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FERTILITY OF IGNEOUS ROCKS RELATED TO PORPHYRY COPPER DEPOSITS: INDICATIONS FROM ZIRCON COMPOSITIONS

Keiko HATTORI[1], Samuel MORFIN[1], Regina BAUMGARTNER[2], Ping SHEN[3], Duane PETTS[1]

[1] University of Ottawa, 25 Templeton St., Ottawa, Canada (khattori@uottawa.ca)
[2] Goldfields La Cima, Lima, Peru (Regina.Baumgartner@goldfields.com.pe)
[3] Chinese Academy of Science, Beijing, China (pshen@mail.iggcas.ac.cn)

1. Introduction

Porphyry copper deposits are associated with relatively oxidized granitic intrusions, reflecting their source and origin at depth. The oxidized character of igneous rocks are shown by the primary mineral assemblages, such as the occurrence of magnetite and magmatic epidote (e.g., Ishihara, 1977), but many rocks hosting porphyry copper deposits are intensely altered, which obliterate the primary igneous minerals. This makes it difficult to assess the oxidation state of the parental magmas for the intrusions. Zircon is a common accessory mineral in igneous rocks, especially granitic rocks. It crystallizes in melt and records the compositional variation of the parental magmas. In addition, it is a physically and chemically sturdy mineral that retains its original composition once it crystallizes, and it resists hydrothermal alteration. Zircon has the mineral formulae of $ZrSiO_4$, and its structure can incorporate many minor and trace elements depending on composition and conditions of the parental magmas. Among minor and trace elements, rare earth elements are useful. They are trivalent under most conditions, but Ce and Eu may have different valence states reflecting the oxidation condition of the parent magma.

In oxidized magmas, Ce occurs primarily as Ce^{4+} and is readily incorporated into the Zr^{4+} site of zircon (Fig. 1). In reduced magmas, Eu occurs as Eu^{2+} and is depleted in magmas as a result of its incorporation into the Ca^{2+} site of plagioclase. Ca-plagioclase is an early crystallizing phase and zircon most commonly crystallizes later in magmas. Therefore, the melt is depleted in Eu when when zircon starts crystallizing in the melt. Therefore zircon in granitic rocks commonly shows pronounced negative anomalies of Eu. However, fertile magmas related to porphyry copper mineralization contain high water contents so that the magmas release magmatic aqueous fluids for the mineralization. High water content of melt suppresses plagioclase crystallization. Therefore, zircon crystallizing from such magmas have less pronounced negative Eu anomalies. Furthermore Eu is mostly Eu^{3+} in oxidized magmas and not readily incorporated into plagioclase structure. Fertile melt for porphyry copper mineralization, thus, crystallizes zircon with relatively high Eu (Fig. 1). These two features of the behaviours of rare earth elements are reflected in their abundances in zircon grains and can be utilized to distinguish fertile (oxidized and water-rich) magmas from likely barren intrusions. This can be tested in different terranes with intrusions that are associated with porphyry copper deposits of different ages.

2. RESULTS

In the Central Asian Orogenic belt, porphyry copper deposits of varying size are hosted by Paleozoic granitoids. These rocks contain zircon grains with high Ce^{4+}/Ce^{3+} ratios and the ratios are correlated with the tonnage of copper (Shen et al., 2015; Fig. 2). Zircon from deposits containing >1 Mt Cu shows Ce^{4+}/Ce^{3+} values greater than 100 in 75% of grains. Eu/Eu* anomalies of zircon grains (excluding Erdenet and Tuwu) are all > 0.5 (Fig. 3). On the other hand, zircon from small deposits (Borly, Baogutu, with <1 Mt Cu) have low Ce^{4+}/Ce^{3+} ratios, <76, and Eu anomalies are <0.5 in 75% of grains. These findings from the Central Asian Orogenic belt are applicable to other terranes. Granitoids associated with the Chuquicamata-Radomiro Tomic deposits (126 Mt Cu, 33-35 Ma) contain zircon with relatively high Eu/Eu*, >0.5, and Ce^{4+}/Ce^{3+} ratios >800 for over 50% of grains (Ballard et al., 2002). Similarly high values in zircon are associated with the El Salvador deposit (17 Mt Cu, 42 Ma; Lee, 2008). Granitoids in the Cerro Corona porphyry Au-Cu deposit (0.9 Mt Cu, high Au/Cu ratio; 14.3 Ma) in northern Peru have significantly high Eu/Eu*, >0.59, and Ce^{4+}/Ce^{3+} >110 for 75 % zircon grains. Granitoids associated with the Highland Valley Copper deposit in British Columbia, Canada (1.82 Mt Cu, 210 Ma) have zircons with Ce^{4+}/Ce^{3+} ranging from 61 (first quartile) to 175 (third quartile).

