

Ronner Bendezú · Lluís Fontboté · Mike Cosca

Relative age of Cordilleran base metal lode and replacement deposits, and high sulfidation Au–(Ag) epithermal mineralization in the Colquijirca mining district, central Peru

Received: 28 August 2002 / Accepted: 18 February 2003 / Published online: 12 June 2003
© Springer-Verlag 2003

Abstract At Colquijirca, central Peru, a predominantly dacitic Miocene diatreme-dome complex of 12.4 to 12.7 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$ biotite ages), is spatially related to two distinct mineralization types. Disseminated Au–(Ag) associated with advanced argillic alteration and local vuggy silica typical of high- sulfidation epithermal ores are hosted exclusively within the volcanic center at Marcapunta. A second economically more important mineralization type is characterized as “Cordilleran base metal lode and replacement deposits.” These ores are hosted in Mesozoic and Cenozoic carbonate rocks surrounding the diatreme-dome complex and are zoned outward from pyrite–enargite–quartz–alunite to pyrite–chalcopyrite–dickite–kaolinite to pyrite–sphalerite–galeña–kaolinite–siderite. Alunite samples related to the Au–(Ag) epithermal ores have been dated by the $^{40}\text{Ar}/^{39}\text{Ar}$ method at 11.3–11.6 Ma and those from the Cordilleran base metal ores in the northern part of the district (Smelter and Colquijirca) at 10.6–10.8 Ma. The significant time gap (~ 0.5 My) between the ages of the two mineralization types in the Colquijirca district indicates they were formed by different hydrothermal events within the same magmatic cycle. The estimated time

interval between the younger mineralization event (base metal mineralization) at ~ 10.6 Ma and the ages of ~ 12.5 Ma obtained on biotites from unmineralized dacitic domes flanking the vicinity of the diatreme vent, suggest a minimum duration of the magmatic–hydrothermal cycle of around 2 Ma. This study on the Colquijirca district offers for the first time precise absolute ages indicating that the Cordilleran base metal lode and replacement deposits were formed by a late hydrothermal event in an intrusive-related district, in this case post Au–(Ag) high-sulfidation epithermal mineralization.

Keywords Epithermal · Alunite · $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology · Cordilleran · High-sulfidation

Introduction

Einaudi (1977, 1982, 1994) points out that some sulfide-rich polymetallic ores were formed late in the evolution of porphyry-related hydrothermal systems. He noted that in certain systems (e.g., Yauricocha and Cerro de Pasco, Peru and Bisbee, Arizona) these ores are well developed, whereas in others (e.g., Ely, Nevada and El Salvador, Chile) they are only incipient or even barren. Irrespective of the degree of development, he refers to this late stage as the “lode stage” and to the ores, if they are formed, as “Cordilleran base metal lode deposits.” In order to better integrate the frequent massive development of replacements in carbonate rocks, as is the case of the Colquijirca district, we extend here this denomination to “Cordilleran base metal lode and replacement deposits.”

The main characteristics of deposits formed by this late Cordilleran stage (Einaudi 1982) include the following: (1) high sulfidation and oxidation states of the mineral assemblage with associated advanced argillic to sericitic alteration, (2) massive texture and sulfide content of lodes of up to more than 50% in volume, which is considerably higher than in other porphyry-related mineralization types, and (3) a common suite of

