# Mineral Zoning and Geochemistry of Epithermal Polymetallic Zn-Pb-Ag-Cu-Bi Mineralization at Cerro de Pasco, Peru\*

## REGINA BAUMGARTNER<sup>†,\*\*</sup> LLUÍS FONTBOTÉ,

Department of Mineralogy, University of Geneva, 13 Rue des Maraichers, 1205 Genève, Switzerland

### AND TORSTEN VENNEMANN

Institute of Mineralogy and Geochemistry, University of Lausanne Anthropole, 1015 Lausanne, Switzerland

#### Abstract

The large Cerro de Pasco Cordilleran base metal deposit in central Peru is located on the eastern margin of a middle Miocene diatreme-dome complex and comprises two mineralization stages. The first stage consists of a large pyrite-quartz body replacing Lower Mesozoic Pucará carbonate rocks and, to a lesser extent, diatreme breccia. This body is composed of pyrite with pyrrhotite inclusions, quartz, and black and red chalcedony (containing hypogene hematite). At the contact with the pyrite-quartz body, the diatreme breccia is altered to pyrite-quartz-sericite-pyrite. This body was, in part, replaced by pipelike pyrrhotite bodies zoned outward to carbonate-replacement Zn-Pb ores bearing Fe-rich sphalerite (up to 24 mol % FeS).

The second mineralization stage is partly superimposed on the first and consists of zoned east-west-trending Cu-Ag-(Au-Zn-Pb) enargite-pyrite veins hosted in the diatreme breccia in the western part of the deposit and well-zoned Zn-Pb-(Bi-Ag-Cu) carbonate-replacement orebodies; in both cases, sphalerite is Fe poor and the inner parts of the orebodies show typically advanced argillic alteration assemblages, including aluminum phosphate sulfate (APS) minerals. The zoned enargite-pyrite veins display mineral zoning, from a core of enargite-pyrite ± alunite with traces of Au, through an intermediate zone of tennantite, chalcopyrite, and Bi minerals to a poorly developed outer zone bearing sphalerite-galena ± kaolinite. The carbonate-hosted replacement ores are controlled along N35°E, N 90° E, N 120° E, and N 170° E faults. They form well-zoned upward-flaring pipelike orebodies with a core of famatinite-pyrite and alunite, an intermediate zone with tetrahedrite-pyrite, chalcopyrite, matildite, cuprobismutite, emplectite, and other Bi minerals accompanied by APS minerals, kaolinite, and dickite, and an outer zone composed of Fe-poor sphalerite (in the range of 0.05–3.5 mol % FeS) and galena. The outermost zone consists of hematite, magnetite, and Fe-Mn-Zn-Ca-Mg carbonates. Most of the second-stage carbonate-replacement orebodies plunge between 25° and 60° to the west, suggesting that the hydrothermal fluids ascended from deeper levels and that no lateral feeding from the veins to the carbonate-replacement orebodies took place.

In the Venencocha and Santa Rosa areas, located 2.5 km northwest of the Cerro de Pasco open pit and in the southern part of the deposit, respectively, advanced argillic altered dacitic domes and oxidized veins with advanced argillic alteration halos occur. The latter veins are possibly the oxidized equivalent of the second-stage enargite-pyrite veins located in the western part of the deposit.

The alteration assemblage quartz-muscovite-pyrite associated with the pyrite-quartz body suggests that the first stage precipitated at slightly acidic pH. The sulfide mineral assemblages define an evolutionary path close to the pyrite-pyrrhotite boundary and are characteristic of low-sulfidation states; they suggest that the oxidizing, slightly acidic hydrothermal fluid was buffered by phyllite, shale, and carbonate host rock. However, the presence in the pyrite-quartz body of hematite within quartz suggests that, locally, the fluids were less buffered by the host rock. The mineral assemblages of the second mineralization stage are characteristic of high- to intermediate-sulfidation states. High-sulfidation states and oxidizing conditions were achieved and maintained in the cores of the second-stage orebodies, even in those replacing carbonate rocks. The observation that, in places, second-stage mineral assemblages are found in the inner and outer zones is explained in terms of the hydrothermal fluid advancing and waning.

