Assessing the zircon compositional evolution from the Guichon Creek Batholith and Highland Valley Copper deposit, south-central B.C.

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Abstract. The Late Triassic Guichon Creek batholith formed over a period of four million years and hosts the deposits of the Highland Valley Copper porphyry Cu ± (Mo) district. The batholith consists of multiple granodiorite to quartz monzonite intrusions that have zircon as an accessory phase. Zircon compositions were investigated from fifteen samples from the edge to the centre of the batholith to evaluate their potential as an indicator of mineralizing processes. Europium and titanium concentrations were used to determine Eu/Eu* values and calculate temperatures of formation. Zircon from the early phases have Eu/Eu* values of 0.20-0.55 and calculated temperatures of 850°-750°C. Later phases that host mineralization generally have zircons with higher Eu/Eu* up to 0.75 and calculated temperatures down to 600°C. The increase in Eu/Eu* suggests increasing oxidation state in the magma towards conditions favourable for mineralization. Dikes from the porphyry copper deposits that are syn- to post-mineral have higher trace element content and trend from high Eu/Eu* values to lower, thus reflecting exsolution of fluids from the melt and subsequent ore deposition. Evaluating zircon compositions from evolving batholiths emphasizes a broad scale potential for exploration of porphyry deposits.

1 Introduction

The Guichon Creek Batholith (GCB) located in south-central British Columbia, is an elongate, concentrically zoned body that intrudes the sub-marine volcanic and sedimentary units of the Late Triassic Nicola Group. Several moderate to large tonnage porphyry copper deposits are hosted within the centre of the GCB and make up the Highland Valley Copper district (HVC) which is fully-owned and operated by Teck Resources Limited and makes up one of the largest copper resource in Canada (Byrne et al. 2013; Teck 2016). New U-Pb TIMS and Re-Os ages indicate that the GCB formed from up to three magmatic pulses that culminated in the formation of the economic ore deposits at HVC circa ~208.4 Ma

(D'Angelo et al. 2017). Trace element composition of zircon from samples dated by D'Angelo et al. (2017) were analysed to characterize evolutionary changes in zircon chemistry from the early edge of the batholith to the syn- to post-mineral dikes at the HVC deposits. Zircon (Zr[Hf]SiO$_4$) incorporates multiple minor and trace elements into its structure, the concentrations of which can be used to determine the temperature and oxidation state of the parental melt. Recent studies in zircon compositions from intrusive rocks associated with economic porphyry copper deposits are characterized by decrease in SO_2, increased oxidation state and water-rich composition of these granites (Ballard et al. 2002; Dilles et al. 2015; Shen et al. 2015; Lee et al. 2017). Evaluating the zircon compositions from the GCB phases and dikes with precise age dates provides a means by which the usefulness of this method as an exploration and evaluation tool can be determined.

2 Geology of GCB and HVC deposits

The Late Triassic GCB is a compositionally zoned calc-alkalic body that hosts multiple porphyry Cu ± (Mo) deposits including the past producing Bethlehem and the currently mined Valley, Lornex, and Highmont deposits (Figure 1; McMillan 1985; Byrne et al. 2013). Fifteen samples of fresh to altered rocks from the various batholith phases were collected from the margin of the batholith to the core, including late dikes from within the Bethlehem, Valley and Highmont pits (Fig.1). All ages referenced are from D'Angelo et al. (2017) except the Gump Lake phase.

