Elemental mass balance and REE behavior in the hydrothermal alteration associated with the Ticlio porphyry stock, Morococha district, Peru

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Abstract: The Ticlio porphyry stock in the western part of the Miocene Morococha district (Peru) shows alteration and mineralization features typical for shallow porphyry Cu-Au systems. This paper discusses the mineralogy, whole-rock geochemistry and elemental mass balance of the hydrothermal alteration zones (potassic, phyllic and superimposed sericitic) related to the subeconomic porphyry mineralization at Ticlio. Major elements (Ca, Na, Mg, Fe) decrease as a consequence of breakdown of hornblende, biotite, and feldspars with increasing alteration intensity. In parallel, REE considered generally as immobile during alteration processes, show high mobility – as evidenced by REE depletion in the phyllic alteration zone due to acid leaching of the potassically altered precursor rock.

Keywords. Cu-Au porphyry, hydrothermal alteration, mass balance, REE, Ticlio, Morococha district

1 Introduction

The Morococha mining district is part of the Miocene metallogenic belt of central Peru and is located about 150 km east from Lima, on the eastern flank of the western Cordillera (Petersen 1965; Noble and McKee 1999). The Miocene polymetallic belt is defined by a large number of hydrothermal deposits of different types belonging to the porphyry-skarn-epithermal suite that formed mainly between 6 and 20 Ma (Noble and McKee 1999; Bissig et al. 2008). Ore deposits are associated in space and time with high-K calc-alkaline intrusions or domes of granodioritic composition (Bissig and Tosdal 2009).

The Ticlio stock, cropping out in the western part of the Morococha district and sharing mineralization and alteration features with shallow-level porphyry Cu-Au deposits, is atypical for this area where Cu-Mo porphyry systems are predominant (e.g., the giant Toromocho porphyry Cu-Mo deposit; Lowell and Alvarez 2005; Kouzmanov et al. 2008). The Ticlio magmatic-hydrothermal system consists of a single porphyritic stock with granodioritic composition in the center of which a stockwork of dense quartz-magnetite, quartz and hairline magnetite veinlets was developed. Several hydrothermal alteration zones, typical of porphyry Cu systems, overprinted the stock. The present study focuses on the mineralogy, whole-rock geochemistry and mass balance of the different alteration styles at Ticlio. Particular attention has been paid to the REE behavior during alteration processes.

2 Geological setting

A large anticline dominates the eastern part of the Morococha district. Permo (?) - Triassic volcaniclastic rocks (Mitu Group) crop out in the core of the anticline. Overlying the Mitu Group is the Triassic-Jurassic Pucará Group, consisting of carbonate sediments interlayered with chert and volcaniclastic and volcanic rocks. The Cretaceous Goyllarisquizga and Chulec Formations crop out to the northeast and southwest of the anticline. Tertiary volcanic rocks cover the southwestern part of the district. These formations are intruded by Miocene porphyries of different compositions (Bendezú et al. 2008). Magmatic activity began in the Mid-Miocene (~14 Ma) with the emplacement of a large dioritic intrusion (Anticona) that covers most of the western part of the district. In the Late-Miocene (9-7 Ma) a series of dioritic to granodioritic porphyries was emplaced.

The Ticlio stock is a single granodioritic intrusion emplaced during the Late-Miocene between the Anticona diorite and Cretaceous dolomitic limestones of the Jumasha Formation. The intrusion covers about 0.25 km^2 at surface. A series of basaltic xenoliths marks the eastern and southeastern fringe of the intrusion. An intrusive contact with the Anticona diorite delimits the stock to the east. A 10 cm-thick porphyritic dike trending N70-75 and several aplitic dikes having almost the same orientation crosscut the Ticlio intrusion. Three systems of fractures (NE-SW, WNW-ESE and less important N-S) host porphyry-style quartz-magnetite veins. Some of the NE-SW faults host also some late polymetallic meso-epithermal veins.

