha et al., 2017). This compositional sensitivity allows for integrated petrographic, geochemical and thermobarometric information to place high-resolution constraints on the pressure–temperature ($P$–$T$) evolution of a rock.

1.3 Project objectives and implications

I have conducted a field campaign in BTC with the aim of investigating in detail the nature of this reported c. 1.4 Ga orogenic event (Picuris Orogeny). I will aim to determine whether it represents a pervasive overprint of all units within BTC, or if it is localized in specific regions, isograd zones or lithologies. This data will have been integrated with new petrographic observations, field measurements, whole-rock and mineral geochemistry, and thermobarometry to place new constraints on the $P$–$T$ evolution of BTC metasediments.

There are two key research objectives for this study, which have implications for both BTC and the surrounding regions of the Colorado Front Range:

- Constrain the $P$–$T$ conditions of metamorphism of monazite-bearing metasediment rocks within Big Thompson Canyon
- Identify the age of metamorphism in different isograd zones across Big Thompson Canyon, with the aim of identifying the existence (or not) of the cryptic Picuris Orogeny and how it affected this region.
CHAPTER TWO

GEOLOGIC BACKGROUND

The Colorado Front Range preserves a complex history of metamorphism, magmatism, deformation and continental growth (Condie and Martell, 1983). The aluminous metasedimentary rocks of Big Thompson Canyon retain a clear record of Barrovian-style metamorphism, with metamorphic grades increasing from biotite all the way to migmatite from east to west (Mahan et al. 2013). Big Thompson Canyon is located within the Yavapai Province (~1.8-1.7 Ga), a primary block associated with the southward growth of North America.

2.1 Structural History of the Colorado Front Range

The geology of Colorado and neighboring states records an ancient period of supercontinent growth during the Proterozoic. This growth is the product of a combination of juvenile island arc and continental arc terranes accreting to the southern margin of Laurentia. This study focuses on the basement rocks in north-central Colorado that document the southward growth of Laurentia from ~1.8 to 1.0 Ga (Mahan et al., 2013). This >1000-km-wide domain, commonly referred to as the Colorado Province, is composed of five major tectonostratigraphic belts/provinces: the Mojave (~2.4–1.7 Ga), the Yavapai (~1.8–1.7 Ga), the Mazatzal (~1.7–1.6 Ga), the Granite–Rhyolite or Picuris (~1.5–1.3 Ga), and finally the Grenville (~1.3–1.0 Ga) (Figure 2.1). Each of these domains is hypothesized to represent a discrete fragment of continental lithosphere that was sequentially accreted to the growing southern margin of Laurentia during this period.

There is a clear distinction between the Archean Wyoming craton to the north and the Proterozoic provinces that lie to the south. The well-defined suture that divides these domains along the state line of Colorado and Wyoming is the Cheyenne Belt (Medicine Bow Orogeny, ~1.78–1.75 Ga) in Southern Wyoming (Karlstrom and Houston, 1984, Chamberlain, 1998). Other boundaries that exist
between provinces are more diffuse, such as that between the Yavapai and Mazatzal provinces. Previous mapping of structural features in this region has revealed a 300-km-wide transition zone where the boundary between these provinces lies (Shaw and Karlstrom, 1999). This northeastward trending transition zone has been defined by geochemical, geochronological and xenolith data, and runs through northern New Mexico and into Colorado (Shaw and Karlstrom, 1999). Although there is no clearly defined suture zone between the Yavapai and Mazatzal provinces, Big Thompson Canyon lies demonstrably in the Yavapai Province (Figure 2.1).

2.2 Geology of Big Thompson Canyon

Big Thompson Canyon is dominated by alternating ~1.7-1.8 Ga pelitic and psammitic layered metasedimentary and metavolcanics rocks, which include pelitic phyllite, schist, meta-conglomerate, quartzite, quartzofeldspathic gneiss, minor amphibolite and calc-silicate schist (Mahan et al. 2013) (Figure 2.2).
During the time of accretion and growth of these northward moving domains into the southern margin of the Wyoming craton, there was also a significant amount of intrusive activity. Important intrusive suites within BTC include the Routt Plutonic Suite (~1.7 Ga) and the Berthoud Plutonic Suite (~1.4 Ga) (Mahan et al. 2013).

The Routt Plutonic Suite has a composition ranging from monzogranite to tonalite/trondhjemite, and includes the Boulder Creek Granodiorite (1714 ± 5 Ma) and the Palisade tonalite/trondhjemite intrusion (1726 ± 15 Ma) (Mahan et al., 2013). In Big Thompson Canyon, the Berthoud Plutonic Suite comprises batholiths of “Silver Plume-type” granite, granodiorite, quartz diorite and pegmatite (Mahan et al., 2013). “Silver Plume-type” intrusions form irregular batholiths, ovoid plutons and dikes (Boos and Boos, 1934). The largest intrusive body is the Longs Peak-St Vrain batholith, which consists of a mica-rich monzogranite to syenogranite (Mahan et al., 2013). The Canyon also has a large amount of muscovite-bearing alkali-feldspar granite pegmatite dike and sills that include minerals such as biotite, tourmaline, garnet and beryl (Mahan et al., 2013).

Paleoproterozoic (c. 1.75–1.68 Ga) supracrustal rocks in BTC are some of the oldest known regionally metamorphosed rocks containing a coherent, mappable isograd sequence (Mahan et al., 2013). This sequence of mappable mineral isograds may be a usable record of arc accretion, crustal thickening, and burial metamorphism during the Proterozoic (Mahan et al., 2013). At lower metamorphic grades within the canyon, well preserved turbidite sequences display graded bedding, cross-bedding and scour and fill structures (Condie and Martel 1983). These features describe a depositional setting congruent with a continental shelf or a reworked sub-marine fan in a foreland setting (Condie and Martel 1983). The mappable isograd sequence within this canyon displays an increasing metamorphic grade from east to west. Isograd zones comprise of biotite-, garnet-, staurolite-, andalusite-, sillimanite-, K-feldspar-, and migmatite zones (Mahan et al., 2013). Nesse (1984) suggests that these isograd zones define a set of synformal surfaces whose axis plunges eastward, although other researchers suggest that this region has experienced multiple stages of metamorphism and deformation (e.g. Shah and Bell, 2012). The canyon also has kilometer scale isoclinal folding and is bound to the north by the Buckhorn Creek kilometer-scale ductile shear zone and by the Moose Mountain shear zone to the south (Cavosie and Selverstone., 2003).
Figure 2.2 Simplified geological map of Big Thompson Canyon, northern Front Range, Colorado. Isograds are drawn in purple and record increasing metamorphic grade from east to west. Samples specific to this study are shown by a yellow star and the sample number. Igneous intrusions are shown as dikes and large bodies, with ages of ~1.7–1.4 Ga, and cut through the metasediments of ~1.8–1.7 Ga age (modified from Mahan et al., 2013).
The dominant metasedimentary rocks within BTC are metapelites that are interlayered with quartz-rich layers of greywacke and metapsammmites. The mouth of the canyon which hosts the biotite-, garnet-, and staurolite-zones, displays distinctive banding of pelitic and psammitic layers (Figure 2.3). As the metamorphic grade increases to the andalusite-, sillimanite- and K-feldspar-zones, these distinct alternating layers are much harder to distinguish in the field because the rocks are much more weathered, showing oxidization (Figure 2.3). The variable composition of the psammitic and pelitic protoliths allow for an in-depth investigation of the \( P-T \) conditions of metamorphism during the accretion of local provinces such as the Yavapai and Mazatzal.

2.3 Previous work in Big Thompson Canyon

Much of the previous petrological work performed in this region was executed in the 1960’s to 1990’s by William Braddock and his graduate students at the University of Colorado. These studies included extensive mapping of this structurally complex area (Mahan et al., 2013). In 1984, William Nesse identified the increasing metamorphic grade within BTC and began to put constraints on the peak metamorphic conditions in the canyon. Using chemical composition and experimentally calibrated equilibria, he concluded that the peak metamorphic conditions for the sillimanite/K-feldspar zones was ~3-4 kbar and \( 650 \pm 30 \) °C with a geothermal gradient of ~60 °C/km (Nesse, 1984). Later, Shah and Bell (2012) attempted to unravel the deformation history of BTC by using inclusions within foliations defining FIA’s (foliation inflection/intersection axes). They also used \textit{in-situ} monazite geochronology to further define the porphyroblast growth of the samples, producing three significant tectonic events: 1760.5 ± 9.7, 1719.7 ± 6.4 and 1674 ± 11 Ma, followed by 250 Ma of thermo-tectonic quiescence (Shah and Bell, 2012). The Berthoud Orogeny then defined the fourth FIA at 1415 ± 16 Ma (Shah and Bell, 2012). However, there is much dispute about their correlation between ages of metamorphism and structural features, whereby the oldest detrital zircons within along-strike sediments in the BTC-forming sedimentary basin have an age of c. 1755 Ma (cf. Baird pers. comms). If true, the work of Shah and Bell (2012) would imply that burial metamorphism has begun to affect the region after just 5 Myr of surficial sedimentation.
Figure 2.3: Left: Field photograph from the biotite-zone of Big Thompson Canyon demonstrating the alternating pelitic (darker) and psammitic (lighter) metasedimentary layers at the mouth of the canyon. Right: Field photograph from the sillimanite-zone of Big Thompson Canyon describing the lack of visible layered metasedimentary rocks. This isograd zone also has abundant nodules of metamorphic minerals, and many outcrops are highly oxidized or retrogressed.
CHAPTER THREE

ANALYTICAL TECHNIQUES

3.1 Field investigation and sample preparation

During the Summer of 2018, forty-five samples were collected from Big Thompson Canyon. Outcrops listed in the Geological Society of America (GSA) field guide (Mahan et al., 2013) were visited alongside additional roadside stops in each isograd zone to ensure complete sampling of all key isograd zones and lithologies in the region. However, due to the uneven terrain and steep cliff faces, no off-road sampling was conducted. Each sample was documented with a GPS location, a field description, and a photograph showing large-scale structural relationships with adjacent units. Representative samples collected from each isograd zone, which form the focus of this research, are outlined in figure 2.2. Table 3.1 documents the location, isograd zone and mineralogy of each sample collected, and highlights the suite of samples chosen for each type of analysis.

Upon return to the Colorado School of Mines, all samples were cleaned and classified according to protolith/composition (i.e. pelite or psammite). Out of the forty-five samples that were collected, twenty-seven thin sections were made, which allowed examination of at least one metapelite and metapsammite from each isograd zone. Picking fresh samples was difficult in the zones of high-grade metamorphism, as most of these samples were highly oxidized and/or showed retrogression.