By contrast, barren igneous rocks of various ages from Australia and Europe show low values of Ce^{4+}/Ce^{3+}, up to 5 in most zircon grains (Fig. 2). Furthermore, granitoids that host tin-tungsten deposits are known to be relatively reduced (e.g., Ishihara et al., 1980; Lehmann, 1982). The zircon data from a Brazilian tin deposit reported by Nardi et al. (2012) confirm this, with zircon in the granite host shows prominent negative Eu anomalies (Eu/Eu* <0.25) an essential lack of Ce anomalies, shown with low Ce^{4+}/Ce^{3+} of <5.

Summary

Zircon grains from granitoids hosting porphyry copper deposits show relatively high Eu/Eu* and very high Ce^{4+}/Ce^{3+}. Zircon is a physically and chemically robust mineral that retains its original composition during subsequent hydrothermal alteration, chemical weathering and sedimentary transport. Furthermore, its heavy density makes it easy to separate from rocks and sediments for grain analysis. The compositions of zircon grains can help during district-scale exploration to identify water-rich and oxidized igneous rocks that would have been fertile to form porphyry copper deposits.

Acknowledgements

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References

Ballard, J.R., Palin, J.M., Campbell, I.H. 2002. Relative oxidation states of magmas inferred from Ce(IV)/Ce(III) in zircon: application to porphyry copper deposits of northern Chile. Contri. Mineral. Petrol., v. 144, p. 347-364.

Belousova, E.A., Griffin, W.L, O'Reilly, S.Y., 2006. Zircon crystal morphology, trace element signatures and Hf isotope composition as a tool for petrogenetic modelling: examples from eastern Australian granitoids. J. Petrology, v.47, p. 329-353.

Ishihara, S., 1977. The magnetite-series and ilmenite series granitic rocks. Mining Geology, v.27, p. 293-305.

Ishihara, S., Sawata, H., Shibata, K., Terashima, S., Arrykul, S., Sato, K., 1980. Granites and Sn-W deposits of peninsula Thailand. Mining Geology Spec Issue 8, p.223-241.

Lee, R. 2008. The Genesis of the El Salvador Porphyry Copper Deposit, Chile and Distribution of Epithermal Alteration at Lassen Park, California. Oregon State Univ. Unpub. PhD Thesis.

Lehmann, B., Metallogeny of tin: magmatic differentiation versus geochemical heritage. Econ. Geol. V. 77, p.50-59.

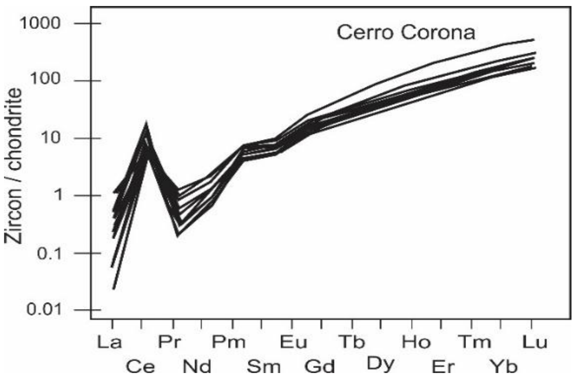
Lukács, R., Harangi, S., Bachmann, O., Guillong, M., Danisik, M., Buret, Y., vonQuadt, A., Dunkl, I., Fodor, L., Sliwinski, J., Soos, I., Szepesi, J. 2015. Zircon geochronology and geochemistry to constrain the youngest eruption events and magma evolution of the Mid-Miocene ignimbrite flare-up in the Pannonian Basin, eastern central Europe. Contr. Mineral. Petrol. v.170, 52 (on-line first)