3 Hydrothermal alteration and veining

The Ticlio granodiorite is characterized by phenocrysts of plagioclase (~25-30%), biotite (~5-10%), quartz (~3-7%) and magnetite (<1%). The phenocrysts are set in aplitic, medium-grained groundmass consisting of K-feldspar (40-60%), quartz (40-50%) and albite (<10%). The predominant phenocrysts consist of plagioclase, generally euhedral and uniform in size (2-3 mm) with complex compositional zoning. Quartz phenocrysts (0.5-5 mm across) are usually rounded, commonly containing small inclusions of other minerals. Magmatic biotite forms euhedral grains with a typical length of 0.5-5 mm. Magmatic hornblende is completely pseudomorphed by hydrothermal biotite. Zircon and apatite are ubiquitous accessory phases, set in the groundmass, or as inclusions in the euhedral phenocrysts.

Mineralization and alteration at Ticlio developed in four main stages: (i) an early stage of biotite ± K-feldspar (potassic) alteration, accompanied by a dense quartz or quartz-magnetite stockwork zone, developed in the central part of the stock; (ii) a transitional stage consisting of chlorite ± epidote ± hematite affects principally the SW fringe of the intrusion; (iii) a phyllic alteration zone developed on the southern periphery of the stock; and (iv) illite-sericite alteration related to the formation of late polymetallic meso-epithermal veins overprints the porphyry-style mineralization and alteration.

Along the contact with Cretaceous carbonate sedimentary rocks, at the western border of the intrusion, a narrow zone of endo- and exoskarn developed, both dominated by garnet-diopside assemblages. In the endoskarn, hydrothermal titanite is commonly intergrown with diopside. Late epidote ± carbonate veinlets overprint the anhydrous assemblages.

4 Mass balance calculations

Whole-rock geochemical data (XRF analyses for major oxides and LA-ICP-MS on molten pellets for both traces and REE) were used to evaluate quantitatively the mass balance of major and minor elements that accompanied hydrothermal alteration (Fig. 1).

The mass balance method is based on the assumption that some elements (e.g. Ti, Al, Zr) can be considered as immobile during alteration and can be used as reference to calculate changes in element concentrations. These changes were calculated following the formula below using Zr as immobile element:

$$\Delta C = (C^F_{Zr}/C^A_{Zr})*C^A - C^F$$

where C^F_{Zr} and C^A_{Zr} are the concentration of the immobile element in the least altered (F) and altered (A) sample. C^A and C^F are the element concentrations in the altered and least altered sample, respectively, and ΔC denotes the gain or loss in grams per 100 g of rock for major elements or in ppm for trace elements.
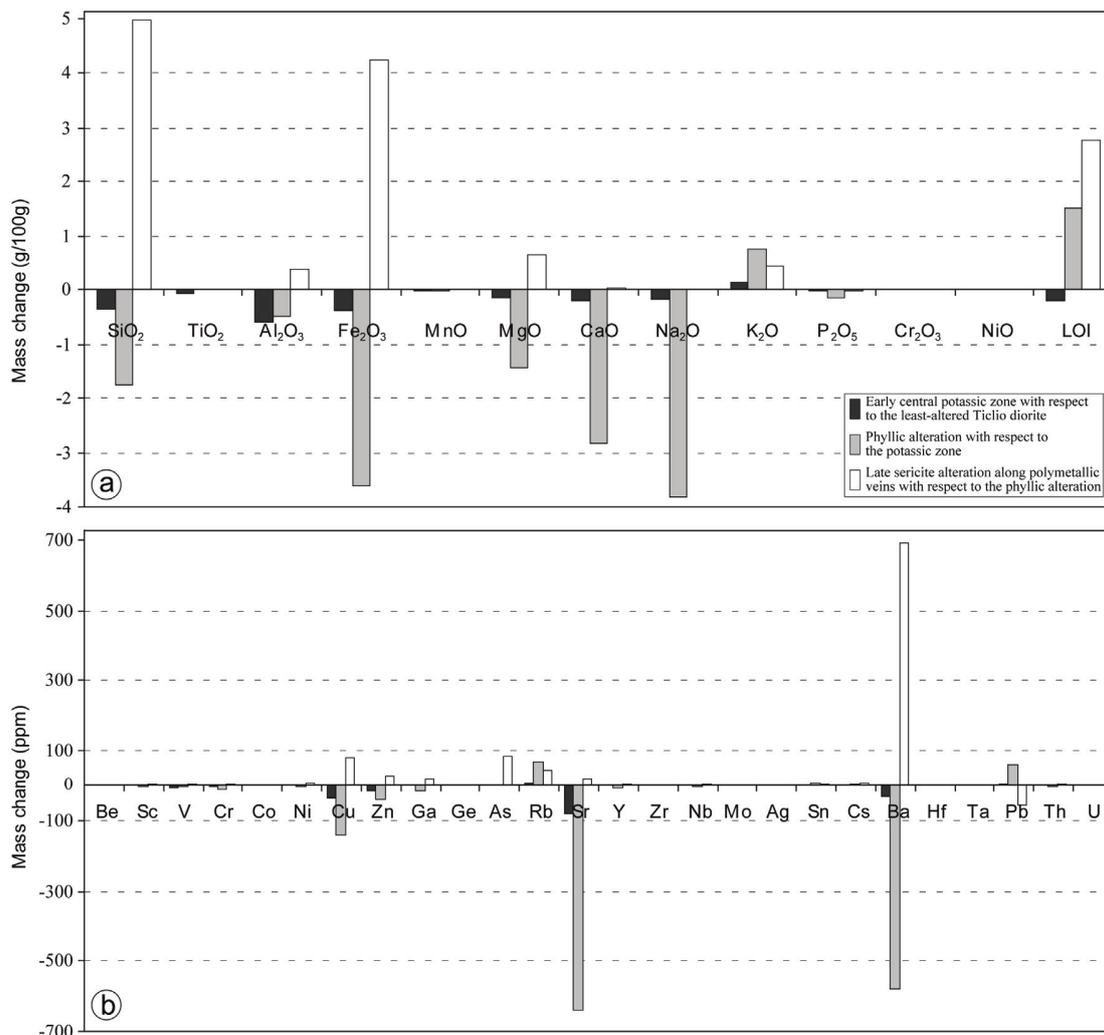
Figure 1 Mass balance diagrams - gain and loss of major (a) and trace (b) elements in different alteration zones of the Ticlio stock with respect to the fresh or altered precursor rock.

Chemically, the alteration trend (from early potassic to late sericitic) is expressed by a general decrease in Ca, Na, Sr, Mg and Fe, as a consequence of the destruction / replacement of plagioclase and mafic minerals. The increase of Fe, Si, As and Cu in the sericite alteration zone related to the polymetallic veins relative to the precursor phyllically altered rock is consistent with abundant sulfide precipitation and silicification.

5 REE behavior

Chondrite-normalized REE concentrations in the least-altered granodiorite, potassic, phyllic and sericitic alteration zones at Ticlio are shown in Figure 2.
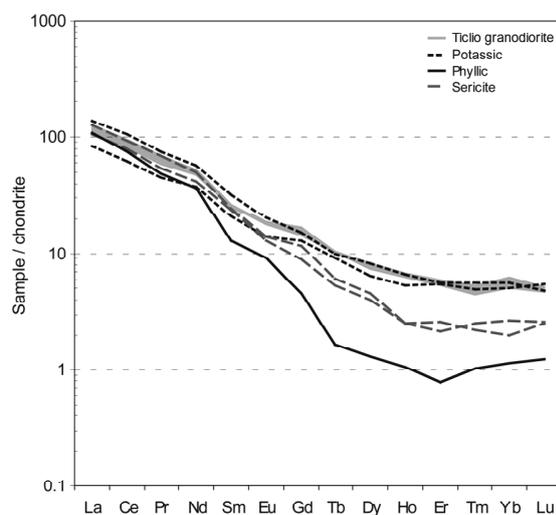
Figure 2. REE-chondrite (C1) normalized patterns discriminating various alteration zones at Ticlio. C1 chondrite normalization values are from Sun and McDonough (1989). The shaded area corresponds to the least-altered Ticlio granodiorite.