2.1 Pre-GCB Gump Lake phase

The Gump Lake phase is an elongate 3x10 km granodiorite to quartz monzonite located along the eastern edge of the GCB. Sampled for this study (KB132), the intrusive phase has previously been mapped as syn- to post-GCB (McMillan et al., 2009), however, new U-Pb TIMS dating puts the age of formation at 218.01 ± 0.18 Ma. The phase is geochemically different from the early marginal phases of the GCB and this, with the new age data, suggests that magmatic activity and batholith formation is older than had been previously recognised in the region.
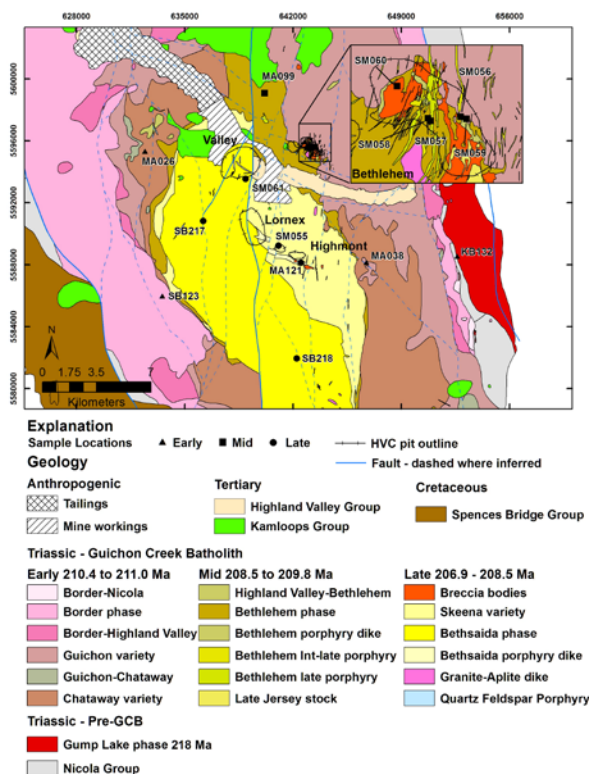
Figure 1. Geologic map of the Guichon Creek batholith modified after ongoing CMIC-Footprint contributions and referenced within Byrne et al. (2017). Samples referenced in D'Angelo et al. (2017) except KB132 (Gump Lake phase) from this study. Main economic deposits include Valley, Lornex, Highmont, and Bethlehem (inset).

2.2 Early GCB phases

The margin of the GCB comprises an equigranular and mafic Border phase and a Highland Valley facies, which consists of the Guichon and Chataway sub-facies. Contacts between the Guichon and Chataway sub-facies are generally gradational from granodiorite to quartz monzodiorite; however, local sharp boundaries can occur (Byrne et al. 2013; D'Angelo et al. 2017). Samples of all three phases and the transitional zone of the Highland Valley phase were collected. U-Pb ages for these phases range from 211.0 to 210.4 Ma and are generally within error of each other (Fig. 1).

2.3 Middle GCB phases

The Bethlehem facies and associated porphyry dikes, stocks, and brecciated phases from the HVC Bethlehem pit are here defined as part of the middle GCB units. The Bethlehem facies is a weakly porphyritic granodiorite that occurs between the Highland Valley phase and later Skeena facies but is in contact with the Guichon phase in the Bethlehem deposit. Dikes sampled for this study from the Bethlehem deposit include the early feldspar and quartz phyric Bethlehem porphyry, the equigranular to porphyritic Jersey stock, and the late-mineral feldspar and quartz-

phyric porphyry dike (FQPC). The age of these units ranges from 208.5 to 209.8 Ma and they are associated with an earlier mineralization event at the Bethlehem deposit relative to the main mineralization at the Valley and Lornex deposits (Byrne et al. 2013).

2.4 Late GCB phases

The youngest phases (206.9 to 208.5 Ma) of the GCB are in the centre of the batholith and consist of felsic granodiorite to monzogranite (Skeena facies) and the weakly porphyritic granodiorite and monzogranite of the Bethsaida facies. These units host the main copper mineralization at the Valley, Lornex, and Highmont deposits. Two samples of Bethsaida facies were collected from outside of the main deposits and one of Skeena facies is from the Lornex pit. Two syn- to post-mineral dikes are from Valley drill core and the Highmont pit. The biotite-phyric porphyry 'salt and pepper' (S&P) Bethsaida dike from Valley was dated at 208.2 Ma and the quartz and feldspar phyric, quartz-rich porphyry dike (QFPQ) from Highmont was dated at 206.9 Ma bounding the minimum age of the GCB (D'Angelo et al. 2017).