Editorial handling: O. Christensen

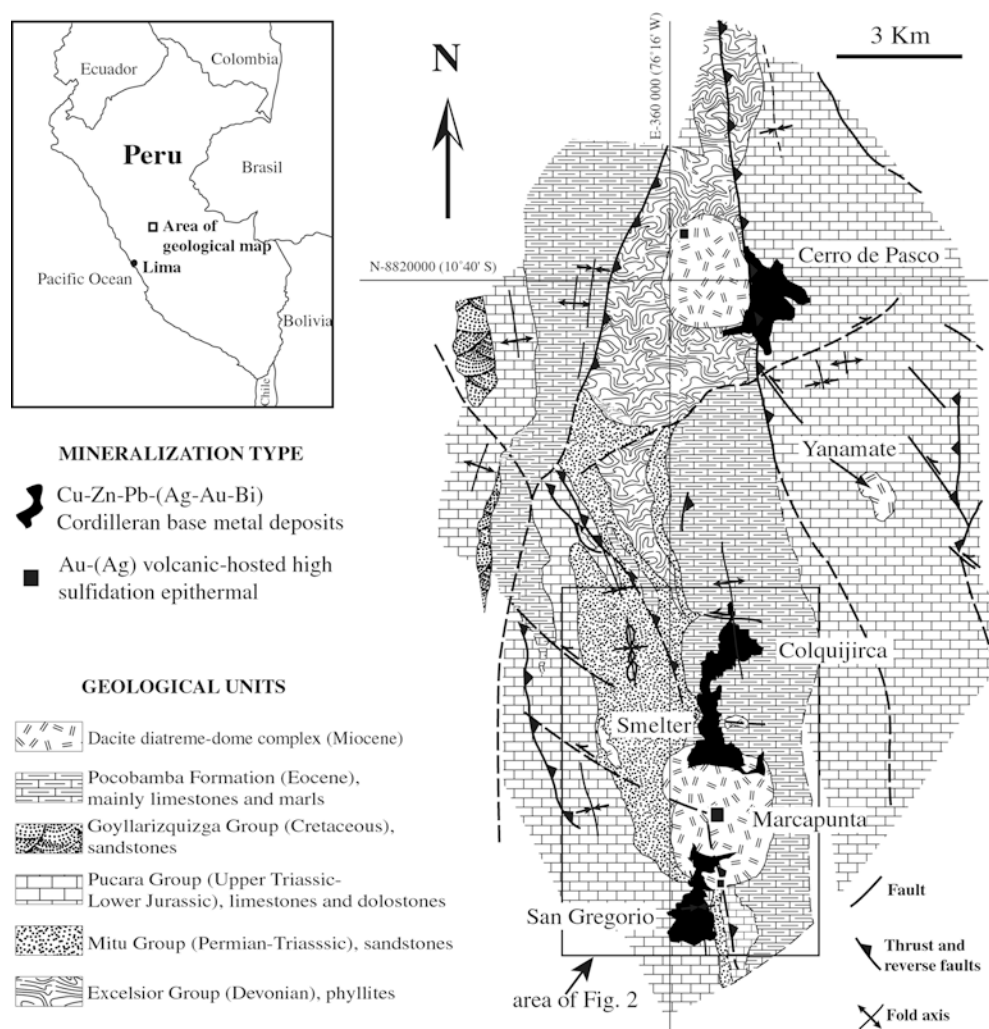
Electronic Supplementary Material Supplementary material is available for this article if you access the article at <http://dx.doi.org/10.1007/s00126-003-0358-z>. A link in the frame on the left on that page takes you directly to the supplementary material.

R. Bendezú (✉) · L. Fontboté
Section des Sciences de la Terre,
Université de Genève, Genève, Switzerland
E-mail: Ronner.Bendezu@terre.unige.ch
Tel.: +41-22-702-6645
Fax: +41-22-320-5732

M. Cosca
Institut de Minéralogie et Pétrographie,
Université de Lausanne, Lausanne, Switzerland

Present address: R. Bendezú
Sociedad Minera El Brocal S. A., Lima, Peru

Fig. 1 General geology and main mineralization types along the Miocene metallogenic belt at Cerro de Pasco and Colquijirca districts. Geology compiled from Angeles (1999), Sociedad Minera El Brocal S. A. staff, and this study



economically interesting metals, mainly Cu–Zn–Pb(Ag–Au).

Multidisciplinary research over the past 3 decades on epithermal deposits and their active equivalents in volcanic arcs, has helped decipher many of the formation mechanisms of the Au–(Ag) high-sulfidation epithermal deposits (Hedenquist 1987; Stoffregen 1987). Recently, their genetic links with porphyry copper–gold deposits have been supported (Hedenquist et al. 1998; Muntean and Einaudi 2001).

A review of existing literature shows that most of the detailed studies on Cordilleran base metal deposits were on deposits not spatially linked to the presumed parental porphyry copper mineralization or to any other recognizable ore-forming environment. This reflects the infrequent occurrence of Cordilleran base metal lode and replacement deposits and contemporaneous igneous activity, as was already discussed by Guilbert and Park (1986 p. 465).

The Colquijirca district offers the rare opportunity to study Cordilleran base metal lode and replacement deposits that are closely related in space, with Au–(Ag) high-sulfidation epithermal mineralization produced

within a Miocene diatreme-dome volcanic complex. In this paper, we establish, through $^{40}\text{Ar}/^{39}\text{Ar}$ dating of hydrothermal alunite and magmatic biotite, the timing of the mineralization of these two ore types and their relationship to the magmato–volcanic activity in the district.