3.2 Petrography

Detailed petrography was conducted on all thin sections using a Leica DM750P polarizing microscope with a Leica EC3 digital camera and a 0.55 c-mount, and the LAS EZ software version 3.3.0. Full slide scans were produced using a Nikon Coolscan IV with unpolarized and polarized light filters. These scans were used to aid electron-beam analyses and the placement of spots for obtaining mineral composition data, described below. Petrography was important to this study to better understand changes in mineralogy as well as prograde and retrograde reactions that took place within each isograd zone. Two representative samples from
the garnet-, staurolite-, andalusite-, sillimanite- and K-feldspar- isograd zones were chosen for
detailed mineralogical analysis, bulk-rock geochemistry, thermobarometry, and geochronology
(where applicable). These samples are highlighted in Table 3.1.

3.3 Bulk-rock geochemistry (XRF)

Ten representative samples from the Big Thomson Canyon transect were crushed and
milled down to a fine powder to be analyzed for major, minor and trace element via X-Ray
fluorescence (XRF) analysis at ActLabs Ltd., Ontario, Canada. These XRF analyses were used
for discrimination of the tectonic provenance of the protolith sediments and as input parameters
for phase equilibria modeling-based thermobarometry.

Samples analyzed via XRF were thoroughly cleaned and trimmed to remove weathered
edges or areas with large quartz veins. Then ~ 1 kg of each of the samples was crushed using the
RockLabs Boyd Crusher, the resulting material was then laid out and separated into equal
quarters. Two of the four quarters were then taken and put into the RockLabs standard ring mill
to be milled into a powder of <74 microns. After crushing and milling each individual sample the
machines were cleaned using water to remove rock dust, scrubbed with a wire brush, sprayed
with compressed air and wiped down with acetone and a clean Kimtech wipe. This process was
repeated if the Kimtech wipe did not turn up clean to avoid contamination between samples.
Surfaces for sample preparation were covered in thick paper that was changed after each sample
to prevent contamination between samples. Sample BTC-20 was split into two to make BTC-20S
with a psammitic composition and BTC-20P with a pelitic composition. Therefore, there was
eleven samples sent for XRF analysis. The samples were sent to ActLab in Ontario, Canada
where the XRF analysis took place. For each analysis ~10 grams of powder was needed;
therefore, for each sample, ~25 grams was sent to account for possible errors or problems.
Sample preparation for geochemical analysis at ActLabs included the samples being dissolved in
a weak nitric acid then a lithium metaborate/tetraborate fusion of the sample was done to digest
the powder and molten bead. Analyses can then be performed on the resulting homogenous
mass.
Table 3.1 Sample number, location, mineralogy and isograd zone for each petrographically analyzed sample. Samples used for further investigation are marked with an “X”. TIMA = Tescan Integrated Mineral Analyzer; EPMA = electron probe microanalyzer; Geo. = geochronology; Thermo. = thermobarometry; qtz = quartz; pl = plagioclase; ms = muscovite; bt = biotite; chl = chlorite; ilm = ilmenite; ser = sericite; grt = garnet; tour = tourmaline; sil = sillimanite; st = staurolite; and pseudo = andalusite pseudomorph, srp = serpentinite.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Location</th>
<th>Mineralogy</th>
<th>Isograd-zone</th>
<th>TIMA</th>
<th>EMPA</th>
<th>Geo.</th>
<th>Thermo.</th>
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<td>N 40 27°.286, W 105 26&quot;.088</td>
<td>qtz, bt, ms, pl, ser, sil</td>
<td>k-feldspar</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>BTC-20</td>
<td>N 40 25°.214.0, W 105 13' 44.71</td>
<td>qtz, ms, bt, chl, ilm</td>
<td>biotite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTC-21</td>
<td>N 40 25°.214.0, W 105 13' 44.71</td>
<td>qtz, pl, bt, ms</td>
<td>biotite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTC-22</td>
<td>N 40 24°.903, W 105 14°.907</td>
<td>qtz, pl, bt, ms, chl, ilm</td>
<td>staurolite</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>BTC-23</td>
<td>N 40 24°.903, W 105 14°.907</td>
<td>qtz, ser, bt, chl, ms, st, ilm</td>
<td>staurolite</td>
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<tr>
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<td>N 40 24°.903, W 105 14°.907</td>
<td>qtz, pl, bt, ms, chl, ilm</td>
<td>staurolite</td>
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<tr>
<td>BTC-25</td>
<td>N 40 24°.903, W 105 14°.907</td>
<td>qtz, pl, bt, ms, chl, ilm</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTC-26</td>
<td>N 40 25°.063, W 105 16°.226</td>
<td>qtz, ser, bt, chl, ms, and pseudo</td>
<td>andalusite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTC-27</td>
<td>N 40 25°.063, W 105 16°.226</td>
<td>qtz, ms, ser, grt, chl, bt, and pseudo, ilm</td>
<td>andalusite</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>BTC-28</td>
<td>N 40 25°.063, W 105 16°.226</td>
<td>qtz, ser, bt, chl, ms, and pseudo, ilm</td>
<td>andalusite</td>
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<tr>
<td>BTC-29</td>
<td>N 40 25°.063, W 105 16°.226</td>
<td>qtz, ser, bt, chl, ms, and pseudo, ilm</td>
<td>andalusite</td>
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<td>qtz, ser, bt, chl, ms, and pseudo, ilm</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTC-31</td>
<td>N 40 25°.257, W 105 17°.097</td>
<td>qtz, ms, chl, g rt, bt, st, and, and pseudo, ilm</td>
<td>andalusite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTC-32</td>
<td>N 40 25°.257, W 105 17°.097</td>
<td>qtz, ms, bt, chl, g rt, ser, st pseudo</td>
<td>andalusite</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>BTC-33</td>
<td>N 40 25°.257, W 105 17°.097</td>
<td>qtz, ms, bt, g rt, pseudo, ilm</td>
<td>andalusite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTC-36</td>
<td>N 40 25°.257, W 105 17°.097</td>
<td>qtz, pl, ser, ms, bt, chl, and pseudo, ilm</td>
<td>andalusite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTC-37</td>
<td>N 40 27°.488, W 105 20°.926</td>
<td>qtz, ms, bt, tour, ilm,</td>
<td>sillimanite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTC-43</td>
<td>N 40 27°.488, W 105 20°.926</td>
<td>qtz, ms, bt, ser, ilm</td>
<td>sillimanite</td>
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<tr>
<td>BTC-44</td>
<td>N 40 27°.488, W 105 20°.926</td>
<td>qtz, pl, bt, ms, ser, ilm</td>
<td>sillimanite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.4 Tescan Integrated Mineral Analyzer (TIMA) analysis

Automated mineralogy via bright-phase TIMA analysis was performed on the eleven selected samples to determine the size and distribution of monazite. These analyses were done at Colorado School of Mines FE-SEM lab under the supervision of Dr. Katharina Pfaff. Prior to analysis, the chosen thin sections were carbon coated to ~250 angstroms. Carbon coating of these samples were also performed in the FE-SEM lab. This FE-SEM based analysis system provides a quantitative analysis of monazite in my samples based on a user defined resolution pixel grid. Automated point counting is performed on this grid to determine the distribution of specific minerals. A bright-phase search with a step size of 20 µm was used when scanning for monazite. A bright-phase search for monazite is critical to this study because monazites must be located for geochronology. After these high-resolution maps were made, it became evident that monazite in these samples were small (>100 microns) and very sparse in the chosen samples. This step was essential to sample selection for geochronology, as these results were compared to bulk-rock composition and the eleven samples were narrowed down to five (one from each isograd zone).

3.5 Electron probe microanalysis (EPMA) and Back-scattered electron imaging (BSE)

The EPMA (JEOL JXA-8230) located at the University of Colorado Boulder was used to obtain major mineral compositions of metamorphic minerals under the supervision of Dr. Aaron Bell. For these analyses, the ten representative samples (sample BTC-20 as one sample) that were chosen for XRF and TIMA were analyzed. The running conditions for the EPMA were a 40 degree take off angle, 15 keV beam energy and a 10 nA beam current with a 2-micron spot size. The standards used for these analyses are listed in table C.1. Major minerals such as biotite, muscovite, garnet, plagioclase, ilmenite and chlorite were analyzed in these samples to understand their elemental compositions and if there were any zoning patterns present. Biotite, muscovite, plagioclase, ilmenite and chlorite were analyzed selecting linear transects of 3-5 points with varying step sizes on 3-5 different grains around the thin section. Garnet in this sample suite were only present in two samples. The garnet contained in these samples are highly fractured and/or retrogressed; therefore, taking core to rim transects was impossible. Also, when checking with the BSE function of the EPMA, it appeared that there was no distinct zoning of garnet either. Analyses instead were taken as random points around the garnet to obtain an
average garnet composition. The quality of analysis was considered as well, and only major minerals that appeared minimally fractured and well-polished were chosen for investigation and were checked using stoichiometry to ensure accuracy. A BSE image was also taken of each area of analysis to document where analyses were taken. These photos were taken to determine the intra- and inter-grain relationships within each sample.

The raw EPMA results were re-calculated into molar proportions of oxides and normalized to produce mineral formulae. To perform this re-calculation the data from the Excel spreadsheets was run through a program called AX by Holland (2009). This program also estimates the proportions of ferrous iron vs. ferric iron based on a charge balance procedure.

3.6 U–Th–Pb in-situ monazite geochronology (EPMA)

Quantitative age determination of monazites was performed following the EPMA U–Th–Pb\textsubscript{total} dating protocol outlined by Allaz et al. (2013). During the summer of 2019, geochronology was performed at the same EPMA facility at University of Colorado Boulder under the supervision of Dr. Aaron Bell.

3.6.1 Element mapping of monazite (EPMA)

To prepare the selected samples specifically for geochronological analysis, they were coated in gold simultaneously with the standards to a thickness of 100 angstroms. The next step was to make composition maps of the monazites that were chosen for analysis. The wavelength dispersive X-ray maps were acquired for U, Th, Ce, Pb and Y. These elements were chosen because of their correlation to surrounding minerals such as the correlation of Y content and garnet, and because of their ability to define specific domains within the monazites. Recognizing domains and zoning of these elements within the monazites allows for a more specific point selection, correlation of ages and general concentration of these specific elements to be determined.

