Mineral markers of porphyry copper mineralization: Work in progress at the Gibraltar deposit, British Columbia

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Abstract

Indicator minerals that can persist within glacial sediments offer the potential to be tracers towards buried porphyry mineralization. This study is examining the composition of epidote, rutile and zircon in till and bedrock from the Gibraltar copper-molybdenum porphyry deposit, British Columbia, to test their utility as indicators of mineralizing system fertility. Some rutile grains in till at Gibraltar have a composition comparable to rutile from the El Teniente porphyry copper deposit in Chile. Comparison of the composition of rutile in till and bedrock at Gibraltar is in progress. Other studies have indicated that high Ce/Ce* values in magmatic zircon are indicative of oxidizing conditions that are favourable for the formation of porphyry deposits. At Gibraltar, zircon from the mineralized phase of the intrusion yields high Ce/Ce* values (average of 133) relative to the barren intrusive phases. Epidote is more abundant in till in the region of the host intrusion. Such distribution was originally interpreted to be derived from the propylitic alteration related to porphyry mineralization. Detailed analysis of the epidote shows that epidote in till could be derived from the contact zone between the Granite Mountain batholith and the Nicola volcanic rocks.

Introduction

Significant interest is dedicated to the study of mineral chemistry indicative of fertile porphyry copper mineralization. For example, the compositions of zircon (Ballard et al., 2002; Lee et al., 2017a; Hattori et al., 2017; Zhang et al., 2017), epidote (Cooke et al., 2014; Jago et al., 2014), magnetite (Canil et al., 2016; Pisiak et al., 2017), apatite (Bouzari et al., 2016; Mao et al., 2016; Rukhlov et al., 2016), tourmaline (Baksheev et al., 2012; McClenaghan et al., 2017, 2018), titanite (Che et al., 2013; Celis et al., 2014; Celis, 2015; Kobylinski et al., 2016), plagioclase (Williamson et al., 2016) and chlorite (Wilkinson et al., 2015) have been investigated to understand the controls and ore formation processes related to mineral chemistry. The ultimate objective of this research is to be able to use these ore, magmatic and alteration minerals in rocks and/or sediments as indicators and vectors in mineral exploration for copper porphyry deposits.

This study aims to define a suite of minerals that are indicative of porphyry copper mineralization (e.g. zircon, epidote and rutile) and to test their utility in defining the fertility of porphyry systems within a glaciated landscape. The activity relies on till heavy mineral concentrates previously collected from four areas with porphyry copper mineralization in British Columbia (Ferbey et al., 2016; Plouffe and Ferbey, 2016; Plouffe et al., 2016). These sites include the Highland Valley Copper, Gibraltar and Mount Polley deposits and the Woodjam prospect (Fig. 1). The till sampling surveys completed around these copper porphyry systems revealed that a number of minerals recovered from till may be indicative of copper porphyry mineralization. Certain minerals such as chalcopyrite and jarosite are more abundant in till close to mineralization and generally decrease in abundance with increasing distance down ice from ore zones (Hashmi et al., 2015; Plouffe and Ferbey, 2015a; Plouffe et al., 2016). Other minerals that can be derived from a variety of rock types (e.g. apatite and magnetite) need to be chemically characterized to be linked to a porphyry copper source (Rukhlov et al., 2016; Pisiak et al., 2017; Plouffe and Ferbey, in press). Herein we report on work in progress on zircon, rutile and epidote composition in till and bedrock at the Gibraltar porphyry copper-molybdenum deposit in south-central British Columbia.

Background

The Gibraltar Mine is a calc-alkaline porphyry copper-molybdenum deposit hosted within the Late Triassic Granite Mountain batholith, which intruded volcanic and sedimentary rocks of the Upper Triassic to Lower Jurassic Nicola Group of the Quesnel Terrane (Fig. 1). At least three intrusive phases have been recognized in the Granite Mountain batholith including from west to east, the border, mine, and Granite Mountain phases (Fig. 2). The mine phase contains the economic copper-molybdenum porphyry mineralization. Including past production and current resources, the deposit represents 1.22 billion tonnes of ore with a Cu grade of 0.317% and an estimated Mo