Geologic setting and mineralization

The Colquijirca district is located 8–16 km south of the world famous Cerro de Pasco mine (Fig. 1). It contains one of the largest concentrations of massive polymetallic ores within the Miocene metallogenic belt of central and northern Peru (Vidal et al. 1997), where numerous other Cordilleran base metal lode and replacement deposits occur (Petersen 1965; Einaudi 1977, 1982, 1994; Guilbert and Park 1986; Bartos 1988). Indeed, from a metallogenetic point of view, the Colquijirca district is part of a larger belt that also comprises the giant ore concentrations of Cerro de Pasco. Spatially linked with the ores, magmatism in the Colquijirca–Cerro de Pasco districts is manifested through explosive calc–alkalic volcanism of intermediate composition, particularly as diatreme

complexes accompanied by subsequent multiple intrusion of porphyritic domes (Bowditch 1935; Lacy 1952). The diatreme-dome complexes of Cerro de Pasco, Yanamate and Colquijirca (Fig. 1) intrude thick sequences of carbonate rocks that host most of the ores (Angeles 1993, 1999; Sillitoe 2000).

The Colquijirca mining district

In the center of the Colquijirca district, the Marcapunta diatreme-dome complex intrudes an Eocene sequence more than 300 m thick of folded carbonate rocks, continental limestones, marls, and detrital sediments (Pocobamba Formation) to the north, and Triassic–Jurassic marine, nearly pure limestones, and dolostones (Pucará Group) and Permian red beds of the Mitu Group to the south (Figs. 1, 2, 3). The sedimentary rocks around the diatreme, including red beds of the Permo–Triassic age, have subsided about 500 m into the diatreme neck (Fig. 3).

Intense alteration, dominated by advanced argillic and argillic alteration related to Au–(Ag) epithermal mineralization, is present in large parts of the diatreme-dome complex (Figs. 2, 3). Mixtures of quartz–alunite–dickite–kaolinite ± (zunyite, pyrophyllite, illite) occur within or immediately surrounding mineralized areas, and kaolinite–illite ± (smectite)–sericite–chlorite–calcite occur in weakly mineralized or barren areas.

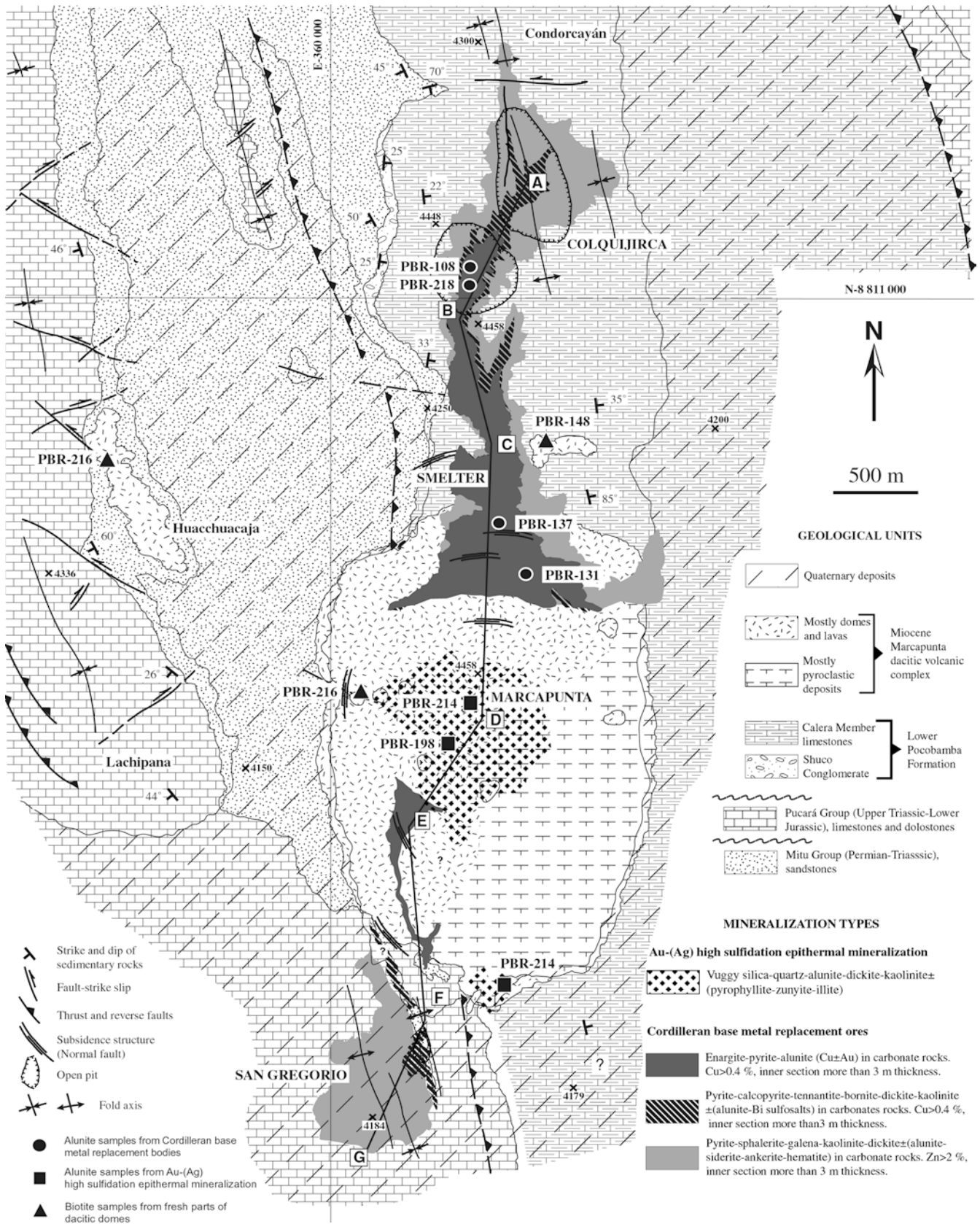
Au–(Ag) high-sulfidation epithermal mineralization is hosted within oxidized shallowly emplaced “vuggy silica” bodies (Fig. 3) with vertical dimensions of up to 100 m and gold values around 1 to 2 ppm (Vidal et al. 1997). The tonnage of the resources is not known. The bodies have been recognized mainly in the central portion of the complex, mostly within the diatreme breccia and pyroclastic infill. The morphology apparently is controlled by both lithological and structural permeability. Less abundant gold-bearing zones of completely oxidized veinlets have been recognized, particularly toward the surface. As in other high-sulfidation epithermal deposits (e.g., Summitville, Gray et al. 1994), deep portions of unoxidized ores characteristically contain less than 5 vol% of finely disseminated sulfides, which is mainly pyrite—and very minor enargite and sphalerite. The original sulfide content of the oxidized veinlets is estimated to be no more than 10 vol%.