3.6.2 Geochronology procedure

The running conditions for the geochronology analyses was a 40-degree takeoff angle, 15 keV beam energy and a 200 nA beam current, and a 1-micron beam diameter. The standards used to calibrate the EPMA for this procedure are outlined in table C.2. On-peak interference
corrections were applied for UMα (Uranium M alpha x-ray line) interference by Th and to Pb for interference by Y, Th and La. Off-peak count times for elements included 120 seconds for Th and U, and 240 seconds for Pb. The matrix correction method used was the Pouchou and Pichoir-Full (PAP) correction. A non-linear multipoint background model was utilized for the background subtraction beneath the U, Pb, and Th X-ray lines that were being quantified. The individual positions for the multipoint background model were chose from a careful examination of several high-resolution wavelength scans over the spectral region of interest. These WDS scans were performed on both the standards, as well as several of the monazites targeted for analysis. Along with U, Th and Pb analyzed in this analysis suite, other elements measured include CaO, Y₂O₃, La₂O₃, Ce₂O₃, Nd₂O₃, Pr₂O₃, Sm₂O₃, Tb₂O₃, Eu₂O₃, Dy₂O₃, Gd₂O₃, Er₂O₃, Yb₂O₃, P₂O₅. All elements were analyzed using the Mean Atomic Number Background method to ensure the accurate assessment of the major element composition of each monazite. (Allaz et al., 2013)

Once calibration and corrections were complete and applied, then homogeneous monazite domains were chosen for analysis. Individual analyses took ~20 to 30 minutes per analysis point, with five points per domain. The first point within the group of five was a background point or “throw away point”. The background point was the analysis that defined the interference correction for the group of points. A BSE image of each monazite was also taken to document the monazite/matrix correlation. A matrix correction was also applied, and oxygen was calculated using cation stoichiometry. Secondary monazite age standards were also used to ensure that the machine was calibrated correctly. The standards used were Burnett (1088 Ma) and Moacyr (508 Ma) (Allaz et al., 2013). These standards were analyzed after each set of 25 monazite spot analyses. This method was expected to take around two days for five samples after calibration was complete. Since the EPMA data obtained is a self-contained chemical analysis performed in-situ, relationships between the analyzed dates, microstructure, and the relation of monazite with other rock-forming minerals (e.g. inclusion vs. matrix) can be determined to provide robust geochronological interpretations. Once compositions of U, Th, and Pb were obtained the equation from Montel et al. 1994 was used alongside the Steiger and Jäger, 1977 decay constants for Th and U to calculate the compositional ages of monazites.

3.6.3 Data reduction process
The U, Th, and Pb contents of monazite were used to calculate a so-called “chemical” age for each grain (or its internal domains). This calculation used the following equation from Montel et al. (1994):

\[
Pb = \frac{Th}{232} \left[ \exp(\lambda_{232}T) - 1 \right]208 + \frac{U}{238.04} 0.9928 \times \left[ \exp(\lambda_{238}T) - 1 \right]206 + \frac{U}{238.04} 0.0072 \times \left[ \exp(\lambda_{235}T) - 1 \right]207
\]

where Pb, U, Th are in ppm, and radioactive decay constants were taken from Steiger and Jäger (1977): \( \lambda(^{238}\text{U}) = 1.55125 \times 10^{-10}/\text{yr} \), \( \lambda(^{235}\text{U}) = 9.8485 \times 10^{-10}/\text{yr} \), and \( \lambda(^{232}\text{Th}) = 4.9475 \times 10^{-11}/\text{yr} \). To ensure the accuracy of these calculations, monazite standards Moacyr (TIMS \(^{207}\text{Pb}/^{235}\text{U} \ 506.7 \pm 1.4 \text{ Ma}\) and \(^{208}\text{Pb}/^{232}\text{U} \ 506.4 \pm 1.8 \text{ Ma}\) (Allaz et al., 2013) and Burnet (1088 Ma: University of Colorado Boulder in-house standard) were checked after every 25 analysis.

After all monazites were analyzed for compositions and an age was calculated for each point of analysis data reduction took place. Each zone of monazite was analyzed in groups of five points, the first point determined the background correction for the grouping of points. When the data was reduced, these background points were taken out of the average age calculation for each zone. Therefore, unless there were clear outliers, points 2 through 5 of each monazite zone were averaged to give a mean age for the grain and a standard deviation. By eliminating outliers, weighted mean averages using Isoplot were calculated for each zone and monazite.

All compositional ages (minus the background point and including outliers) were taken and compared to the calculated U/Th ratio. By doing this, the relationships between age and U/Th can be determined. All points were plotted on probability density diagrams using Isoplot to understand the distribution of ages from the canyon as a whole, and each isograd zone individually.

The average age for each zone within each monazite was then compared to the element maps of the specific monazite. This comparison determined that there is little to no correlation between age and zoning of monazite.
CHAPTER FOUR

PETROLOGY

Eleven samples of metasediment were chosen from the Big Thompson Canyon suite for detailed petrological analysis. These are the same eleven samples that were sent for XRF and TIMA analysis. These comprised of one metapelite and one metapsammite from each isograd zone, which enabled examination of up-sequence changes that may be interpreted within the context of prograde metamorphism and parallel evolution of distinct protolith types. The samples that were chosen from the full suite collected during fieldwork are outlined in table 3.1.

4.1 Bulk-rock geochemistry

Bulk-rock geochemical analysis of 11 key samples from BTC was conducted according to the procedures outlines in chapter 3. Measured compositions of selected major elements are provided in table 4.1. Measured compositions of major, minor, and trace elements for each sample are given in table C.3 and C.4.

Table 4.1 Bulk-rock compositions for select samples as determined by X-ray fluorescence (wt.
% ). Only major oxides are displayed, trace elements can be found in appendix C.3 and C.4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isograd zone</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃(T)</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>LOI</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTC-02</td>
<td>Andalusite</td>
<td>69.8</td>
<td>13.8</td>
<td>0.05</td>
<td>1.26</td>
<td>0.9</td>
<td>2.8</td>
<td>0.7</td>
<td>0.1</td>
<td>1.6</td>
<td>0</td>
<td>6</td>
<td>99.72</td>
</tr>
<tr>
<td>BTC-04</td>
<td>Andalusite</td>
<td>76.3</td>
<td>11.1</td>
<td>0.05</td>
<td>0.56</td>
<td>2</td>
<td>0.23</td>
<td>5</td>
<td>9</td>
<td>2</td>
<td>0</td>
<td>6</td>
<td>98.77</td>
</tr>
<tr>
<td>BTC-17</td>
<td>K-feldspar</td>
<td>68.2</td>
<td>14.1</td>
<td>0.05</td>
<td>0.56</td>
<td>2</td>
<td>0.23</td>
<td>5</td>
<td>9</td>
<td>2</td>
<td>0</td>
<td>6</td>
<td>98.77</td>
</tr>
<tr>
<td>BTC-20S</td>
<td>Biotite</td>
<td>56.3</td>
<td>21.8</td>
<td>0.06</td>
<td>1.55</td>
<td>3</td>
<td>2.76</td>
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<td>2</td>
<td>8</td>
<td>6</td>
<td>100.2</td>
<td></td>
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<tr>
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<td>Biotite</td>
<td>70.9</td>
<td>13.1</td>
<td>0.06</td>
<td>2.02</td>
<td>2</td>
<td>1.90</td>
<td>1</td>
<td>8</td>
<td>5</td>
<td>4</td>
<td>0</td>
<td>100.7</td>
</tr>
<tr>
<td>BTC-22</td>
<td>Staurolite</td>
<td>70.8</td>
<td>14.0</td>
<td>0.05</td>
<td>1.37</td>
<td>0</td>
<td>1.42</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>9</td>
<td>99.48</td>
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</tr>
<tr>
<td>BTC-23</td>
<td>Staurolite</td>
<td>61.0</td>
<td>19.5</td>
<td>0.04</td>
<td>3</td>
<td>0.66</td>
<td>0.29</td>
<td>3.0</td>
<td>100.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>BTC-27</td>
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<td>62.8</td>
<td>18.0</td>
<td>0.07</td>
<td>1.69</td>
<td>0</td>
<td>0.89</td>
<td>0</td>
<td>9</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>100.5</td>
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<tr>
<td>BTC-31</td>
<td>Andalusite</td>
<td>64.8</td>
<td>15.0</td>
<td>0.08</td>
<td>0.73</td>
<td>0</td>
<td>1.63</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>100.1</td>
</tr>
<tr>
<td>BTC-37</td>
<td>Sillimanite</td>
<td>70.7</td>
<td>13.1</td>
<td>0.05</td>
<td>1.77</td>
<td>1</td>
<td>0.20</td>
<td>7</td>
<td>6</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>100.7</td>
</tr>
</tbody>
</table>
Bulk-rock composition from these 11 samples are shown on a sediment provenance diagram based on the compositional criteria Log (Fe₂O₃/K₂O) vs. Log (SiO₂/Al₂O₃) in Figure 4.1. In general, samples from lower isograd zones plot into the “shale” zone of this diagram and are not enriched enough in Fe to be considered Fe-shale. The samples and isograd zones that fall into this category are BTC-20S (biotite/garnet), BTC-23 (staurolite), BTC-27 (andalusite) and BTC-31 (andalusite). The majority of the rest of the samples fall into the “greywacke” area of the plot. These samples and isograd zones are BTC-43 (sillimanite), BTC-02 (andalusite), BTC-17 (K-feldspar), BTC-22 (staurolite), BTC-20P (biotite/garnet), BTC-37(sillimanite). Compared to the samples that plot into the “shale” composition, samples of greywacke composition are from mostly higher-grade metamorphic zones in BTC. One sample, BTC-04 (andalusite) plotted as a litharenite because of its higher SiO₂/Al₂O₃ ratio. Following these trends seen in figure 4.1, it can be noted that there is a possibility for low to mid-grade metamorphic rocks from BTC to have pelitic and psammitic compositions, however, samples from higher isograd zones (andalusite, sillimanite, and K-feldspar) tend to be more SiO₂-rich. From this compositional data, samples for petrographical modeling were chosen.
Figure 4.1 Big Thompson Canyon samples plotted on sedimentary provenance diagram (Log (SiO$_2$/Al$_2$O$_3$) vs. Log (Fe$_2$O$_3$/K$_2$O) using geochemical classification of sediments (after Hu et al., 2015). Sample number and isograd zone are noted in legend.

Tectonic setting discrimination diagrams were created using trace element values obtained by bulk-rock geochemical analysis. Figure 4.2 shows the relationships between Th-Sc-La, Zr/10-Th-Sc, Co-Th-Zr/10 and Ti/Zr vs. La/Sc. All of the investigated sample, excluding BTC-02 plot within the continental island arc (CIA) zone of the ternary plots. This suggest that based on trace element concentration in these samples, these sediments were deposited in association with continental island arcs. The Ti/Zr versus La/Sc graph shows different results. Here, the samples plot on the edge of the CIA zone as well as the active continental margin (ACM) zone. Sample BTC-02 is the only sample the plots differently than the others in this study. This sample falls into the passive margin (PM) zone of the ternary plots, as well as the binary plot.
Figure 4.2 Tectonic setting discrimination diagrams for metasediments from Big Thompson Canyon after Hu et al. (2015). OIA ocean island arc, CIA continental island arc, ACM active continental margin, PM passive margin. Sample number and isograd zone are delineated for context.

4.2 Petrography

Petrographic examination of thin sections has shown the mineral assemblages and microstructures that occur in the biotite-, staurolite-, andalusite-, sillimanite- and K-feldspar-zones. The results of this examination are discussed below, and mineralogy is summarized in table 3.1.

Most of the BTC metasediments are schistose and contain abundant quartz, plagioclase, and micas. These minerals make up the foliation of the samples. Porphyroblasts vary in each sample according to the protolith chemistry (pelite vs. psammite) and the metamorphic grade. The biotite/garnet-zone seen in figure 4.3 has a mineral assemblage of muscovite + quartz +
biotite + chlorite. This lower grade isograd zone does have distinct compositional zones. Figure 4.3 shows this by a red line dividing the 20S and 20P sections of the thin section. When looking at the figure the top of the image is of greywacke composition and the lower portion is of shale composition based on figure 4.1.