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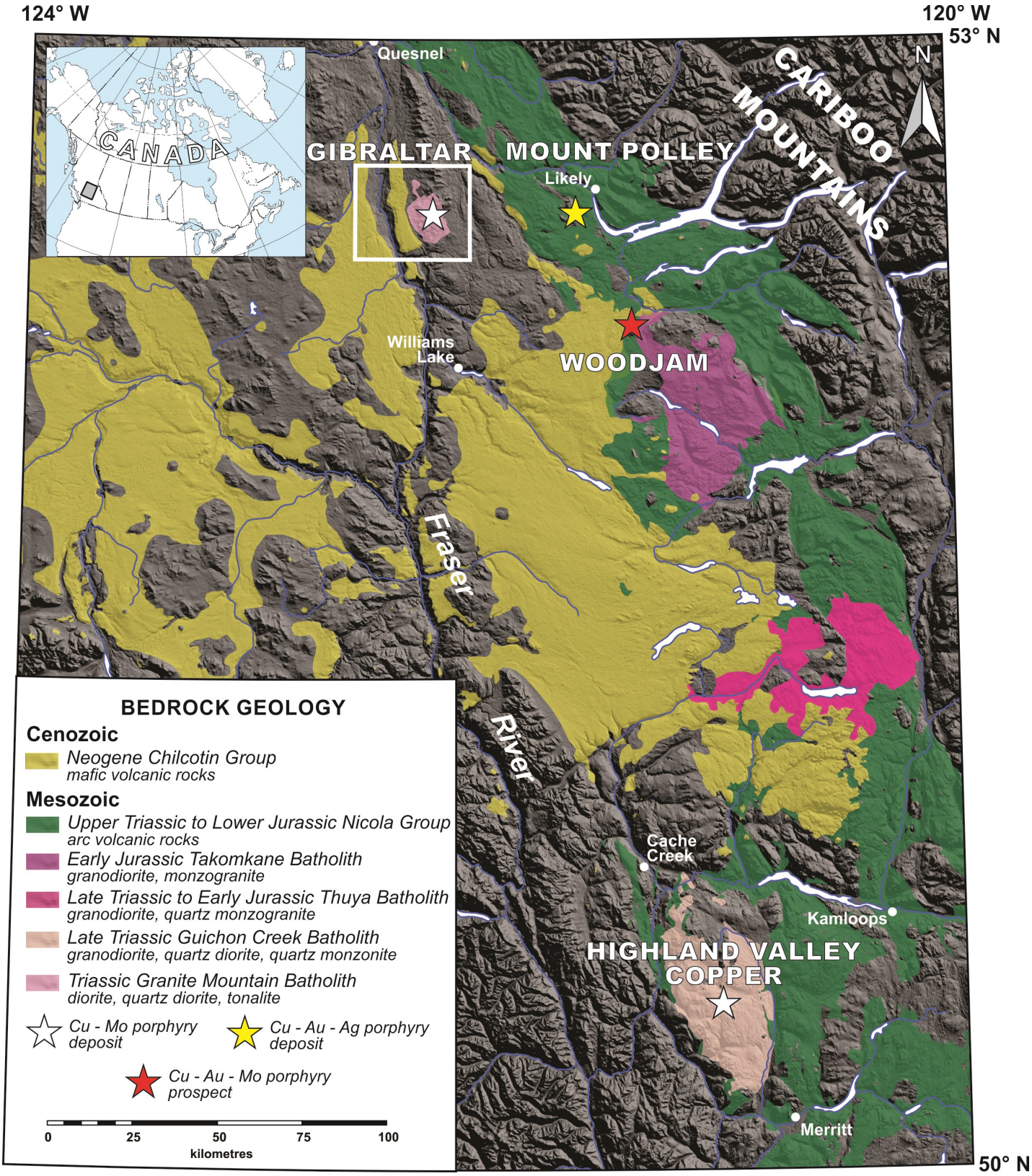

Figure 1. Location map of the Gibraltar and Highland Valley Copper porphyry copper-molybdenum deposits in British Columbia (modified from Plouffe et al., 2017). The white frame around Gibraltar represents the extent of Figures 2, 5, 6a and 8.