3 Methods

Twenty to twenty-four zircon grains from each sample were analysed for trace element composition using laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS) technique. Approximately twenty-five, 47 μm core to rim spots (Fig. 2) were conducted on each sample over a fifteen hour session yielding >375 analyses, not including standards. Isotopes measured include Ca^{48} to monitor for apatite inclusions and Ti^{49} to calculate temperatures after Watson et al., (2006). Additional elements measured included Y, Nb, Ta, REE, Hf, U, Th, and Pb.
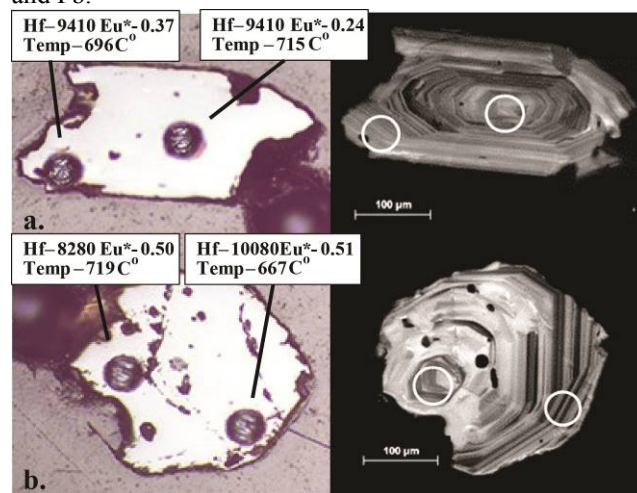

Figure 2. Reflected light and cathodoluminescent images of zircon with spot locations for **a** Gump Lake phase, and **b** Bethsaida phase. Hafnium concentration, Eu/Eu* (Eu*) value, and calculated temperature given for each spot location. Grains from all samples varied in zoning characteristics but where able a core and rim spot analysis was taken for each zircon grain.

4 Discussion

Hafnium content in zircon can generally be used as a proxy for crystallization percent as concentration increases due to Hf incompatibility in the parent melt (Hanchar and Watson 2003; Dilles et al. 2015). In the GCB phases Hf concentration generally varies from less than 7000 to 14000 ppm, whereas the Gump Lake phase clusters around 9000 ppm (Fig. 2). Using Hf as a proxy for crystallization and comparing with Eu/Eu* values $\{[Eu]_N/([Sm]_N*[Gd]_N)^{0.5}$ where $[Eu]_N$, $[Sm]_N$, $[Gd]_N$ are chondrite-normalized$\}$, the general oxidation state can be determined as increased water content decreases plagioclase crystallization resulting in a lower negative europium anomaly in zircon (Dilles et al. 2015). The Gump Lake, Guichon, and Guichon-Chataway (Highland Valley transitional unit) phases have Eu/Eu* values ranging from 0.20 to 0.40, whereas the Border phase varies from 0.30 to 0.55 (Fig. 3A). The Chataway phase shows a distinct trend relative to the other early phases in that the Eu/Eu* values increase from 0.30 to 0.70 with increasing Hf concentration. The middle GCB Bethlehem phases and late GCB Skeena and Bethsaida phases have Eu/Eu* values ranging from 0.30 to 0.70, suggesting an increase in aqueous fluids in the melt and higher oxidizing conditions through time (Figs. 3B, 3C). The dikes associated with or post-mineralization from the Valley and Highmont pits ('S&P' Bethsaida; QFPQ) trend from higher Eu/Eu* values 0.70 to lower 0.20 with increasing Hf content (Fig. 3D). Although variation within individual samples is high the overall trend shows increasing Eu/Eu* values from the early phases to the Bethsaida facies followed by a sharp decrease with the 'salt and pepper' Bethsaida and QFPQ dikes (Fig. 4). There is a slight difference between the two Bethsaida samples with sample SB217 located southwest of the Valley pit (Fig. 1) having a lower variation than sample SB218 located to the east. This could be the result of heterogeneity in the Bethsaida facies but the overall Eu/Eu* values in the Bethsaida facies fall above 0.40. Decreasing Eu/Eu* values with increasing Hf content within individual samples have been observed in other porphyry copper deposits (Lee et al. 2017) and indicates either early fluid saturation and release in the parental melt or alternatively mixing between an upper oxidized melt with a reduced melt. The younger 'salt and pepper' Bethsaida and QFPQ dikes have higher concentrations of Y, Ta, Nb, and REE relative to the other samples suggesting they crystallized from a more enriched source. Calculated Ti^{49} temperatures (calculation referenced in Watson et al. 2006) for the samples show a higher temperature range for the early GCB phases relative to the later phases (Fig. 5). Additionally the temperature range for the 'salt and pepper' Bethsaida dike shows a subtle increase with increasing Hf content suggesting probable mixing with a late higher temperature melt (Fig. 5D). Zircon composition from these dikes reflect the melt composition during the main mineralization event at HVC suggesting that the possible mixing event released the buildup of aqueous fluids in the GCB allowing for the