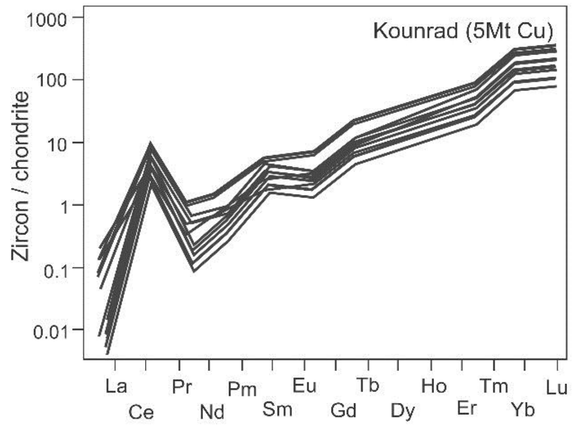
Nardi, L.V.S., Formoso, M.L.L., Jarvis, K., Oliveira, L., Nato, A.C. B, Fontana, E., 2012. REE, Y, Nb, U and Th contents and tetrad effect in zircon from a magmatic-hydrothermal F-rich system of Sn-rare metal-cryolite mineralized granites from the Pitinga Mine, Amazonia, Brazil. J. S Amer. Earth Sci. v. 33, p.34-42.

Shen, P., Hattori, K., Pan, H., Jackson, S., Seitmuratova, E., 2015. Oxidation condition and metal fertility of granitic magmas: zircon trace element data from porphyry Cu deposits in the Central Asian Orogenic Belt. Economic Geology, v. 110, p.1861-1878.

Ward, R., 2008. Isotope Geochemistry of Zircons from the Guichon batholith, Highland Valley Copper deposit: Southern British Columbia: Relationship between Ce^{4+}/Ce^{3+} in zircon, oxidation state in magmas and ore genesis. BSc Thesis at Carleton University, Ottawa.

Figures





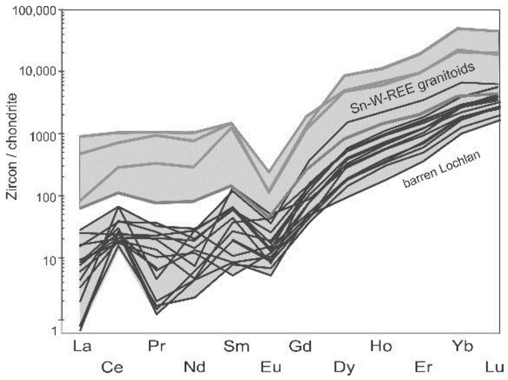


Figure. 1. Examples of typical normalized REE patterns of zircon grains in granitoids associated with porphyry Cu deposits (upper, middle) and Sn-W deposits (lower). Cerro Corona in Peruvian Cordillera with 0.9 Mt Cu (upper diagram) and Kounrad in the Central Asian Orogenic belt in Kazakhstan with 5 Mt Cu (middle diagram). The third diagram shows the REE patterns for zircon from Sn-W-REE deposits (Nardi et al., 2012) and barren granitoids in the Lachlan fold belt, Australia (Belousova et al., 2006). The abundances of rare earth elements in zircon grains are determined in situ using a laser-assisted inducted coupled mass spectrometer (LA ICP-MS). The detailed procedure for the analysis of Kounrad samples is described by Shen et al (2015). The analytical procedure for Cerro Corona samples is similar to that for the Kounrad samples.