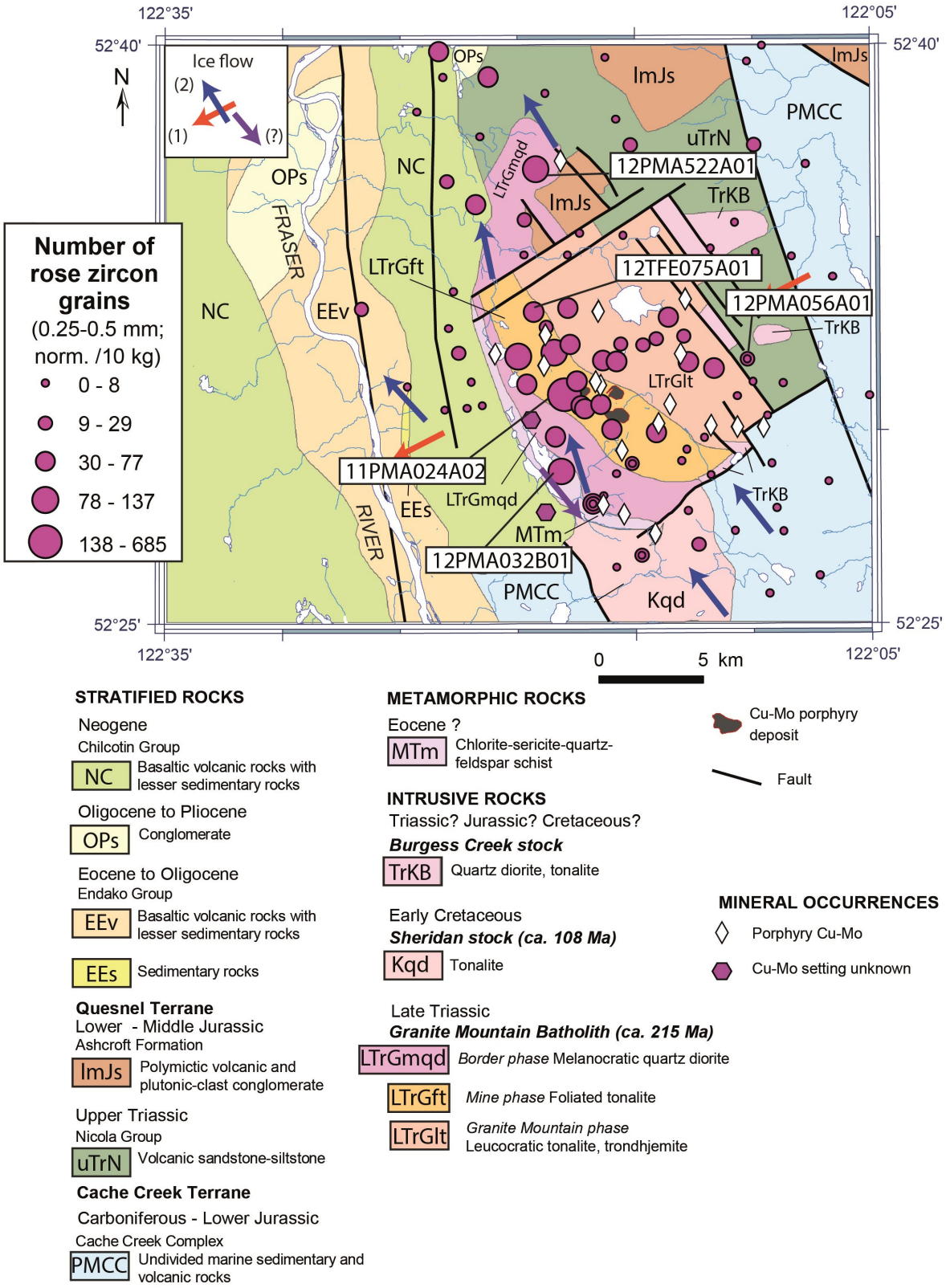

Figure 2. Rose zircon grain counts in the 0.25–0.5 mm, >3.2 SG fraction of till normalized to 10 kg sample weight at Gibraltar and distribution of samples collected for analysis. Figure modified from Plouffe and Ferbey (in press). Mineral grain count data is from Plouffe and Ferbey (2016). Till samples from which zircon grains were analyzed are labelled (e.g. 12P-MA522A01).

grade of 0.010% (van Straaten et al., 2013). The main ore minerals at Gibraltar are chalcopyrite, molybdenite and bornite. Propylitic hydrothermal alteration is present in the batholith extending outward at least 5 km from mineralization and includes epidote, chlorite and albite (Drummond et al., 1973, 1976; van Straaten et al., 2013; Kobylinski et al., 2017).

The Gibraltar region was last glaciated during the Late Wisconsin Fraser Glaciation (Clague and Ward, 2011). Most of the region is covered by till with lesser amounts of glaciofluvial sand and gravel deposits in valleys (Plouffe and Ferbey, 2015b). Three ice movements have been identified in the Gibraltar region: i) an initial local ice movement towards the southeast likely derived from a mountain ridge with cirques and arêtes located ca. 12 km north of the mine; ii) a regional movement to the southwest derived from the Cariboo Mountains; and iii) a third movement, likely the dominant one, towards the north to northwest, derived from an ice divide around 52° latitude (Plouffe et al., 2016). The till surface was marked by drumlins, flutings and crag-and-tails during this last event.

Analytical methods

Zircon, rutile and epidote compositions from till and bedrock were determined by a combination of laser ablation – inductively coupled plasma mass spectrometry (LA-ICP-MS), scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS) and electron probe microanalyses (EPMA) at the University of Ottawa. Analyses were conducted on polished thin section (bedrock samples) and individual grains recovered from heavy mineral concentrates (till and bedrock samples).

Zircon composition

A number of studies point out the potential of zircon as a fertility indicator for porphyry mineralization (Ballard et al., 2002; Liang et al., 2006; Chapman et al., 2012; Dilles et al., 2015; Shen et al., 2015; Hattori et al., 2016, 2017; Lu et al., 2016; Lee et al., 2017a, b; Yang et al., 2017; Zhang et al., 2017). In summary, the rare earth element (REE) composition of magmatic zircon reflects melt oxidation state, which correlates with the potential of an intrusion to host porphyry-style mineralization. For example, in the above listed studies, magmatic zircons from fertile porphyry systems typically have higher ratios of Eu/Eu* (>0.3), Ce^{+4}/ Ce^{+3} (typically >100), 10000(Eu/Eu*/Y) (>1), (Ce/Nd)/Y (>0.01) compared to zircons from barren intrusions. It is recognized that the presence of other REE-bearing minerals, such as titanite, can influence the REE composition of zircon, but even in such conditions the Eu/Eu* might remain a good proxy for fertile versus barren intrusions (Loader et al., 2017).