Figure 4.3 Sample BTC-20 from the biotite/garnet-zone showing a 5 mm field of view in plane polarized light and a mineral assemblage of muscovite + quartz + biotite + chlorite.

Figure 4.4 shows the pelitic and psammitic samples, BTC-23 and BTC-22 respectively from the staurolite-zone. Sample BTC-23 is more mica dominated, plotting in the shale domain of figure 4.1 and has a mineral assemblage of muscovite + quartz + biotite + plagioclase + chlorite. Sample BTC-22, which is more quartz rich and has a greywacke composition, has the same mineral assemblage of muscovite + quartz + biotite + plagioclase + chlorite. Of all the samples investigated, the andalusite-zone shows the most range of mineral assemblages and intriguing textures compared to those from other isograd zones. Figure 4.5 shows samples BTC-02 and BTC-27. Sample BTC-02 plots in the greywacke zone of figure 4.1 and has a mineral
assemblage of muscovite + quartz + biotite + plagioclase. Sample BTC-27 of pelitic composition has a mineral assemblage of muscovite +

![BTC-23 Image](image1)

![BTC-22 Image](image2)

Figure 4.4 Sample BTC-22 and BTC-23 from the staurolite-zone showing a 5 mm field of view in plane polarized light and a mineral assemblage for each sample of muscovite + quartz + biotite + chlorite + plagioclase.

quartz + biotite + plagioclase + chlorite + garnet. This sample is important because it describes the nature of garnets found during my study. Garnet within BTC is mostly broken up and rimmed or replaced by chlorite, thus making data collection to describe zoning profiles of garnet impossible. Sample BTC-27 also has an abundance of sericite and pseudomorphs of andalusite to fine grained white mica.
Sample BTC-02 from the andalusite-zone showing a 5 mm field of view in plane polarized light and a mineral assemblage of muscovite + quartz + biotite + plagioclase. Sample BTC-27, also from the andalusite-zone showing a 7 mm field of view in plane polarized light with a mineral assemblage of muscovite + quartz + biotite + plagioclase + chlorite + garnet. Abundant sericite and pseudomorphs of andalusite to fine-grained white mica are also present in this sample.

Sample BTC-31, also from the andalusite-zone displays curious overgrowths and replacement textures of fine-grained white mica pseudomorphing andalusite along what appears to be a twinning plane (figure 4.6). Further growth of staurolite within the fine-grained white mica is also present. Chlorite in these zones is found as replacement textures around garnet and biotite. The sillimanite zone (figure 4.7) displays samples BTC-37 and BTC-43. BTC-37 has a mineral assemblage of quartz + plagioclase + muscovite + biotite + tourmaline. Sample BTC-43 has a mineral assemblage of muscovite + quartz + biotite + sillimanite. Both samples plot in the greywacke domain of figure 4.1.
Figure 4.6 Sample BTC-31 from the andalusite-zone showing an 8 mm field of view in plane polarized light and a mineral assemblage of muscovite + quartz + biotite + chlorite + plagioclase + staurolite.

Figure 4.7 Sample BTC-37 and BTC-43 from the sillimanite-zone showing a 5 mm field of view in plane polarized light. BTC-37 has a mineral assemblage of muscovite + quartz +
biotite + plagioclase + tourmaline and BTC-43 has an assemblage of muscovite + quartz + biotite + sillimanite.

Also, in figure 4.8 sample BTC-17 from the K-feldspar-zone has a mineral assemblage of quartz + plagioclase + muscovite + biotite + sillimanite, and a greywacke composition based on figure 4.1. It is important to note that lower grade zones show a finer grain matrix and fewer porphyroblasts relative to the higher grade isograd zones. There is also more evidence of retrogression in the mid metamorphic zones (staurolite- and andalusite-zones) compared to that of the highest-grade zone in this study (K-feldspar-zone).

Figure 4.8 Sample BTC-17 from the K-feldspar-zone showing a 5 mm field of view in plane polarized light and a mineral assemblage of muscovite + quartz + biotite + plagioclase + sillimanite.

4.3 Mineral compositions

Compositional data collected using EPMA at the University of Colorado Boulder was used to quantify changes in mineral chemistry as a function of increasing grade of metamorphism from the biotite-, staurolite-, andalusite-, sillimanite- and K-feldspar zones. Mineral compositions were collected from species that commonly show pressure- or temperature-sensitive element substitutions (e.g. Fe–Mg exchange). These minerals included garnet, biotite, muscovite, plagioclase, ilmenite and chlorite. The following discussion outlines compositional variation within these species as a function of metamorphic grade.
**Plagioclase:**

Plagioclase compositions in metasediments typically trend towards higher anorthite content \((\text{Ca}/(\text{Ca+Na+K}))\) with increasing temperatures (Noguchi et al., 2004). An EPMA cannot accurately measure the content of Na, therefore the Ca content will vary based on the approximated content of Na. To verify whether this pattern is preserved in the BTC rocks, plagioclase compositions were plotted on a binary diagram where anorthite (Ca) content is calculated in two ways: one using Al-to-Si ratios \([(\text{Al}-1)/(\text{Al}+\text{Si}-3)]\) and the other using the ratios of alkali elements \([\text{Ca}/(\text{Ca+Na+K})]\). Ideally, both values for an individual analysis will be equivalent and fall within the 1:1 line of the plot. The Al-to-Si ratio shows the true Ca content of plagioclase.

EPMA-derived analyses from BTC rocks are shown in Figure 4.9. Most fall within ± 0.04 (4%) of the ideal 1:1 line for anorthite content determined via both elemental ratios. This implies that analyses are of good quality. If these analyses were more than ± 0.05 from the 1:1 line, this indicates that the EPMA measured a Na content that is too low. When the Na content is measured to low then there is going to be an elevated Ca content when calculated by alkalis.

This method of plagioclase stoichiometry can also aid in determining general trends of plagioclase composition between different units. In general, there appears to be no consistent progression in XCa up-grade, as staurolite-, sillimanite-, and K-feldspar-zone samples all have similar ranges (~0.20-0.26).
Figure 4.9 Plagioclase stoichiometry of four samples over three isograd-zones. This plot describes the quality of analysis that were taken using the EPMA based on $(\text{Al-1})/(\text{Al+Si-3})$ vs. $\text{Ca/(Ca+Na+K)}$. Analyses mostly fall within 0.04 error of the 1:1 ratio line.

**Mica**

Grade-dependent compositional patterns in dioctahedral and trioctahedral micas in BTC rocks were examined using the classification scheme of Tischendorf et al. (2007). In this scheme, EPMA compositional data of micas was plotted in terms of $\text{Mg + Li (c.p.f.u.)}$ and $[(\text{Fe}^{2+}+\text{Mn+Ti})-\text{Al}^{IV}]/2$ for an 11-oxygen calculation. The graphed data is shown in figure 4.10. For muscovite composition analysis, sample BTC-20 was not separated into compositional domains, therefore there are no longer eleven samples being analyzed, there are ten.
Figure 4.10 End member plot displaying mica compositions for the ten samples in the sample suite (after Tischendorf et al., 2007). The x-axis value represents the Mg c.p.f.u as calculated for 11-oxygens and the y-axis represents \( [(Fe^{2+}+Mn+Ti)-Al^{IV}] / 2 \). Each of the five studied isograd-zones are represented in this graph.

Most dioctahedral micas from BTC plot very close to the ideal muscovite composition. This indicates limited substitution of other elements, such as Na for K, although minor Mg (or Fe) + Si for Al is evident. The average calculated XMg for biotite from each zone are; biotite/garnet 0.37, staurolite 0.41, andalusite 0.40 with an outlier from sample BTC-02 which has shown enrichment in XMg with a value of 0.62. The sillimanite zone has an average XMg value of 0.39, and finally the K-feldspar zone with an average biotite XMg composition of 0.36. Muscovite XMg values for each isograd zone are as follow; biotite/garnet 0.55, staurolite 0.42,
andalusite 0.54, sillimanite 0.54 and the k-feldspar zone with a value of 0.47. Biotite in BTC rocks is more compositionally complex, but analyzed compositions lie mostly within a field delimited by Tischendorf et al. (2007) showing the most common types of biotite in crustal rocks (as shown by density contours). Almost all analyses plot within the Fe-rich biotite field, trending towards annite, although those from BTC-02 (andalusite zone) are more Mg-rich.

Garnet

Garnet is rare within the metasediments of BTC isograd sequence and is never present in meta-psammite units due to their low Al$_2$O$_3$ contents. Although other workers have documented it, garnet was not observed in “garnet-zone” units collected during this study. Only two metapelites contained garnets: BTC 37 and BTC 31. Both of these samples were collected from the andalusite zone. Garnets in BTC 37 were highly fractured and being replaced by chlorite, whereas sample BTC-31 only had one garnet, which showed no retrogression.

Point analyses were taken on these garnets at various radial distances, although high fracture densities and alteration limited the ability to make core-to-rim transects across these grains. As a result, all point analyses were plotted on an XMg vs. c.p.f.u. of Mg, Ca, Mn and Fe diagram to reveal compositional trends, as XMg is expected to decrease from the core to the rim of a garnet that grows during prograde metamorphism (Kohn and Spear, 2000). Figure 4.11 of garnet analyses from sample BTC-27 shows that Fe content decreases linearly with increasing XMg content. At ~0.27 c.p.f.u. Fe, XMg values are ~0.46, then when the Fe c.p.f.u. is quite lower at a value of ~0.035, XMg values are almost 0.85. Mn content within this garnet has no correlation with XMg contents; however, there is quite a range of Mn c.p.f.u with values ranging from ~0.25 c.p.f.u. Mn up to ~0.42 c.p.f.u. Mn. The c.p.f.u. values of Mg and Ca stay constant with varying XMg values. Mg c.p.f.u. values have an overall average of 0.21 c.p.f.u., where the average of Ca is 0.14 c.p.f.u.

The other sample that where garnet is present is sample BTC-31. The single garnet in this sample was a fresh matrix garnet; however, it is still highly fractured therefore no transects could be taken. Twelve points of analysis were taken within this garnet, and then plotted on the same XMg versus c.p.f.u. of Ca, Mn, Mg and Fe. All values for c.p.f.u. stay steady when the XMg is changes. One important trend to note is that as the value of Mg and Fe have a slight increase
from ~0.21-0.24 c.p.f.u. and ~0.25-0.265 c.p.f.u. respectively the value of Ca decreases (~0.11-0.07 c.p.f.u. Ca). (figure 4.12)

Figure 4.11 Compositions of garnet plotted based on values of XMg versus cation mole fraction units of Mg, Ca, Mn and Fe for two garnets from sample BTC-27.