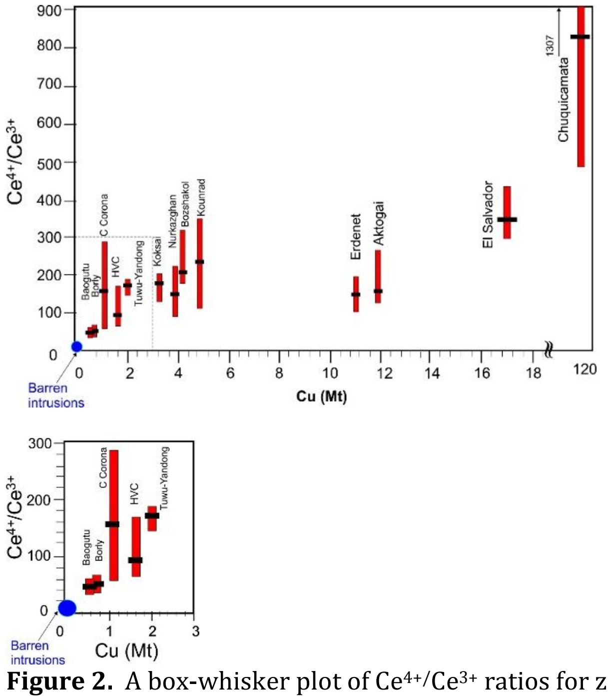


Figure 2. A box-whisker plot of Ce^{4+}/Ce^{3+} ratios for zircon grains in granitoids associated with porphyry copper deposits. The lower diagram enlarge the area covering the copper tonnage up to 3 Mt (shown in dashed line in the upper diagram). The amount of Ce^{3+} in zircon is calculated from the concentrations of Nd, Sm, Gd, Tb, Dy, Yb, Lu and Y in zircon and bulk rocks using expected partition coefficient between Ce^{3+} in zircon and bulk rocks. The calculation method is similar to that described by Ballard et al (2002) and Shen et al (2015).

Data sources: deposits in the Central Orogenic Belt (Shen et al., 2015), Highland Valley Copper (HVC, Ward, 2008), El Salvador (Lee, 2008), Chuquicamata (Ballard et al., 2002), barren granitoids and ignimbrites and tin deposit (Belousova et al., 2006; Nardi et al., 2012; Lukacs et al., 2015).

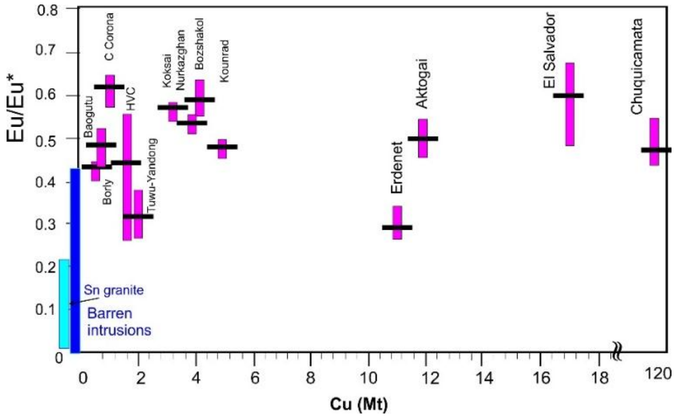


Figure 3. Europium anomalies of granitoids. Europium anomalies, Eu/Eu*, is defined as $[Eu]_N / ([Sm]_N*[Gd]_N)$^$^{0.5}$ where $[Eu]_N$, $[Sm]_N$ $[Gd]_N$ are the chondrite-normalized values. Data sources are the same for Fig. 2

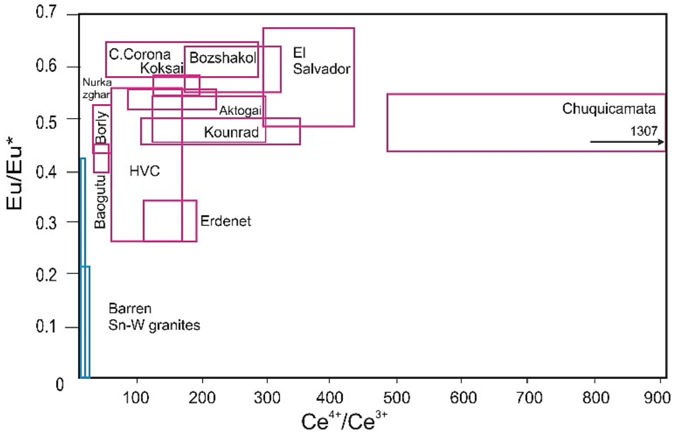


Figure 4. Europium anomalies vs Ce^{4+}/Ce^{3+} of zircon grains from mineralized granitoids (lower and upper quartile values are shown as squares in pink) compared to those of barren and Sn-W bearing granitoids (light blue)