With this background knowledge at hand, we are testing zircon as a potential porphyry copper indicator mineral given its presence and regional distribution in till in the Gibraltar region (Fig. 2). In an oxidized magma potentially fertile for porphyry mineralization, Ce can occur in a +4 valence (Ce^{+4}) and substitute for Zr^{+4} in zircon, which can produce positive Ce anomalies in chondrites normalized rare earth element (REE) plots. The ratio Ce/Nd is a means of depicting the Ce enrichment in zircon and hence the relative oxidation state (and the fertility potential) of the magma (Hattori et al., 2017). The Ce/Nd ratio becomes useful when studying detrital zircon grains for which the Ce anomaly (Ce/Ce*; determined with La and Nd concentrations) cannot be calculated because the La concentrations are close or below the detection limit. At Gibraltar, zircon grains with the highest Ce anomaly are from the mine phase, which hosts the economic mineralization (Fig. 3a, b). Similar REE patterns are observed in zircon grains in till (Fig. 3c) but the Ce anomaly cannot be directly calculated for these grains, because the La concentrations are below detection limit or low

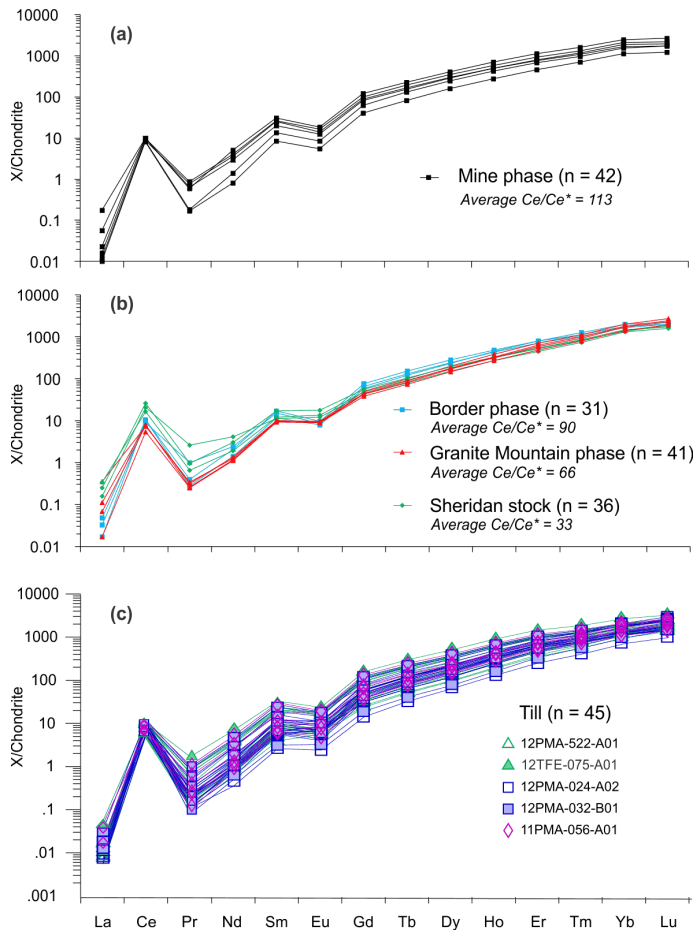

Figure 3. Chondrite-normalized rare earth element (REE) concentrations in zircon grains from: (a) the mine phase; (b) the border and Granite Mountain phases, and the Sheridan Creek stock; and (c) till. Till sample locations shown in Figure 2. Zircon from the mine phase (a), host of the copper-molybdenum mineralization, yields high Ce/Ce* values relative to the other intrusive phases. Samples taken from the barren Sheridan stock have low average Ce/Ce* (33). Chondrite values are from McDonough and Sun (1995).

and not precise. On the other hand, the Ce/Nd ratios in zircon grains from till provide an indication of the presence of a fertile intrusion. Till sample 11PMA024A02 located < 1 km from mineralization, contains three zircon grains with high Ce/Nd ratios (>18) which are indicative of more oxidizing magmatic conditions compared to the other grains (Fig. 4). Further investigation of the zircon rare earth element composition in intrusive rocks and till at Gibraltar is in progress.

Additionally, we have calculated the crystallization temperature of zircon grains in intrusive rocks and till at Gibraltar using the Ti in zircon thermometry method of Ferry and Watson (2007) assuming an activity of 0.7 for TiO_2 and 1.0 for SiO_2. This shows that the crystallization temperatures of the intrusive rocks at Gibraltar are generally hotter near mineralization (748–817°C) compared to distal sites (712–747°C) (Fig. 5). Similar temperatures have been calculated from zircon grains recovered from till (Fig. 4).

Rutile

We completed the analyses of red rutile grains obtained from five till samples located up- and down-ice of mineralization (Fig. 6a; Wolfe, 2017). Four out of five till samples contain at least one grain of rutile with a Mo and Sb content corresponding to the composition of rutile in the high- and low-grade ore at the El Teniente copper deposit in Chile (Fig. 6b; samples 11PMA024A02, 11PMA038A01, 12PMA042A01, and 12PMA536A01) (Rabbia et al., 2009; Wolfe et al., 2017).