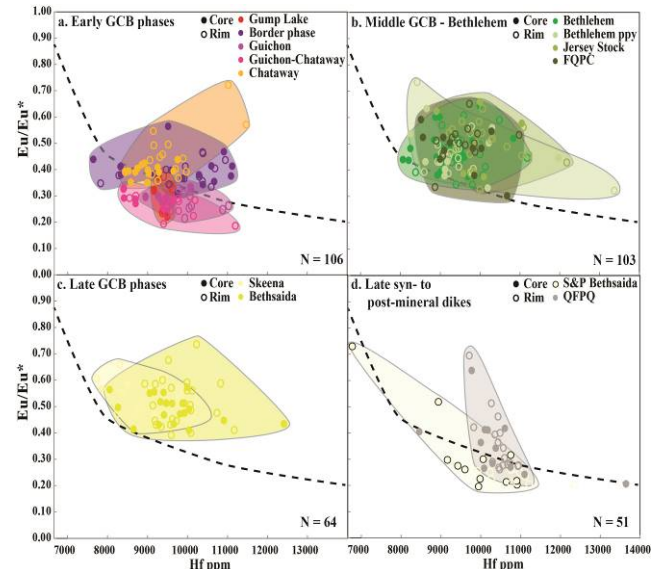extraction and deposition of the main ore deposits at HVC.

Figure 3. Eu/Eu* vs. Hf concentration in zircon point samples from: **a** early GCB phases; **b** middle GCB Bethlehem phases and dikes; **c** late GCB phases; and **d** syn- to post-mineral dikes from Valley and Highmont deposits. Dashed line conceptualized after Dilles et al. (2015) denoting normal zircon crystallization path under reduced conditions (below line) and increasing oxidation and SO_2 release (above line). Early GCB phases generally fall below dashed line with later phases starting with Chataway sub-facies having a higher Eu/Eu* value with increasing Hf content. The syn- to post-mineral dikes from Valley and Highmont have an opposing trend with decreasing Eu/Eu* value with increasing Hf content. ppy = porphyry, S&P = salt and pepper.
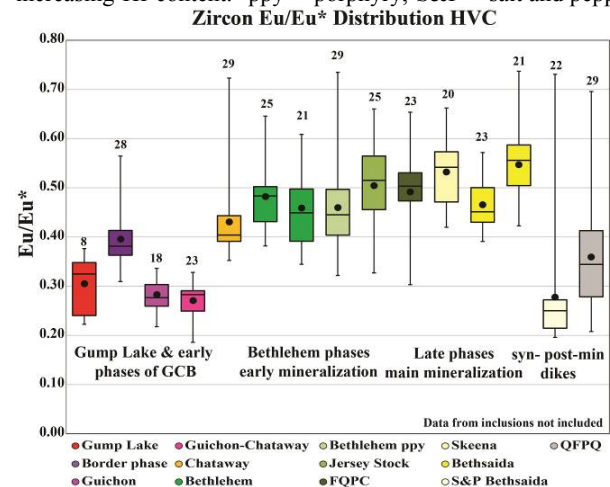