Figure 4.12 Compositions of garnet plotted based on values of XMg versus cation mole fraction units of Mg, Ca, Mn and Fe for two garnets from sample BTC-31.
Monazite geochronology was performed on four samples from the BTC suite that contained enough grains of sufficient size for chemical dating. Unfortunately, the lowest metamorphic zone, the biotite/garnet-zone there were no monazite to analyze. There were no monazite to analyze because monazite in sample BTC-20 from the biotite/garnet-zone were no larger than 10 µm across, and were not of high enough quality to take measurements. However, the other four samples yielded monazite that was able to be studied. These samples were BTC-02, BTC-17, BTC-23 and BTC-37. While EPMA dating is known to be less precise than other forms of isotope geochronology commonly applied to monazite, such as TIMS or LA-ICP-MS, it is most suited to the rocks in this study due to the small size (~10 microns) of monazite and their complex internal zoning. For example, laser ablation techniques would not have the spatial resolution to resolve ages from discrete domains, and techniques (e.g. TIMS) that require mineral separation lead to a loss of microstructural context with which to interpret age data. Monazites chosen for this analysis range in size from 15- 100 µm and were located within the matrix along biotite grain boundaries.

5.1 Monazite element mapping and interpretation (spot selection)

High-resolution element mapping of U, Th, Ce, Y and Pb was performed via EPMA at the University of Colorado Boulder. These element maps are important to understanding the zoning and homogeneous domains that are present within each monazite grain. Understanding the intra-grain intricacies of each monazite led to logical spot selection for each monazite.

Element mapping of Th in monazites from these samples revealed that there are three distinct domains within most monazite grains. First, there is a dark grey zone that usually is within the core of grains. Next, a light grey zone that generally was around the dark grey zones. The dark grey and light grey zones are the most common throughout all of the monazites, and often showed strange stripy or intermingling zoning within monazite grains. Finally, a bright domain was present within monazites. This domain is most common around the edges of monazites. When picking points for analysis the domains that are present in the Th maps are
considered and groupings of points were plotted only within one of the three domains. This is demonstrated in figure 5.1. The idea behind this is that each domain will have an age correlation (i.e., dark grey is older than light grey). Also, since analyses were taken in groups of five points with the first point being the background calculation point, more precise compositions will be calculated when the background calculation is made within the same domain as the four following points.

As a whole, mapping of Y in samples BTC-02, BTC-17 and BTC-23 show that there is minimal to no concentration or zoning of Y. Element maps of Y in monazite show up very dark describing a low concentration of Y. It can be seen in figure 5.1 that Y concentration of monazite
4 from sample BTC-23 is so low that the monazite grain cannot be seen in the image. Monazites from sample BTC-17; however, show the most present zoning of Y, with higher concentrations (lighter color) in the core and lower concentrations (darker color) around the edges (Appendix D). Another thing to note about Y zoning is in sample BTC-17. In this sample Y zoning closely reflects the zoning of Th in each monazite grain. Monazites in sample BTC-37 were mapped for Pb instead of Y. These Pb maps for sample BTC-37 show little to no zoning and are quite homogenous as well.

5.3 Results

All calculated ages are shown on a graph of age (Ma) versus U/Th ratio and are compared to the major orogenic events that affected Colorado during the Proterozoic. Figure 5.2 displays this data from each of the four analyzed isograd zones. The trends that arise from this plot are that there are two distinct grouping of ages. One of these groupings is from ~1300-1400 Ma. This grouping is mostly from andalusite-zone monazites and corresponds to the Granite-Rhyolite Province of this region. The Granite-Rhyolite Province is also associated with the Picuris Orogeny that is found much further south, but evidence from BTC points to the idea that overprinting from this orogeny is found as far north as north-central Colorado. The other large grouping of ages is from ~1600-1700 Ma. These ages correspond to the Mazatzal Orogeny that is part of the building blocks of northern Colorado. In general, the U/Th ratio for the staurolite, andalusite and sillimanite-zones is within a suitable range reflecting “typical metamorphic” ratios with most values being between ~0.03-0.20 (Palin et al., 2013). U/Th ratios are significantly higher for the K-feldspar-zone. Values for this zone range from as low as ~0.05, but most fall into the range of ~0.21-0.45.
Figure 5.2 Geochronology results. This plot describes the relationship between calculated elemental age of monazite in millions of years vs. the U/Th ratio. For context, important orogenic events to have affected north-central Colorado are shown. The analyses taken in this study fall into two areas of the plot, most of which are within the Mazatzal Orogeny and then the Granite-Rhyolite province or the Picuris Orogeny. Each point represents one compositional age analysis.

A probability density diagram (figure 5.3) was made using the compositional age data to show the distribution of calculated ages for BTC as a whole. This plot used all the calculated ages, omitted the background calculation point and was made using Isoplot. Figure 5.3 displays the distribution of all the collected ages from all monazites and isograd zones. Figure 5.3 shows that there are three areas of high probability within these 188 points of analysis. The highest relative probability is 1650 Ma. There are two smaller peaks that are apparent at 1325 Ma and 1400 Ma as well. Taking this understanding of the whole data set, the ages were then plotted in probability density diagrams for each individual isograd zone. Figure 5.4 describes the probability density for each of the studied zones; staurolite, andalusite, sillimanite and K-feldspar zones. As seen in the figure, the 56 points of analysis for the staurolite-zone has one main population at 1651 Ma. Moving up the isograd zones, the andalusite-zone shows three populations within the 44 points of analysis, two that show younger ages of 1323 Ma and 1398
Ma. The older age population for the andalusite-zone is at 1647 Ma. The sillimanite-zone’s 56 points of analysis has

![Figure 5.3 Probability density diagram for all collected compositional ages from BTC.](image)

one population of high probability at 1670 Ma. Lastly, the K-feldspar zone, with 32 points of analysis has two populations of high probability, one at 1420 Ma and another at 1700 Ma.

The results from this EPMA compositional age analysis for individual monazite from specific zones are outlined in figure 5.5. To display data this way, the raw data was combed through to omit outliers or points of analysis that appear to not be of high quality. The criteria to omit outliers was dependent on the standard deviation of the analysis groups. If a grouping of analysis has an age that produced larger than ~20 Ma standard deviation, that point was omitted from the average for the group of analysis. Sample BTC-23 from the staurolite-zone yielded a
weighted mean average of 1643 ± 7 Ma of seven monazites that were investigated. It can be seen in figure 5.3 that all the monazite grains in this zone have an age range that encompasses the weight mean average.

Figure 5.4 Probability density diagrams for each isograd zone from BTC showing distribution of compositional age data.

From the andalusite-zone, five monazites were analyzed from BTC-02. Figure 5.5 shows that the weighted mean average for this group of analysis was 1556 ± 140 Ma. This zone has the highest margin of error, and the lowest calculated age out of the four samples investigated. It is also important to note that there is a distinction of three zones within monazite 5 (figure 5.6). The first zone, labeled monazite 5a has an average age of 1661 ± 7 Ma, monazite 5b has an average age of 1151 ± 14 Ma, and finally monazite 5c has an average age of 1392 ± 9 Ma. The large amount of error within this zone, and the calculated ages are some of the highest out of all the samples and some of the lowest. This large range of ages can also be seen for the andalusite-
zone in the probability density diagram (figure 5.4). At higher metamorphic grades, sample BTC-37 (sillimanite-zone) contained seven monazites that were dated to give a weighted mean average age of 1674 ± 22 Ma. Finally, the K-feldspar zone was the highest metamorphic grade analyzed for geochronology. Five monazites from sample BTC-17 were investigated and a weighed mean average of 1674 ± 19 Ma was calculated. It can be seen in figure 5.5 that there is an outlier in this set of data. Monazite 1a was not included in this weighted mean average calculation, but is still shown to describe an outlier for this sample.

Figure 5.5 Weighted mean average plots of calculated compositional ages of monazite from Big Thompson Canyon. Samples BTC-23, BTC-02, BTC-37 and BTC-17 are displayed with y-axis values of age in millions of years (Ma). Average age for each isograd-zone is denoted by an orange line, and each colored bar represents a 2σ error from the weighted mean for a specific monazite.
Figure 5.6 Detailed element map of monazite 5 from sample BTC-02 (andalusite-zone) showing concentration of Y, Th, U, Ce and the backscattered electron image. Specific zones are circled in red, and corresponding ages are listed.

BTC-02 Monazite 5
Zone A: 1661.4 ± 7 Ma
Zone B: 1151.2 ± 14 Ma
Zone C: 1392 ± 9 Ma

- Point of analysis (~1 μm)
- Approx. zone boundary
Various forms of thermobarometry were used to provide $P-T$ constraints on the prograde and peak metamorphic history of BTC samples. These comprised conventional techniques, which consider individual mineral compositions, and petrological modeling techniques, which use bulk-rock geochemistry and mineral assemblages. The results of each are discussed below.

### 6.1 Ti-in-biotite thermometry

A useful thermometer for peraluminous metapelites is the Ti content of biotite. This thermometer can be used on metapelites that contain ilmenite or rutile and are of relatively low pressure (4-6 kbar) (Henry et al., 2005). The thermometer works by combining natural biotite sets with petrogenetic grids of Spear et al. (1999). Given that the calculated Ti-saturated surface is curved based on the value of XMg, then the Ti concentrations increase as a function of temperature in a nonlinear fashion (Henry et al., 2005). For a given temperature Ti concentrations decrease given an increase of XMg (Henry et al., 2005). Biotite compositions were collected using the EPMA at CU Boulder, and the discussed results for each point of analysis of biotite are summarized in figure 6.1. Temperature ranges for each sample are summarized in figure 6.2 by increasing isograd zone.

Biotite that was analyzed for this thermometer did not have any obvious zoning in the BSE images that were taken. Figure 6.3 is a comparison of biotite grains from the garnet/ biotite zone (sample BTC-20) and the K-feldspar zone (sample BTC-17). The lower grade isograd zone biotite has a large range of grain sizes (>1 µm – 300 µm) with granoblastic textures. Larger grains have abundance of inclusions including muscovite, quartz, zircon and monazite. The foliation is not well defined in this lower isograd zone; therefore biotite grains have random orientations. Sample BTC-17 from the k-feldspar zone has biotite grains that are larger in size (100 µm – 300 µm). These porphyroblasts are subidioblastic and have very few inclusions. Points chosen for measurements were chosen with the goal of obtaining an overall composition of biotite within the whole sample.
Ti-in-biotite thermometry shows that the biotite/garnet-zone has the lowest Mg content, most between 0.36-0.38, but some as high as 0.44, Ti content of 0.18-0.21 cation per 22 oxygen, and temperatures of 534-582 °C (Figure 6.1). Comparing this to the higher-grade zones, it can be seen that these are some of the lowest calculated temperatures and are the lowest Mg values for the canyon, thus aligning with the lowest grade of metamorphism.

Ti-in-biotite thermometry for the staurolite-zone yields Mg values of 0.38-0.40, Ti content of 0.16-0.18 cation per 22 oxygen, and temperatures ranging from 515-536 °C. Although the Mg values for this zone are higher, the temperatures are slightly lower than that of the biotite/garnet zone.

Figure 6.1 Ti-in-biotite thermometry for samples from each isograd-zone. Samples from higher metamorphic grades have higher amounts of Ti per 22 oxygen, which also yields higher temperatures. For examples, the K-feldspar-zone displays the highest temperatures (>750 °C).