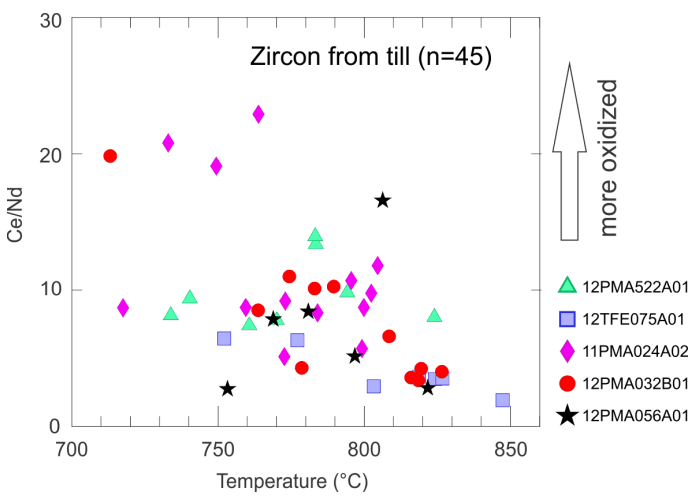

Figure 4. Ce/Nd ratio in zircon grains from till as a proxy to the Ce anomaly in zircon and hence the relative oxidation state of the magma (Hattori et al., 2017). Grains with the higher ratios are from more oxidized magma and could be indicative of fertility (e.g. Ballard et al., 2002). Sample 11PMA024A02 with three zircon grains characterized by an oxidized magma signature is located <1 km from mineralization. Modified from Wolfe et al. (2017). Sample locations are shown in Figure 2.

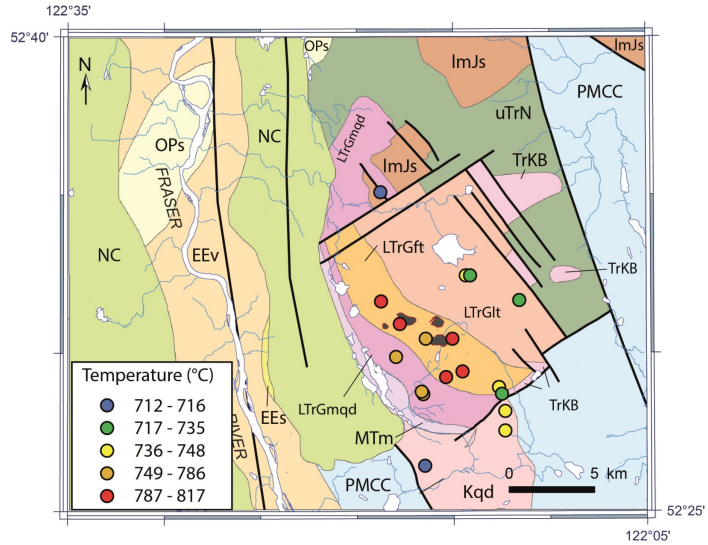

Figure 5. Distribution of zircon crystallization temperatures from the Granite Mountain batholith based on Ti in zircon thermometry (°C) calculated using the methodology of Ferry and Watson (2007), and assuming an activity of 0.7 for TiO_2 and 1.0 for SiO_2.

The only till sample with not a single grain of rutile within the El Teniente compositional field (12PMA056A01) is located approximately 7 km east (up-ice) from mineralization. Comparison of the rutile composition in till and bedrock at Gibraltar is in progress.

Epidote

Epidote is a common mineral in the hydrothermal alteration zones of copper porphyry deposits (e.g. Sinclair, 2007; Sillitoe, 2010) and has the potential to be a porphyry copper indicator mineral for exploration (e.g. Cooke et al., 2014). For instance, Hashmi et al. (2015), Plouffe et al. (2016), and Plouffe and Ferbey (in press) have suggested that the greater abundance of epidote in till (determined in the >3.2 specific gravity, 0.25–0.5 mm size, and 0.8–1 amp electromagnetic fraction) near porphyry copper mineralization compared to background regions could be derived from hydrothermal alteration related to the porphyry mineralization. However, a clear link between epidote abundance in till and a hydrothermal alteration source based on mineral attributes remains to be established. The challenge in developing epidote as a porphyry copper indicator mineral in the Canadian Cordilleran context is to differentiate epidote derived from alteration zones of fertile porphyry copper systems versus "background" epidote derived from: i) altered but non-fertile intrusions; ii) rocks of regional greenschist metamorphic facies; and iii) rocks from contact metamorphic aureoles such as the Nicola Group volcanic rocks of the Quesnel Trough, which are known to contain epidote (Campbell and Tipper, 1971).