Figure 4. Box and whisker plots for zircon Eu/Eu* values from the fifteen GCB samples, number of analyses per sample labelled above each plot. Distribution of Eu/Eu* values tend to have large variance within individual samples but show a general trend of increasing from 0.20 to 0.70 suggesting an increase in the oxidation state of the magma chamber from the edge of the batholith inwards to the late Bethsaida phase. The younger 'salt & pepper' Bethsaida and QFPQ dikes from Valley and Highmont respectively show a large range but dominantly with values below 0.4 indicating a trend to a lowered oxidation state with larger negative Eu anomaly relative to the Skeena and Bethsaida phases.
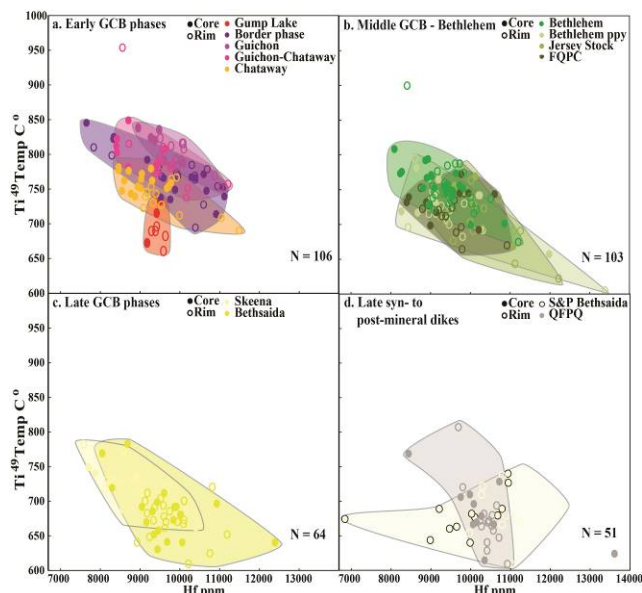
Figure 5. Calculated Ti^{49} temperatures after Watson et al. (2006) corrected for TiO$_2$ activity of ≈ 0.7 after Ferry and Watson (2007) vs. Hf concentration in zircon samples from: **a** early GCB phases; **b** middle GCB Bethlehem phases and dikes; **c** late GCB phases; and **d** syn- to post-mineral dikes from Valley and Highmont deposits. Early phases have higher calculated temperatures except for Gump Lake phase relative to the middle and late GCB phases which are at or near solidus temperatures. The late 'salt and pepper' Bethsaida dike has a subtle increase in temperature with increasing Hf content suggesting possible mixing with a higher temperature melt. ppy = porphyry, S&P = salt and pepper.

4 Summary

Acquisition of zircon trace element concentration via LA ICP-MS allows for lower cost, rapid analysis of multiple data points that is still viable relative to other more precise techniques such as sensitive high resolution ion microprobe - reverse geometry (SHRIMP-RG). Data acquired from the GCB and associated HVC porphyry deposits indicate an increase in Eu/Eu* values with time to conditions where fluid content is high and potential for metal extraction from the melt is greater. The youngest sampled dikes have a trend of decreasing Eu/Eu* values with crystallization, suggesting potential mixing with an oxidized upper chamber and an enriched higher temperature melt. This is interpreted to have contributed to the formation of the large tonnage ore deposit at HVC due to fluid release and metal extraction from the lower source magma. Zircon composition when analysed over a large districts has potential to determine ore fertility of large regional granite systems.

Acknowledgements

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