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## **GEOCHRONOLOGICAL, FLUID INCLUSION AND ISOTOPIC CONSTRAINTS IN THE CERRO DE PASCO DISTRICT, PERU**

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The Cerro de Pasco deposit is located in Central Peru and constitutes one of the largest polymetallic resources in the world with post-1950 production plus known resources amounting more than ~175 Mt @ 7% Zn and 2% Pb as well 3 oz/t Ag. In addition, prior to 1950, 1200 Moz Ag, 2 Moz of Au, and around 50 Mt @ 2% Cu were mined (compiled from Einaudi, 1977; Fischer, 1977; Geological staff of Cerro de Pasco Corporation, 1950; Jiménez, 1924, and Cerro de Pasco geological staff, pers.com.). The deposit is located at the eastern flank of a mid-Miocene dacitic diatreme-dome complex which intruded Devonian weakly metamorphosed Excelsior Group shales and quartzites, Permian-Triassic Mitu sandstones and conglomerates, and Upper Triassic-Lower Jurassic carbonate rocks from the Pucará Group. Emplacement of the diatreme may be controlled by a regional NS fault already active during deposition of the Pucará Group.

An early phreatomagmatic episode produced a diatreme breccia (Rumiallana Agglomerate), tuffs bearing accretionary lapilli, and dacitic to rhyodacitic porphyritic domes (Rogers, 1983). Late E-W trending quartz-monzonite dykes cut the diatreme-dome complex and carbonate rocks of the Pucará Group. Ring faults are recognized in the northern (Venencocha) and western part of the diatreme-dome complex.

### **MINERALIZATION AND ALTERATION**

Cerro de Pasco hosts several mineralization stages. An early vertical funnel shaped body (Einaudi, 1977) composed of pyrite and quartz replaced carbonate rocks as well as, subordinate the diatreme breccia. This body was partly replaced by pyrrhotite pipes zoned outward to Zn-Pb mineralization bearing Fe-rich sphalerite (up to 25 mol % FeS), pyrite, and arsenopyrite forming an assemblage characteristic of a low sulfidation states. A late stage of well zoned base metal ores formed mainly large replacement bodies and veins in carbonate rocks but also veins in the diatreme breccia and the pyrite-quartz body (Baumgartner et al., 2003). The core zone includes the pyrite-famatinite assemblage, accompanied by quartz and alunite. The intermediate zone is composed of pyrite, tetrahedrite, Bi-minerals (cuprobismuthite and bismuthinite-stibnite solid solution series) as well as Ag-minerals such as matildite, with alteration minerals including kaolinite, quartz, the alunite group mineral hinsdalite, and alunite. The outer zone consists of pyrite, sphalerite, galena, including the same alteration minerals as the intermediate zone except alunite. The outermost zone is composed of hematite, magnetite, and Mn-Zn-Fe bearing carbonates. These mineral assemblages reflect high to intermediate sulfidation and oxidation states (i.e., acid fluids) characteristic of Cordilleran base metal (or zoned base metal) veins and replacement bodies in the sense of Einaudi (1977), Einaudi et al.,(2003) and Bendezú et al (2003).

### **GEOCHRONOLOGICAL STUDY**

Step-wise IR-CO<sub>2</sub> laser <sup>40</sup>Ar/<sup>39</sup>Ar analyses on biotite from a tuff located inside the diatreme was performed in order to obtain a minimum age for the diatreme-dome complex event. Results show an age

of  $15.92 \pm 0.07$  Ma (plateau age). Preliminary U/Pb analyses in single grain zircon from an accretionary lapilli tuff also located in the diatreme is consistent with the  $^{40}\text{Ar}/^{39}\text{Ar}$  age. Zircon from a late E-W trending quartz-monzonite dyke yields a mean  $^{206}\text{Pb}/^{238}\text{U}$  age of  $15.35 \pm 0.05$  Ma (2 $\sigma$ , MSWD = 0.86) and a  $^{40}\text{Ar}/^{39}\text{Ar}$  age on biotite of  $15.14 \pm 0.06$  Ma. This latter age is younger than the  $^{206}\text{Pb}/^{238}\text{U}$  one but can be considered equivalent within the  $^{40}\text{K}$  and  $^{238}\text{U}$  decay constant uncertainties. Cathodoluminescence images do not show inherited cores in the zircon.