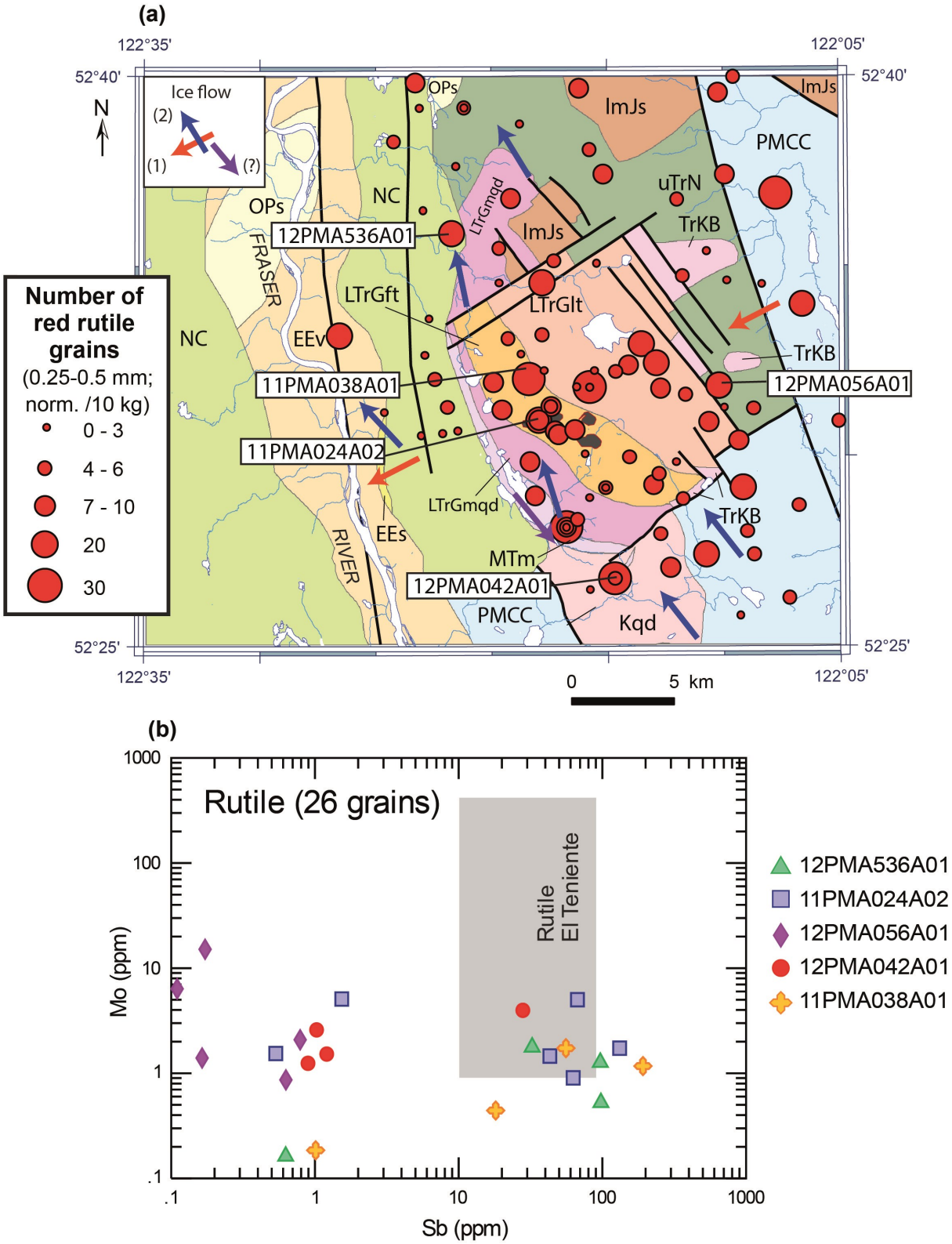

Figure 6. a) Red rutile grain counts in the 0.25–0.5 mm, >3.2 SG fraction of till normalized to 10 kg sample weight at Gibraltar. Figure modified from Plouffe and Ferbey (in press). Mineral grain count data is from Plouffe and Ferbey (2016). Till samples from which rutile grains were analyzed are labelled (e.g. 12PMA536A01). The bedrock legend is the same as Figure 2. b) Mo versus Sb content of rutile recovered from till. The grey field corresponds to the composition of rutile in the high- and low-grade ore at the El Teniente porphyry copper deposit in Chili (Rabbia et al., 2009). Figure modified from Wolfe et al. (2017).

Kobylinski et al. (2017) presented a detailed account of the form and composition of epidote within the Granite Mountain batholith and the intruded Nicola volcanic rocks. In summary, epidote occurs as aggregates, veins and veinlets, and disseminated and isolated grains within the various intrusive phases of the batholith. Most of the alteration epidote in the batholith shows a sharp zoning characterized by a Fe-poor core and Fe-rich rim. Kobylinski et al. (2017) set the Fe-rich / Fe-poor boundary at an Fe(t) / [Fe(t) + Al] ratio of 0.29 (Fig. 7). The zoning is interpreted to reflect the evolution in composition of hydrothermal fluids from an S-rich phase during growth of the epidote core, and S-poor phase during rim growth. The interpretation is that the Fe content of epidote is controlled by preferential precipitation of Fe into sulphides when there is excess S in the hydrothermal system. Furthermore, the rare earth element (REE) plus Y content of epidote varies from 0.01 to 21.7 weight % oxides. Some epidote grains contain >15 weight % REE oxides and therefore qualify as allanite (Kobylinski et al., 2017). Kobylinski et al. (2017) also investigated the composition of epidote in the Nicola volcanic rocks of the Gibraltar region. Epidote in the Nicola rocks does not show Fe zoning, commonly contains apatite and titanite inclusions, but has no detectable amount of REE. The abundance of epidote in the Nicola volcanic rocks is >40 volume % within 500 m of the contact with the batholith compared to <30 volume % at >500 m from the contact. The greater abundance of epidote in the Nicola rocks near the contact with the intrusion can be attributed to contact metamorphism or metasomatic alteration near the intrusion contact zone (Kobylinski et al., 2017).