Ti-in-biotite thermometry for the andalusite-zone shows Mg values of 0.59-0.64, a Ti content of 0.15-0.22 cations per 22 oxygens and temperatures ranging from 581-630 °C with
most of the analysis laying within the 581-602 °C range. The calculated Mg values for this isograd zone are by far the highest of the five isograd zones, thus demonstrating that the andalusite-zone is enriched in Mg. This enrichment is most likely from mineralogical differences between the isograd zones or from the introduction of fluids from magmatic sources that permeated this isograd zone more dominantly than the others.

The three lower isograd zones, the biotite/garnet-, staurolite- and andalusite-zones all have a Ti content that is relatively similar. All of the values lie between 0.15- 0.22 cation per 22 oxygen. The calculated temperatures for each of these zones are within the same range as well. The most notable difference between these three zones is that the Mg content of the andalusite-zone is significantly enriched compared to not only the biotite/garnet, and staurolite-zones, but all of the isograd zones within the canyon.

The sillimanite-zone of Big Thompson Canyon plots in a very narrow range in regard to Ti-in-Bt thermometry. Mg content for this zone ranges from 0.42-0.44, Ti content of 0.26-0.29 cation per 22 oxygens and temperatures ranging from 621-640 °C. These values correlate to moving up the P-T path of the canyon.

Lastly, the Ti-in-Bt thermometry calculations are able to describe the highest Ti substitutions and the highest possible temperatures for all of the isograd zones. By estimating the highest temperature for each zone, upper constraints can begin to be determined for the temperature of each isograd zone. Mg values for the highest metamorphic grade in BTC (K-feldspar-zone) are 0.36-0.37, a Ti content of 0.35-0.37 cations per 22 oxygens and a temperature range of 666-673 °C. It can clearly be seen that the calculated temperatures for this zone are the highest temperatures calculated in this study, which corresponds to the general increasing P-T conditions of the increasing isograd zones. One last important thing to note for the K-feldspar-zone is that it has the highest Ti content per 22 oxygen. There is a general increase while moving up the isograd sequence, for example the biotite/garnet zone has an average Ti value of about 0.20 cation per 22 oxygen, while the K-feldspar-zone has an average Ti content of 0.43 cation per 22 oxygen. The value calculated for the K-feldspar-zone (highest metamorphic grade analyzed in this study) is double that of the lowest isograd zone.
To summarize the final calculated temperatures for each sample analyzed, a box-and-whisker plot was made to display the temperature ranges. Figure 6.2 denotes the calculated temperature ranges for eight samples from the sample suite across four isograd zones.

Figure 6.2 Box and whisker plot displaying the temperatures for the eight samples analyzed out of the sample suite and used for Ti-in-Bt thermometry. Sample number, isograd-zone and temperature ranges are noted on the graph. Boxes are from lowest to highest isograd zone.
Figure 6.3 EMPA backscattered electron image of sample BTC-17 (K-feldspar zone) and below sample BTC-20 (garnet/biotite zone) of BTC. Minerals of interest include biotite (bt), muscovite (ms), plagioclase (pl) and quartz (qtz).

6.2 Petrological modeling

Petrological modeling uses the principles of equilibrium thermodynamics to construct phase diagrams and derive $P$–$T$ information from rocks (White et al., 2014). In the case of Big Thompson Canyon, inverse modeling was employed in order to constrain the P and T conditions
at which observed mineral assemblages formed. For this study, one sample of metapelite from each of the biotite/garnet-, staurolite-, andalusite-, sillimanite-, and k-feldspar zones was investigated using this technique: BTC-20, BTC-23, BTC-02, BTC-37, and BTC-17 (table 3.1).

6.2.1 Modeling Parameters

Modeling was performed using Theriak-Domino (de Capitani and Brown, 1987; de Capitani and Petrakakis, 2010) in an 11-component compositional system MnNCKMASHTO (MnO–Na$_2$O–CaO–K$_2$O–FeO–MgO–Al$_2$O$_3$–SiO$_2$–H$_2$O–TiO$_2$–O$_2$) and the thermodynamic database from Holland and Powell (2011) (update ds62; February 6$^{th}$, 2012). Theriak-Domino uses Gibbs free energy minimization to determine equilibrium assemblages at different P-T conditions representative of the continental crust during collisional orogenesis (de Capitani and Brown, 1987).

6.3 Results

Pseudosections were produced for each sample using XRF-derived bulk-rock compositions (Table 6.1) at P-T conditions of 400–750 °C and 2–10 kbar. These P-T parameters were chosen because they best fit regional metamorphism conditions, assuming lithostatic pressure. Key aspects of these diagrams are labeled included garnet-in phase boundary, solidus and H$_2$O out. Degrees of freedom for each stability field are highlighted with higher variance in lighter colors and lower variance in darker colors. The observed mineral assemblages and estimated P–T conditions are highlighted in grey.

Table 6.1 Bulk-rock compositions (mole % oxide) used to calculate phase diagrams.

<table>
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<tr>
<th>Sample No.</th>
<th>H$_2$O</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>FeO</th>
<th>Fe$_2$O$_3$</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>TiO$_2$</th>
<th>MnO</th>
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<td>BTC-20</td>
<td>7.6</td>
<td>72.13</td>
<td>7.87</td>
<td>0.33</td>
<td>2.84</td>
<td>5.14</td>
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<td>0.23</td>
<td>2.71</td>
<td>5.49</td>
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<td>0.2</td>
<td>0.52</td>
<td>0.04</td>
</tr>
<tr>
<td>BTC-23</td>
<td>10.44</td>
<td>63.47</td>
<td>11.98</td>
<td>0.33</td>
<td>2.62</td>
<td>5.69</td>
<td>0.28</td>
<td>3.71</td>
<td>0.9</td>
<td>0.54</td>
<td>0.04</td>
</tr>
<tr>
<td>BTC-02</td>
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<td>1.11</td>
<td>1.96</td>
<td>4.95</td>
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<td>0.59</td>
<td>0.04</td>
</tr>
<tr>
<td>BTC-17</td>
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<td>2.86</td>
<td>0.58</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Biotite/garnet-zone

Sample BTC-20 from the biotite/garnet-zone has an observed mineral assemblage of plagioclase + muscovite + biotite + staurolite + chlorite + magnetite + ilmenite. This stability
field is highlighted grey in figure 6.4. The P–T conditions for this chosen field are ~420–550 °C and >2–4.5 kbar. Because of the P–T parameters set for this phase diagram; the lower limit of this stability field cannot be seen. It is observed that this field lies just below the garnet-in phase boundary, meaning that these calculated P–T conditions are more likely to represent the biotite-zone.

Figure 6.4 Pseudosection for sample BTC-20 of pelitic composition from the biotite/garnet zone, modeled using the MnNCKMASHTO system. The stability field highlighted in grey represents that peak observed metamorphism for this isograd zone.

Staurolite-zone:

Sample BTC-23 was used to represent conditions from the staurolite-zone of BTC. This phase diagram yielded a peak mineral assemblage of plagioclase + muscovite + biotite + staurolite + chlorite + magnetite + ilmenite (figure 6.5). This mineral assemblage has P–T stability of ~425–550 °C and >2–4.3 kbar. The lower temperature limit of this stability field it also not shown in figure 6.5 because of the P–T parameters set for this model. It should also be
noted that this stability field lies below the garnet-in phase boundary, despite the rock being collected from beyond the garnet-in isograd. Thus, this sample is sub-aluminous compared to other pelites from the region.

Figure 6.5 Pseudosection for sample BTC-23 of pelitic composition from the staurolite-zone, modeled using the MnNCKMASHTO system. The stability field highlighted in grey represents that peak observed metamorphism for this isograd zone.

Andalusite-zone:

Sample BTC-02 was chosen to represent the andalusite-zone of BTC. Plagioclase and biotite are calculated to be stable throughout the entire P–T space of interest. The peak observed mineral assemblage contains plagioclase + biotite + muscovite + chlorite + magnetite + ilmenite ± H₂O. These phases are stable at P–T of ~410–525 °C and >2–5.5 kbar, highlighted in grey on figure 6.6. This stability field displays that there is a progression up P–T conditions as samples from higher isograd zones are investigated, even though the general phases that are stable are the same. The stability field for the andalusite-zone is also below the garnet-in line, since there was no observed garnet within this sample.
Figure 6.6 Pseudosection for sample BTC-02 of pelitic composition from the andalusite-zone, modeled using the MnNCKMASHTO system. The stability field highlighted in grey represents that peak observed metamorphism for this isograd zone.

Sillimanite-zone:

Sample BTC-37 was chosen from the sillimanite-zone for pseudosection calculation (figure 6.7). The observed peak mineral assemblage is plagioclase + muscovite + biotite + sillimanite + magnetite + ilmenite + H₂O. This field is stable at conditions of ~575–700 °C and ~3–6.2 kbar. This field is also below the garnet-in phase boundary; however, the presence of sillimanite and absence of garnet and staurolite in this sample allows for the stability field to be narrowed down. This stability field also lays along the solidus for this sample (~700 °C), thus describing this isograd’s proximity to the K-feldspar and migmatite-zones of this region.
Figure 6.7 Pseudosection for sample BTC-37 of pelitic composition from the sillimanite-zone, modeled using the MnNCKMASHTO system. The stability field highlighted in grey represents that peak observed metamorphism for this isograd zone.

**K-feldspar-zone:**

Phase-diagrams for the K-feldspar-zone were modeled using sample BTC-17 (figure 6.8). The majority of this P–T space has plagioclase, garnet and biotite as stable phases. The peak observed mineral assemblage calculated for this zone is plagioclase + garnet + biotite + magnetite + ilmenite + H₂O. This field is stable at conditions of ~560–735 °C and ~2.8–8.8 kbar. This stability field falls along the solidus, which for this sample is calculated to be ~700 °C along the phase boundary of this field. The amount of H₂O and/or melt in this sample is unknown, but is inferred based on petrographic evidence.
To summarize the phase diagram calculations, a piezo-thermal array was created. This diagram was created by taking the predicted P–T conditions for each isograd zone and overlaying them in common P–T space. Figure 6.9 portrays the clear correlation between metamorphic grade and isograd zone. The lowest grade of metamorphism, the biotite/garnet-zone have the lowest P–T stability space of the five sample. Although the biotite/garnet-zone has the lowest P–T conditions, the staurolite and andalusite-zones share P–T space with the biotite/garnet zone. There is then an increase in P–T from the three lower isograd-zones to the sillimanite and K-feldspar zones. Even though there is shared P–T for the lower grade isograd zones, there is still an increase of P–T from the biotite/garnet-zone to the K-feldspar zone. The aluminosilicate polymorph boundaries were also added to this diagram to show where each
isograd stability falls with relation to possible phase boundaries and stability fields of common metapelite minerals. However, even though the biotite/garnet, andalusite and K-feldspar-zones fall within the kyanite stability field, kyanite has yet to be observed within Big Thompson Canyon (Mahan et al., 2013).