The first documented hydrothermal pulse within the diatreme-dome complex was recorded in Venenchocha at about 14.5 Ma (five  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau ages at  $14.54 \pm 0.06$  Ma,  $14.52 \pm 0.11$  Ma,  $14.52 \pm 0.07$  Ma,  $14.49 \pm 0.08$  Ma, and  $14.41 \pm 0.07$  Ma, ) on alunite from advanced argillic altered Au-bearing (up to 1 g/t Au) oxidized veins and from a dacitic dome (Au up to 0.2 g/t in areas affected by advanced argillic alteration). A second hydrothermal pulse yields a  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau age on alunite at  $12.39 \pm 0.06$  Ma, corresponding to pervasive advanced argillic alteration in a diatreme breccia in the Santa Rosa area (southern part of the open pit). This second pulse is also recorded in a dome in Venenchocha which yields a similar age at  $12.13 \pm 0.07$  Ma (one plateau age on alunite). A plateau age of  $10.94 \pm 0.10$  Ma (plateau age) on alunite in an EW Cordilleran base metal vein hosted in the pyrite-quartz body marks the last recorded hydrothermal pulse. Alunite from the Cordilleran base metal bodies hosted in the carbonate rocks could not be dated so far because it is too small to be separated.

The time span of magmatic activity defined by the  $^{40}\text{Ar}/^{39}\text{Ar}$  results of the tuff ( $15.92 \pm 0.07$  Ma) and the crosscutting E-W trending quartz-monzonite dyke ( $15.14 \pm 0.06$  Ma) represents at least 800'000 years. No field evidences have been found so far that magmatic activity could have begun before the formation of the diatreme-dome complex. The obtained  $^{40}\text{Ar}/^{39}\text{Ar}$  ages reveal three hydrothermal high sulfidation pulses ( $\sim 14.5$  Ma,  $\sim 12.4$  to  $\sim 12.1$  Ma,  $\sim 10.9$  Ma) indicating that hydrothermal activity lasted 3.5 My or more. This pulsed activity and time-life can be compared to other large magmatic-hydrothermal systems such as the porphyry and polymetallic mineralization at Butte (Montana, USA) and the very large Chilean porphyry copper deposits Chuquicamata, El Teniente, and La Escondida.

## FLUID INCLUSIONS AND STABLE ISOTOPE COMPOSITIONS

A fluid inclusion study coupled with cathodoluminescence (CL) in quartz has been performed in the Cordilleran veins and replacement bodies. CL imaging indicates multiple quartz generations in single grains. In general, commonly euhedral quartz grains associated with enargite in the core of the veins show three generations. The first one is a CL-bright luminescing core with complex oscillatory growth zones typical of magmatic quartz, as well as irregular margins indicating dissolution. The second generation is CL-dark and -bright luminescing with irregular banding and weak internal CL zoning; widespread dissolution borders and minute pyrite and anatase grains occur as inclusions. The third generation of quartz is characterized by marked oscillation with predominantly CL-dull to CL-dark luminescing and rare bright-luminescing growth zones. The first generation of quartz contains magmatic inclusions ( $\sim 50$  m glass inclusion with a shrinkage bubble) and liquid and vapor inclusions along cracks. The second generation of quartz does not contain measurable fluid inclusions, mainly because of necking down. The third quartz generation contains abundant measurable fluid inclusions.

CL imaging in several quartz crystals from the center of replacement bodies shows only one generation of quartz, characterized by bright-CL oscillatory luminescence in the center of the crystal that becomes CL-darker toward the borders. No dissolution is visible. Some bands contain pyrite inclusions.