The REE concentrations in the potassic alteration do not show strong difference relative to the least altered rock. In contrast, in the phyllic alteration we measured the strongest depletion in REE, especially in MREE and HREE. This behavior could be explained by the complete breakdown of primary minerals (feldspars, mafic minerals, accessory apatite) in the phyllic alteration zone and the inability of the neo-formed aluminosilicates to capture all the released elements. The sericite-illite alteration along the polymetallic veins which overprints the phyllic alteration shows higher concentrations for MREE and HREE than the phyllic zone. This may be due either to the potential of phyllosilicates (clays in particular) for REE adsorption (Schneider et al., 1988), or to a possible link between the fluids forming epithermal veins and phyllic alteration zones at greater depths.

6 Conclusions

At Ticlio, the major elements Ca, Na, Mg, Fe

concentrations decrease during progressive alteration as a consequence of breakdown of hornblende, biotite and feldspars. The REE content also decreases with increasing alteration intensity. The strong MREE and HREE depletion in the phyllic alteration involved acid leaching at high water/rock ratio. The depletion in HREE points to the presence in the hydrothermal fluids of anionic species such as F^-, Cl^- with which the HREE preferentially complex (Bau, 1991); high SO_4^{2-} activity is also likely. In addition, high F (up to 0.84 wt.%) and Cl-content (up to 0.32 wt.%) of hydrothermal micas and clays (biotite from the K-alteration, muscovite from the phyllic alteration and sericite-illite from the sericitic alteration zone) are indicative of high F and Cl concentrations in the hydrothermal fluids.

Acknowledgements

References

Bau M (1991) Rare-earth element mobility during hydrothermal and metamorphic fluid-rock interaction and the significance of the oxidation state of europium. Chem Geol 93:219-230

Bendezú A, Catchpole H, Kouzmanov K, Fontboté L, Astorga C (2008) Miocene magmatism and related porphyry and polymetallic mineralization in the Morococha district, central Peru. XIII Geological Congress of Peru, Lima

Bissig T, Tosdal RM (2009) Petrogenetic and metallogenetic relationships in the Eastern Cordillera Occidental of Central Peru. J Geol 117:499-518

Bissig T, Ullrich TD, Tosdal RM, Friedman R, Ebert S (2008) The time-space distribution of Eocene to Miocene magmatism in the central Peruvian polymetallic province and its metallogenetic implications. J S Am Earth Sci 26:16-35

Kouzmanov K, Ovtcharova M, von Quadt A, Guillong M, Spikings R, Schaltegger U, Fontboté L, Rivera L (2008) U-Pb and $^{40}Ar/^{39}Ar$ age constraints for the timing of magmatism and mineralization in the giant Toromocho porphyry Cu-Mo deposit, central Peru. XIII Peruvian Geological Congress, 6 p

Lowell JD, Alvarez Angulo A (2005) Deposito porfido-skarn de cobre – Toromocho. In ProEXPLO-2005 (electronic version)

Noble DC, McKee EH (1999) The Miocene metallogenic belt of Central and Northern Perú. Soc Econ Geol Spec Publ 7:155-193

Petersen U (1965) Regional geology and major ore deposits of central Peru. Econ Geol 60:407-476

Schneider HJ, Özgür N, Palacios CM (1988) Relationship between alteration, rare earth element distribution, and mineralization of the Murgul copper deposit, northeastern Turkey. Econ Geol 83:1238-1246

Sun SS, McDonough WF (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In: Saunders AD, Norry MJ (eds) Magmatism in ocean basins. Geol Soc Spec Publ 313-345