Figure 6.9 A piezo-thermal array describing the calculated stability zones for each isograd-zone in Big Thompson Canyon. An increase in pressure and temperature is seen between the three lower isograd zone (biotite/garnet, staurolite and andalusite-zones) to the higher grade isograd zone (sillimanite and K-feldspar-zones). An estimated metamorphic field gradient is denoted as well.
Understanding regional metamorphism in Colorado is key to deciphering the tectonic evolution of North America and formation of Laurentia during the Proterozoic. The data collected in this study provide new constraints on the two research objectives outlined below:

- Constrain the $P$–$T$ conditions of metamorphism of monazite-bearing metasedimentary rocks within Big Thompson Canyon
- Identify the age of metamorphism in different isograd zones across Big Thompson Canyon, with the aim of identifying the existence (or not) of the cryptic Picuris Orogeny in this area

**7.1 Pressure–Temperature variation across Big Thompson Canyon**

Big Thompson Canyon preserves a clear record of increasing metamorphic grade from east to west that is defined by specific isograd zones: biotite, garnet, staurolite, andalusite, sillimanite, K-feldspar, and migmatite. Phase diagram based petrological modeling (Figure 6.9) quantifies the increases in pressure and temperature preserved at peak metamorphism in each zone, referred to as a metamorphic field gradient (or piezothermal array). The lower grade isograd zones (garnet/biotite and staurolite) have a calculated stability field of ~420–550 °C and >2–4.5 kbar. The andalusite-zone also falls within the stability fields of the isograd zones below it; however, this isograd zone has a higher calculated pressure stability (~5.5 kbar). Also, as seen in figure 6.9, there is the potential to have each kyanite, sillimanite and andalusite stable within each of the biotite/garnet-, staurolite- and andalusite-zones. The andalusite-zone appears to act as a transition zone between the lower isograds zones (biotite/garnet and staurolite) and the higher grade isograd zones (sillimanite and K-feldspar). These higher grade isograd zones, starting with the sillimanite-zone have a calculated stability field of ~575–700 °C and ~3–6.2 kbar and then the K-feldspar-zone has a stability field of ~560–735 °C and ~2.8–8.8 kbar. These two higher grade metamorphic zones continue the progression of increasing metamorphism through BTC
with temperatures increasing from 700 °C to 735 °C and pressures increasing from 6.2 kbar to a possible 8.8 kbar from the sillimanite to K-feldspar zones.

Conventional thermobarometry (Ti-in-Bt thermometry) supports this result (figure 6.2). This thermometer calculated based on the composition of biotite from specific analyzed samples yields and average temperature of 558 °C for the biotite/garnet-zone which is just slightly above the phase diagram calculation of 550 °C. The staurolite-zone yielded an average temperature of 530 °C based on this thermometer, which is well within the stability field calculated of 420–550 °C. The average temperature calculated for the andalusite-zone using this method is 590 °C which is about 40 °C higher than that calculated using phase diagrams. Looking at other results from the andalusite-zone, there is consistently non-typical results. The andalusite-zone shows an enrichment in Mg compared to other isograd zones (figure 6.1) and has three age groupings ranging from 1323-1647 Ma were the other zones only had one or two age groupings (figure 5.4). Finally, to compare the higher grade metamorphic isograd zones, the sillimanite-zone has an average temperature of 635 °C, and the K-feldspar-zone has an average calculated temperature of 670 °C. These averages fall well within the predicted stability fields for these samples yielded from phase diagram calculation. Even though Ti-in-Bt temperature calculations vary somewhat from phase diagram calculations, there is a progression of temperature described that corresponds to the increasing metamorphic grade within the canyon. Thus, I interpret that Big Thompson Canyon has a calculated increase in temperature from 550 °C to 735 °C from the lowest isograd zone to the highest isograd zone, and a pressure increase from 4.5 kbar to 8.8 kbar. This defines a metamorphic gradient of approximately 30 °C/km.

7.2 Style of metamorphism in BTC and influence of the Picuris Orogeny

These P-T data can be used to determine the tectonic processes responsible for formation of this metamorphic suite, as shown schematically on Fig. 7.1. For rocks experiencing regional metamorphism, crustal thickening leads to burial of surface sediments during thrusting (stages 1→2 on figure 7.1). In response, pressure increases due to the greater overburden and temperature increases in order to reach a new stable equilibrium at greater depth in the crust. This leads to a characteristic clockwise P-T path. Eventually, the burial rate slows as erosion begins at the surface and an isostatic equilibrium is approached (stage 2). Isotherms become steeper, and rocks may continue to heat up even when erosion is removing topography (2–3),
which produces the characteristic up-T/down-P loop seen in many regionally metamorphosed rocks. Later uplift/erosion/orogenic collapse causes exhumation back to the surface along a retrograde decompression and cooling path (3→…).

For rocks experiencing thermal metamorphism where there is no significant tectonic thickening or deformation, the P-T path is notably different. For instance, emplacement of hot magma (750–900 °C) triggers a temperature increase in surrounding rocks. If this occurs during orogenesis, there may also be some crustal thickening. Nonetheless, there must be a small increase in pressure if a rock is below the intrusion (1–2), although rocks adjacent to and above the intrusion experience a wholly isobaric P-T path. Eventually the intrusion and country rock reach a new thermal equilibrium and peak metamorphism is reached. The later rate of cooling is controlled by factors such as the duration and intensity of erosion and/or timing of later tectonic disturbances.

These tectono-thermal models represent discrete end-members on a natural continuum, and the presence of voluminous granitic plutons at the western end of BTC may invoke the question of whether the isograds, which appear somewhat parallel to these intrusions, are related to them or not. If the BTC isograds formed via thermal metamorphism, one would expect a low-angle (dP/dT) P-T path that reached peak conditions relatively quickly (i.e. within the lifespan of cooling of the magmatic heat source). However, collisional tectonics has a clockwise P-T loop.
Combining the geochronology and thermobarometry of this study supports the hypothesis that BTC was regionally metamorphosed due to tectonic loading associated with the Yavapai and/or Mazatzal Orogenies. It is unlikely that metamorphism was driven by granitic intrusion, since the duration of prograde metamorphism is estimated to be around 31 Ma and is longer than that expected from thermal metamorphism, which is typically <1 or <10 Myr. However, it is possible that thermal metamorphism played a part in developing later c. 1.4 Ga monazite ages in the andalusite- and K-feldspar-zones, which may be temporally associated with the Picuris Orogeny. The andalusite and K-feldspar zones both yielded two distinct age domains within the analyzed monazites. The andalusite zone shows a lower age population from 1323 – 1398 Ma and a higher age population at 1647 Ma. The K-feldspar zone also has two populations, one at 1420 Ma and another at 1700 Ma. These age populations within these two isograds zones are curious because the surrounding isograds zones do not show the lower age population that may
describe the Picuris Orogeny. If the Picuris Orogeny in this region were to have created a widespread regional metamorphic event reaching all the way to northern Colorado, then there should be evidence of this event in monazites from all of the isograd zones in BTC. Because not all of the isograd zones show an age grouping associated with the Picuris Orogeny, then the influence of the Picuris Orogeny in BTC and surrounding parts of northern Colorado may be due to plutonic activity.

Many exposures within Colorado that have Picuris ages are also associated with plutonic activity, such as metamorphic rocks found in the Wet Mountains of Central Colorado (Palmer et al., 2019). This implies that there was extensive magmatism taking place within Colorado around 1.4 Ga. For example, some are S-type granites that are formed via melting of pre-existing continental (felsic) crust, whereas others are A-type granites, which form via melting of more mafic rocks, such as amphibolites. The nature of the Picuris Orogeny is uncertain given the sparse data that currently exist within the continental USA.

The influence of the Picuris Orogeny and notion that BTC is a classic example of regional metamorphism is a curious subject. Regional metamorphism is generally characterized by one major continental building episode, where BTC shows evidence for the possibility of two major deformation events. This brings into question the validity of thermobarometry used in this study. If there is more than one event where these isograd zones reached a peak metamorphic equilibrium, then are the peak stability fields chosen for the isograd zones describing the older or younger event? This question is especially important for this study and the data that describes the andalusite- and K-feldspar zones, and leaves an open space for future work in this region of Colorado.

7.3 Future work

Big Thompson Canyon is a classic example of a regionally metamorphosed terrane with a coherent isograd sequence. Furthering the abundant work already executed on this canyon will lead to many new conclusions. To expand the understanding of the southward growth of North America in the Paleoproterozoic, detailed field mapping of the surrounding area should be done to estimate the extent of this isograd sequence. Determining the extent of regional metamorphism will help in narrowing down the deformation events that built super continents during the Proterozoic. To add to this investigation, in depth petrological studies that include
thermobarometry, and geochronology to constrain peak P–T conditions for the extent of regional metamorphism in this area should be executed. Taking these peak metamorphic conditions and subsequently calculating the duration of metamorphism in the region will only further the understanding of the formation and timing of North America.

Future work that would be beneficial to this study would include extensive geochronology and thermobarometry to build a framework of data for each isograd zone in BTC. Determining the extent of older and younger age domains within each isograd zone would be the major goal of building the data framework. By expanding the amount of data, a clearer picture of regional metamorphism and deformation events can be painted for this area. To better understand the relationship of intrusive bodies and possible thermal metamorphism, geochronological and mineral chemistry studies of intrusive bodies should also be conducted to find the interactions that occurred between the sedimentary and intrusive units. By conducting geochronological studies of intrusive units in this area, the influence and northern extent of the Picuris Orogeny on Colorado will be better understood.
CHAPTER 8

CONCLUSIONS

This in-depth study of Big Thompson Canyon, Colorado has led to new insight of the formation of the northern Colorado front range. As a whole, Big Thompson Canyon exhibits a coherent isograd sequence recording regional metamorphism. The five isograd zones that were looked at for this study shed light on the peak metamorphic conditions within the canyon, as well as an estimated duration of prograde metamorphism. There has not been an extensive study focused on the petrological implication for BTC; therefore, conclusions drawn from this study have not been previously explored. The main goal of this study was to constrain the peak metamorphic conditions from five isograd zones via thermobarometry, conduct a geochronological investigation to estimate the duration of metamorphism, pinpoint the style of metamorphism and begin to understand the influence of the Picuris Orogeny in northern Colorado.

The conclusions of this study are as follows:

- The temperature range from the biotite/garnet isograd zone (lowest) to the K-feldspar isograd zone (highest) increases from 550 °C to 735 °C, and has a predicted pressure increase from 4.5 kbar to 8.8 kbar. This defines a metamorphic gradient of approximately 30 °C/km across BTC.
- BTC is characterized by an initial regional style metamorphic event that is seen across all of the isograd zones due to tectonic loading during arc-continent accretion around approximately 1647-1700 Ma. A second event, most likely a thermal metamorphic event from proximal intrusive as a result of the Picuris Orogeny around 1400 Ma is seen within the andalusite and K-feldspar zones of BTC.
- The influence of the Picuris Orogeny in BTC is likely the result of proximal magmatism during an orogenic event that caused intrusions, crustal underplating and melting.