Fluid inclusions coexisting with vapor inclusions along cracks within magmatic quartz in diatreme-hosted veins have homogenization temperatures between 300 and 230°C and highly variable salinities, with up to 24 wt. percent NaCl eq. Salinities obtained in the other fluid inclusion assemblages, both in veins and replacement bodies, are always <10 wt. percent NaCl. Fluid inclusion assemblages in growth zones in the third quartz generation from the diatreme-hosted veins yield homogenization temperatures from 200 to 270°C and salinities between 0.1 and 5.2 wt. percent NaCl eq. Those in quartz from the core of replacement bodies yield homogenization temperatures between 200 and 250°C and salinities from 0.1 to 9.5 wt. percent NaCl eq. Fluid inclusions in sphalerite from the outer zone of replacement bodies give

slightly lower homogenization temperatures, between 170 and 220°C, and salinities between 0.5 and 10 wt percent NaCl eq.

The isotopic composition of kaolinite (O and H) from the intermediate and outer zone of replacement bodies and of quartz (O) from veins and replacement bodies was measured, as well as alunite (O and H) from the northwestern part of the district. Water compositions were calculated at equilibrium with kaolinite at 250°C for the intermediate zone and at 220°C for kaolinite from the outer zone. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values range from 2 to 9 permil and -65 to -110 permil respectively. Local meteoric water at Cerro de Pasco is assumed to be similar to that at Julcani (Deen et al., 1994), because of close age and elevation, with oxygen and hydrogen isotopic compositions of -17.5 ‰ and -135 ‰, respectively. The isotopic compositions of water in equilibrium with kaolinite lie distinctly lower than the typical composition of magmatic waters. One sample is particularly depleted in the heavy oxygen isotope relative to the other samples. Two populations can be distinguished and correspond to kaolinite from the intermediate zone (with higher  $\delta\text{D}$  values) and from the outer zone (with lower  $\delta\text{D}$  values). Unlike the waters in equilibrium with alunite, the trend depicted by the variations of isotopic compositions of water in equilibrium with kaolinite cannot be explained by simple mixing between magmatic and meteoric waters only. The measured values can be explained, however, with input of meteoric waters having exchanged with host rocks in an open convecting system in the manner proposed by (e.g. Field and Fifarek, 1985). Models of isotopic exchange of meteoric water with (1) volcanic and (2) sedimentary rocks over a range of temperature from 25 to 400°C have been done. High water/rock ratios (0.3 and 0.9, respectively) have been chosen to explain the obtained  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values. These water/rock ratios are in agreement with those estimated for many epithermal districts (Field and Fifarek, 1985; Taylor, 1974). Therefore, the isotopic composition of the fluids that formed kaolinite suggests that magmatic water was mixed with exchanged meteoric water.

Calculated isotopic compositions of water in equilibrium with quartz from veins and replacement bodies, using equations of Zhang et al.(1989). Water in equilibrium with quartz from replacement bodies has similar  $\delta^{18}\text{O}$  values as water in equilibrium with kaolinite. Only one sample has higher values, which could be explained by fluid interaction with carbonate rocks. O isotopic compositions of water in equilibrium with veins are lower than those from the replacement bodies. However, these values must be interpreted with care because vein quartz crystals contain several generations of growth, as revealed by CL imaging.

The stable isotope values obtained indicate several mineralization steps characterized by different fluid compositions:

- The alunite-related water appears to result from mixing between magmatic and meteoric water. The magmatic component likely represents oxidized vapors.

- The Cordilleran polymetallic bodies that replaced carbonate rocks in the eastern and central parts of the deposit formed from moderately saline fluids (<9 wt.% NaCl eq.). Their isotopic composition implies strong dilution of magmatic water by exchanged meteoric water and, possibly, minor input of non-exchanged meteoric water. Therefore, the original magmatic fluid had a high salinity. Temperatures of formation in the center of replacement bodies are between 200 and 250 °C, whereas in the outer zones temperatures were generally lower, 170 to- 220°C.

- The Cordilleran enargite-pyrite veins, principally hosted by the diatreme-dome complex, are characterized by moderately saline fluid (mainly <3.5 wt. % NaCl eq.) with homogenization temperatures of 200 to 270°C. The fluid  $\delta^{18}\text{O}$  values are similar but slightly  $^{18}\text{O}$  depleted compared to those forming the polymetallic replacement bodies. Dilution ratios cannot be estimated because of the lack of OH-bearing minerals.

- Vapor plus hotter and more saline fluids occur in inclusions along healed cracks within magmatic quartz, possibly representing early fluids from deeper parts of the system.

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