Microthermometric data from fluid inclusions in quartz indicate that the different ores of the first mineralization stage formed at similar temperatures and moderate salinities  $(200^\circ-275^\circ\text{C} \text{ and } 0.2-6.8 \text{ wt \% NaCl equiv}$  in the pyrite-quartz body;  $192^\circ-250^\circ\text{C}$  and 1.1-4.3 wt % NaCl equiv in the pyrrhotite bodies; and  $183^\circ-212^\circ\text{C}$  and 3.2-4.0 wt % NaCl equiv in the Zn-Pb ores). These values are similar to those obtained for fluid inclusions in quartz and sphalerite from the second-stage ores  $(187^\circ-293^\circ\text{C} \text{ and } 0.2-5.2 \text{ wt \% NaCl equiv}$  in the enargite-pyrite veins;  $178^\circ-265^\circ\text{C}$  and 0.2-7.5 wt % NaCl equiv in quartz of carbonate-replacement orebodies;  $168^\circ-222^\circ\text{C}$  and 3.2-7.7 wt % NaCl equiv in sphalerite of carbonate-replacement orebodies; and  $245^\circ-261^\circ\text{C}$  and 3.2-7.7 wt % NaCl equiv in quartz from Venencocha). Oxygen and hydrogen isotope compositions on kaolinite from carbonate-replacement orebodies ( $\delta^{18}\text{O} = 5.3-11.5\%$ ,  $\delta\text{D} = -82 \text{ to } -114\%$ ) and on alunite from the Venencocha and Santa Rosa areas ( $\delta^{18}\text{O} = 1.9-6.9\%$ ,  $\delta\text{D} = -56 \text{ to } -73\%$ ). Oxygen isotope compositions of quartz from the first and second stages have  $\delta^{18}\text{O}$  values from 9.1 to 17.8 per mil. Calculated fluids in equi-

<sup>+</sup>Corresponding author: e-mail, regina.baumgartner@teckcominco.com

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°°Present address: Teck Cominco Peru, Psje. los Delfines 159, Las Gardenias, Santiago de Surco Lima 33, Peru.

librium with kaolinite have  $\delta^{18}$ O values of 2.0 to 8.2 and  $\delta$ D values of -69 to -97 per mil; values in equilibrium with alunite are -1.4 to -6.4 and -62 to -79 per mil. Sulfur isotope compositions of sulfides from both stages have a narrow range of  $\delta^{34}$ S values, between -3.7 and +4.2 per mil; values for sulfates from the second stage are between 4.2 and 31.2 per mil. These results define two mixing trends for the ore-forming fluids. The first trend reflects mixing between a moderately saline (~10 wt % NaCl equiv) magmatic end member that had degassed (as indicated by the low  $\delta$ D values) and meteoric water. The second mixing indicates condensation of magmatic vapor with HCl and SO<sub>2</sub> into meteoric water, which formed alunite.

The hydrothermal system at Cerro de Pasco was emplaced at a shallow depth (~500 m) in the epithermal and upper part of a porphyry environment. The similar temperatures and salinities obtained for the first stage and second stages, together with the stable isotope data, indicate that both stages are linked and represent successive stages of epithermal polymetallic mineralization in the upper part of a porphyry system.

### Introduction

RECENT GEOLOGIC studies of magmatic-hydrothermal systems have mainly concentrated on fluid evolution in porphyry copper and epithermal high-sulfidation Au-(Ag) deposits (Einaudi et al., 2003; Bethke et al., 2005; Fifarek and Rye, 2005; Heinrich, 2005). However, less attention has been paid to associated epithermal polymetallic base metal deposits which occur in the upper parts of the same environment and which, according to crosscutting relationships and geochronological data, form later in the evolution of the system than the precious metal deposits. A number of such base metal deposits are superimposed on porphyry copper deposits (e.g., Butte, Morococha), whereas others have no known link to mineralized porphyry deposits (Einaudi et al., 2003). In the porphyry environment, epithermal high-sulfidation Au-(Ag) deposits also may be overprinted by such base metal deposits (e.g., Bendezú et al., 2003).