APPENDIX A

HAND SAMPLE PHOTOGRAPHS

Figure A.1 Hand sample BTC-02. Andalusite-zone.
Figure A.2 Hand sample BTC-04. Andalusite-zone

Figure A.3 Hand sample BTC-17. K-feldspar-zone.
Figure A.4 Hand sample BTC-20. Biotite-zone.

Figure A.5 Hand sample BTC-22. Staurolite-zone.
Figure A.6 Hand sample BTC-27. Andalusite-zone.
Figure A.7 Hand sample BTC-31. Andalusite-zone.

Figure A.8 Hand sample BTC-37. Sillimanite-zone.
Figure A.9 Hand sample BTC-43. Sillimanite-zone.
APPENDIX B

THIN SECTION SCANS

Figure B.1 Thin section scan (2.7 x 4.6 cm) of sample BTC-02. Andalusite zone
Figure B.2 Thin section scan (2.7 x 4.6 cm) of sample BTC-04. Andalusite zone

Figure B.3 Thin section scan (2.7 x 4.6 cm) of sample BTC-17. K-feldspar zone.
Figure B.4 Thin section scan (2.7 x 4.6 cm) of sample BTC-20. Biotite zone.

Figure B.5 Thin section scan (2.7 x 4.6 cm) of sample BTC-22. Staurolite zone.
Figure B.6 Thin section scan (2.7 x 4.6 cm) of sample BTC-23. Staurolite zone.

Figure B.7 Thin section scan (2.7 x 4.6 cm) of sample BTC-27. Andalusite zone.
Figure B.8 Thin section scan (2.7 x 4.6 cm) of sample BTC-31. Andalusite zone.

Figure B.9 Thin section scan (2.7 x 4.6 cm) of sample BTC-37. Sillimanite zone.
Figure B.10 Thin section scan (2.7 x 4.6 cm) of sample BTC-43. Sillimanite zone.
APPENDIX C

Table C.1: Standards used for EPMA analysis of major mineral chemistry

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<thead>
<tr>
<th>Element</th>
<th>Standard</th>
<th>Count Times</th>
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<td>Si</td>
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<tr>
<td>Al</td>
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<td>Mg</td>
<td>Olivine Fo93</td>
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<td>Fe</td>
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<td>Ti</td>
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<td>Na</td>
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<td>K</td>
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Table C.2 Standards used for EPMA *in-situ* monazite geochronology

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<td>LaPO₄</td>
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<td>CePO₄</td>
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<td>PrPO₄</td>
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</tr>
<tr>
<td>Nd</td>
<td>NdPO₄</td>
<td>Harlov GFZ</td>
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<tr>
<td>Sm</td>
<td>SMPO₄</td>
<td>Harlov GFZ</td>
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<tr>
<td>Eu</td>
<td>EuPO₄</td>
<td>Harlov GFZ</td>
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<td>GdPO₄</td>
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<td>TbPO₄</td>
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<td>U</td>
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### Table C.3 Bulk-rock geochemical in weight percent oxides obtained using XRF analysis

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<tr>
<th>Sample</th>
<th>Isograd-zone</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃(T)</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>LOI</th>
<th>Total</th>
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<td>0.12</td>
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<td>1.55</td>
<td>1.23</td>
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<td>0.10</td>
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### Table C.4 Trace element concentrations obtained using XRF analysis

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<th>Be</th>
<th>Co</th>
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APPENDIX D

DETAILED MONAZITE ELEMENT MAPS

Figure D.1 Detailed element map of monazite 1 from sample BTC-02 (andalusite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-02 Monazite 1
diameter: ~40 µm
Zone A: 1329.4 ± 9 Ma
Zone B: 1306.8 ± 13 Ma
Average: 1318 ± 15 Ma

Point of analysis (~1 µm)
Approx. zone boundary
Figure D.2 Detailed element map of monazite 3 from sample BTC-02 (andalusite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-02 Monazite 3
- Diameter: ~100 µm
- Zone A: 1610 ± 22 Ma
- Zone B: 1581.6 ± 24 Ma

- Point of analysis (~1 µm)
- Approx. zone boundary
Figure D.3 Detailed element map of monazite 4 from sample BTC-02 (andalusite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-02 Monazite 4
diameter ~60 µm
Zone A: 1646 ± 10 Ma
Zone B: 1353 ± 34 Ma

- Point of analysis (~1 µm)
- Approx. zone boundary
Figure D.4 Detailed element map of monazite 5 from sample BTC-02 (andalusite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-02 Monazite 5
Zone A: 1661.4 ± 7 Ma
Zone B: 1151.2 ± 14 Ma
Zone C: 1392 ± 9 Ma

- Point of analysis (~1 μm)
- Approx. zone boundary
Figure D.5 Detailed element map of monazite 6 from sample BTC-02 (andalusite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-02 Monazite 6
diameter ~40 μm
Zone A: 1641 ± 6 Ma

- Point of analysis (~1 μm)
- Approx. zone boundary
Figure D.6 Detailed element map of monazite 1 from sample BTC-17 (k-feldspar-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-17 Monazite 1
diameter ~20 μm
Zone A: 1423 ± 7 Ma
Zone B: 1686 ± 4 Ma
- Point of analysis (~1 μm)
/ Approx. zone boundary

Figure D.7 Detailed element map of monazite 2 from sample BTC-17 (k-feldspar-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-17 Monazite 2
diameter ~35 μm
Zone A: 1653 ± 9 Ma
- Point of analysis (~1 μm)
/ Approx. zone boundary
Figure D.8 Detailed element map of monazite 3 from sample BTC-17 (k-feldspar-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-17 Monazite 3
diameter ~20 µm
Zone A: 1657 ± 7 Ma

- Point of analysis (~1 µm)
- Approx. zone boundary

Figure D.9 Detailed element map of monazite 4 from sample BTC-17 (k-feldspar-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-17 Monazite 4
diameter ~50 µm
Zone A: 1685 ± 18 Ma
Zone B: 1632 ± 16 Ma
Average: 1655 ± 30 Ma

- Point of analysis (~1 µm)
- Approx. zone boundary
Figure D.10 Detailed element map of monazite 5 from sample BTC-17 (k-feldspar-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-17 Monazite 5
diameter ~20 µm
Zone A: 1659 ± 2 Ma
Zone B: 1677 ± 9 Ma
Average: 1671 ± 10 Ma

- Point of analysis (~1 µm)
- Approx. zone boundary
Figure D.11 Detailed element map of monazite 2 from sample BTC-23 (staurolite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-23 Monazite 2
diameter ~50 μm
Zone A: 1638 ± 12 Ma

- Point of analysis (~1 μm)
- Approx. zone boundary
Figure D.12 Detailed element map of monazite 3 from sample BTC-23 (staurolite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-23 Monazite 3
- Diameter ~30 µm
- Zone A: 1636.8 ± 10 Ma
- Zone B: 1667 ± 19 Ma
- Average: 1652 ± 20 Ma

- Point of analysis (~1 µm)
- Approx. zone boundary
Figure D.13 Detailed element map of monazite 4 from sample BTC-23 (staurolite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.
Figure D.14 Detailed element map of monazite 5 from sample BTC-23 (staurolite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-23 Monazite 5
diameter ~50 μm
Zone A: 1651 ± 3 Ma
Zone B: 1630 ± 19 Ma
Zone C: 1652 ± 3 Ma
Average: 1644 ± 14 Ma

- Point of analysis (~1 μm
  Approx. zone boundary
Figure D.15 Detailed element map of monazite 6 from sample BTC-23 (staurolite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-23 Monazite 6
diameter ~30 μm
Zone A: 1634 ± 6 Ma
Zone B: 1629 ± 27 Ma
Average: 1632 ± 16 Ma

Point of analysis (~1 μm)
Approx. zone boundary
Figure D.16 Detailed element map of monazite 7 from sample BTC-23 (staurolite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-23 Monazite 7
diameter ~20 µm
Zone A: 1614 ± 15 Ma
Zone B: 1639 ± 4 Ma
Average: 1626 ± 15 Ma

Point of analysis (~1 µm)
Approx. zone boundary
Figure D.17 Detailed element map of monazite 8 from sample BTC-23 (staurolite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.
Figure D.18 Detailed element map of monazite 1 from sample BTC-37 (sillimanite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-37 Monazite 1
diameter ~25 μm
Zone A: 1688 ± 12 Ma
Zone B: 1661 ± 8 Ma
Average: 1674.7 ± 16 Ma

- Point of analysis (~1 μm)
- Approx. zone boundary
Figure D.19 Detailed element map of monazite 2 from sample BTC-37 (sillimanite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-37 Monazite 2
Diameter ~55 µm
Zone A: 1619.8 ± 14 Ma
Zone B: 1620 ± 10 Ma
Average: 1620 ± 10 Ma

• Point of analysis (~1 µm)
/ Approx. zone boundary
Figure D.20 Detailed element map of monazite 3 from sample BTC-37 (sillimanite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-37 Monazite 3
diameter ~25 µm
Zone A: 1652 ± 16 Ma

Point of analysis (~1 µm)
Approx. zone boundary
Figure D.21 Detailed element map of monazite 4 from sample BTC-37 (sillimanite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-37 Monazite 4
diameter ~55 μm
Zone A: 1652 ± 6 Ma
Zone B: 1618.8 ± 10 Ma
Zone C: 1626 ± 14 Ma
Average: 1632 ± 17 Ma

- Point of analysis (~1 μm)
/ Approx. zone boundary
Figure D.22 Detailed element map of monazite 6 from sample BTC-37 (sillimanite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-37 Monazite 6
diameter ~30 μm
Zone A: 1673 ± 7 Ma

Point of analysis (~1 μm)
/Approx. zone boundary
BTC-37 Monazite 7
diameter \~35 \, \mu m
Zone A: 1637 \pm 8 \, Ma
Zone B: 1670 \pm 4 \, Ma

Point of analysis (\~1 \, \mu m)
\slash\ Approx. zone boundary

Figure D.23 Detailed element map of monazite 7 from sample BTC-37 (sillimanite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.
Figure D.24 Detailed element map of monazite 8 from sample BTC-37 (sillimanite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.
Figure D.25 Detailed element map of monazite 11 from sample BTC-37 (sillimanite-zone) showing concentration of Y, Th, U, Ce and the original EPMA backscattered electron image or compo. Specific zones are circled in red, and corresponding ages are listed.

BTC-37 Monazite 11
diameter ≈55 μm
Zone A: 1628.5 ± 24 Ma
Zone B: 1650 ± 23 Ma
Average: 1640.6 ± 22 Ma

- Point of analysis (~1 μm)
- Approx. zone boundary
APPENDIX E

SUPPLEMENTAL ELECTRONIC FILES FOR ELECTRON PROBE MICROANALYZER MONAZITE GEOCHRONOLOGY ANALYSES

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APPENDIX F

SUPPLEMENTAL ELECTRONIC FILES FOR ELECTRON PROBE MICROANALYZER MINERAL ANALYSES

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