A complementary study was conducted on the composition of 93 grains of epidote recovered from four of the till samples collected in the Gibraltar region (Fig. 8; Wolfe, 2017; Wolfe et al., 2017). The epidote grains in till have variable amounts of Ca (22–24 weight %), Fe_2O_3 (12–20 weight %), and Al_2O_3 (20 –25 weight %) (Fig. 9a, b). The distribution of Fe_2O_3 in epidote is not homogeneous and varies by 1 to 2 weight % within single grains following a complex texture. The epidote grains in till are not zoned. The REE content (Sc + Y + La + Ce) of epidote in till is low, attaining a maximum of 0.17 weight % (Fig. 9c). Mineral inclusions are common in the till epidote, including in decreasing abundance titanite, actinolite, zircon, apatite, quartz and magnetite. By comparing the composition, texture and mineral inclusions in epidote, Wolfe (2017) concluded that the epidote in till has more affinity to the epidote in the Nicola volcanic rocks as opposed to the Granite Mountain batholith. The greater abundance of epidote in till in the region of the Granite Mountain batholith could be related to the greater abundance of epidote in rocks of the Nicola Group near the contact with the intrusion.

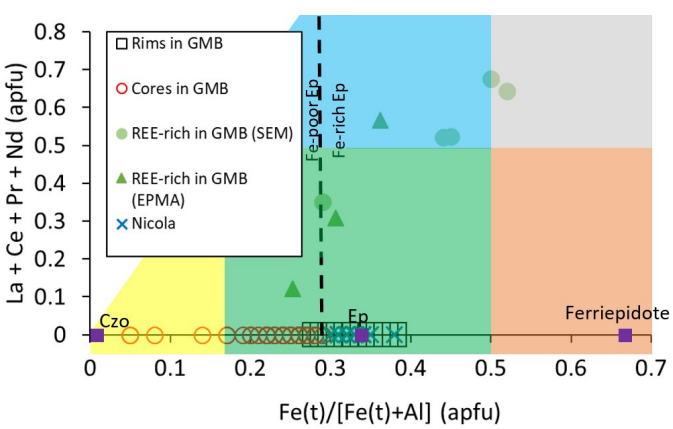

Figure 7. Epidote composition from the Gibraltar deposit. GMB - Granite Mountain batholith; SEM - scanning electron microscope; EPMA - electron probe microanalyses; apfu - atom per formula unit. Figure modified from Kobylinski et al. (2017).

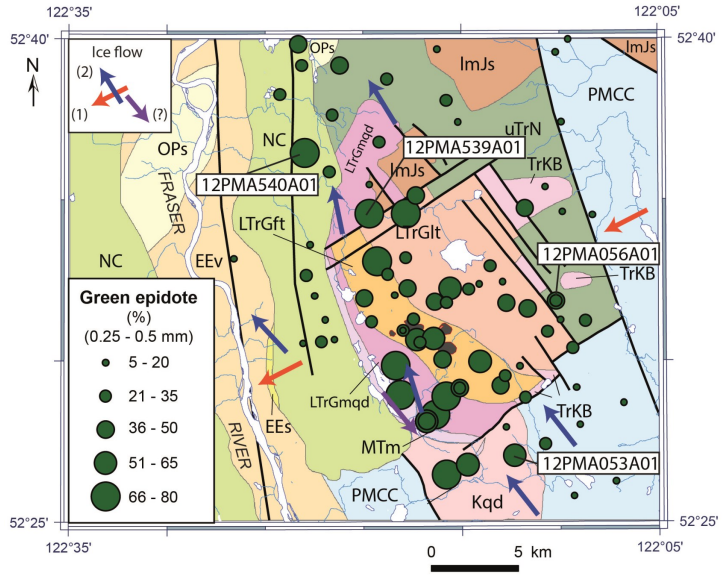

Figure 8. Percentage of green epidote in the 0.25–0.5 mm, >3.2 SG, 0.8–1 amp paramagnetic fraction of till at Gibraltar. Figure modified from Plouffe et al. (2016). Mineral grain count data is from Plouffe and Ferbey (2016). Till samples from which epidote grains were analyzed are labelled (e.g. 12PMA540A01). The bedrock legend is the same as Figure 2.

This first set of results on epidote composition in till and rocks in the region of an economic porphyry copper deposit provides some insight as to the source of epidote in till, but also raises some questions still to be fully addressed:

- In which fraction of till is most of the Fe zoned, intrusion derived epidote present? Could it be present in a paramagnetic fraction other than the one separated at 0.8 to 1 amp? Could it be comminuted to a size fraction <0.25 mm? And, is it abundant enough in till heavy mineral concentrates to be efficiently detected in a 10 kg bulk sample?