Epithermal polymetallic deposits are also referred to as Cordilleran base metal deposits, a term introduced by Sawkins (1972). The term Cordilleran base metal veins and/or deposits was subsequently used by Einaudi (1982), Gilbert and Park (1986), Bartos (1987), Macfarlane and Petersen (1990), Hemley and Hunt (1992), Bendezú and Fontboté (2002), and Bendezú et al. (2003, 2008). Cordilleran deposits have also been termed as Butte-type vein deposits (Meyer et al., 1968), polymetallic veins, and recently zoned base metal veins (Einaudi et al., 2003). The main features of Cordilleran base metal deposits can be summarized as follows, from Bendezú et al. (2008): (1) they have a close association in time and space with calc-alkaline igneous activity (i.e., in the same environment as most porphyry Cu and high-sulfidation epithermal Au-Ag deposits); (2) they form under epithermal conditions at shallow levels beneath the paleosurface; (3) they include Cu-Zn-Pb-(Ag-Au-Bi) metal suites, very rich in sulfides (up to more than 50% total sulfides), and have high Ag/Au ratios; (4) there is a well-developed zonation of ore and alteration minerals (core zones may also include high-sulfidation and advanced argillic alteration); (5) early pyrite-quartz cores are associated with low-sulfidation mineral assemblages containing pyrrhotite-(arsenopyrite) that can be extensive and form large bodies zoned outward to Zn-Pb ores; (6) they occur as open-space fillings (veins, breccia bodies) in silicate host rocks and as replacement in carbonate rocks; and (7) the base metals are deposited late in the evolution of the porphyry system (as seen from abundant crosscutting relationships and sparse geochronological data) after porphyry Cu, skarn, and high-sulfidation Au(-Ag) mineralization. Cordilleran base metal deposits have been historically an important source of Cu as well as Zn, Pb, and Ag in the North American Cordillera and Peru. Table 1 summarizes the characteristics of several of these deposits.

The second largest known Cordilleran base metal deposit, after Butte (Montana), is Cerro de Pasco, in central Peru. It is a Zn-Pb-Ag-Cu-Bi deposit spatially related to a middle Miocene diatreme-dome complex. Post-1950 production plus known resources total more than ~175 million metric tons (Mt) at 7 wt percent Zn and 2 wt percent Pb, as well as 3 oz/t Ag (Einaudi, 1977; Geological staff of Cerro de Pasco, 1950, pers. commun., 2001). In addition, prior to 1950, 1200 million ounces (Moz) Ag, 2 Moz of Au, and about 50 Mt at 2 wt percent Cu were mined (our estimate based on data of Jiménez, 1924; Geological staff of Cerro de Pasco Corporation, 1950; Einaudi, 1977; Fischer, 1977; Baumgartner, 2007). Contributions on the geology and mineralization at Cerro de Pasco include McLaughlin (1924), Bowditch (1935), Graton and Bowditch, (1936), Lacy (1949), Geological staff of Cerro de Pasco Corporation (1950), Jenks (1951), Ward (1961), Petersen (1965), Einaudi (1968, 1977), Silberman and Noble (1977), Mégard (1978), Rivera (1997), Angeles (1999), Baumgartner et al. (2003), and Baumgartner (2007). Several unpublished reports of Cerro de Pasco Corporation, CENTRO-MIN, and Volcán Compañía Minera S.A contain additional information on Cerro de Pasco.

While it is probable that silver was mined at Cerro de Pasco prior to the Spanish conquest, the first historic record of production from the district is in 1630 (Bowditch, 1935, and references therein). In the 19th century, Ag production declined and most claims at Cerro de Pasco were acquired by the American Cerro de Pasco Corporation (1906–1970). Two mineralization stages occur at Cerro de Pasco. The first consists of a large pyrite-quartz body with pipelike pyrrhotite bodies zoned to Zn-Pb ores characterized by marmatitic sphalerite, mainly the Cayac Noruega A, B, and J-337 and K-327A orebodies: see Einaudi, 1977; these orebodies were exploited underground in the late 1940s, as well as the the oxidized portion of the eastern part of the deposit (belonging to the second mineralization stage). The second mineralization stage comprises polymetallic base metal carbonate-replacement orbodies on the eastern part of the deposit and enargite pyrite veins on the western part; the latter narrow and rich copper veins and orebodies (mainly enargite and chalcopyrite) were exploited down to a depth of 700 m at the beginning of Cerro de Pasco Corporation. In the early 1970s, the mine was nationalized and was integrated into the state-owned CENTROMIN. In 1999, Cerro de Pasco was again privatized and Volcán Compañia Minera S.A., the current owner, took the control of the mine.

Mineralization at Cerro de Pasco comprises two stages with contrasting mineralogy (Einaudi, 1977; Baumgartner, 2007).