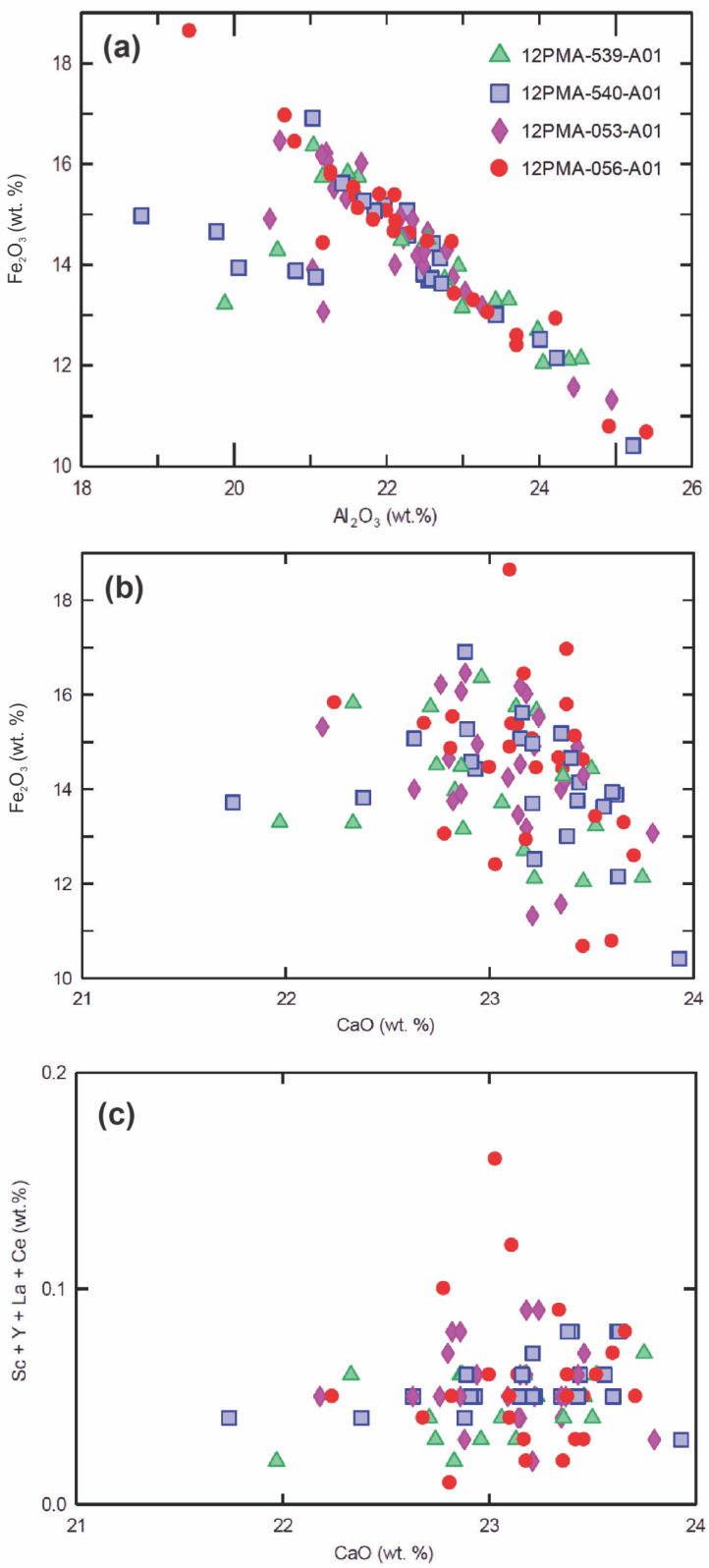

Figure 9. a) Fe_2O_3(t) versus Al_2O_3; b) Fe_2O_3(t) versus CaO; and c) Sc+Y+La+Ce versus CaO in 91 epidote grains from till analyzed by EPMA. Modified from Wolfe (2017).

- Is the Fe zoning observed in epidote at Gibraltar also present in epidote from other copper porphyry deposits, and if so, is the presence of zoning in epidote grains widely applicable as an indication of the presence of porphyry mineralizing processes in detrital sediments?
- Is the greater abundance of epidote in till near porphyry mineralization as outlined in Hashmi et al. (2015) and Plouffe et al. (2016) in large part derived from contact zones between the intrusion and host rocks?
- Can we establish criteria to distinguish between epidote derived from fertile and non-fertile intrusions?

Given that the hydrothermal alteration zones developed in porphyry copper deposits are much larger than the mineralized zones (Lowell and Guilbert, 1970; Sillitoe, 2010), they represent much larger exploration targets (Averill, 2011; Plouffe et al., 2016; Hickin and Plouffe, in press). Establishing hydrothermal alteration minerals (e.g. epidote) as porphyry copper indicator minerals could improve our efficiency at detecting buried porphyry deposits.

Concluding remark

The next generation of mineral deposits to be discovered is unlikely to be an "easy find" that is well exposed at surface. In a glaciated landscape, such as much of Canada, deposits to be discovered are likely covered by glacial and non-glacial sediments. Developing better mineral exploration strategies, including studies of mineral markers of copper porphyry deposits that persist within a glaciated environment will contribute to an improved capacity to detect buried ore that will respond to the needs of future generations.

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