Sulfide-rich polymetallic replacements represent the other distinctive and economically most important type of mineralization in the district. These deposits aggregate at least 150 Mt of carbonate-hosted alunite, kaolinite-bearing Cu–Zn–Pb–Ag ± (Au–Bi), in part massive, replacements (Ahlfeld 1932; Lindgren 1935; McKinstry 1936; Yaringaño et al. 1997; Vidal et al. 1997; BendeZú 1997; Fontboté and BendeZú 1999, 2001; BendeZú and Fontboté 2002a, 2002b, 2002c). The sulfide-rich replacements include the deposits of Colquijirca (30 Mt, at Zn+Pb~8%) and Smelter (50 Mt, at 2% Cu) 3.5 km and 1.5 km north of Marcapunta

respectively, and San Gregorio (70 Mt at Zn+Pb~10%) 3 km south of Marcapunta (Figs. 2, 3). The estimated temperatures from stabilities of alteration assemblages range from around 300° C close to the diatreme-dome complex, to 150° C in external portions of the system (Fontboté and BendeZú 2001). The sulfide-rich replacement ores at Smelter and Colquijirca are hosted by Tertiary Pocobamba Formation carbonate rocks and contain typically between 25 and 60 vol% sulfides, mainly within flat elongated mantos and irregularly shaped, stacked orebodies developed from the external margins of the diatreme vent into the carbonate rocks (Figs. 2, 3). These ores are characterized by massive replacement; however, open space filling and veins as well as breccias are locally important. Exploration drilling indicates that the bodies have their roots within the diatreme complex in deep subvertical narrow veins (from 500 to more than 750 m in depth below the surface) composed mainly of pyrite–enargite–quartz–alunite and minor pyrophyllite (Fig. 2).

The sulfide-rich ores extend continuously from Smelter for almost 4 km north to Colquijirca, where they virtually attain the same shallow elevation as the Au–(Ag) epithermal ores. Along its whole extension, the mantos are zoned in all directions from a core composed of pyrite–enargite–quartz–alunite ± (luzonite, colusite, zunyite, barite; zone I) to the following main zones: pyrite–chalcopyrite–dickite–kaolinite–siderite–quartz ± (tennantite, Bi–Ag sulphosalts, bornite, alunite, barite, quartz; zone II), pyrite–sphalerite–galena–chalcopyrite–dickite–kaolinite–quartz ± (siderite, hematite, magnetite, alunite; zone III), and the outermost known zone of pyrite–galena–sphalerite–siderite ± (kaolinite, dolomite, Zn-bearing carbonates; zone IV) (Figs. 2, 3). A similar zoning is also present to the south (BendeZú 1997; Fontboté and BendeZú 2001), where bodies have developed mainly into Lower Jurassic carbonate rocks of the Pucará Group. This is also the host rock of the recently discovered San Gregorio, one of the largest known Zn–Pb deposits in Peru (> 70 Mt at Zn+Pb~10%; Yaringaño et al. 1997; Vidal et al. 1997).

Due to the absence of direct crosscutting relationships between the Au–(Ag) epithermal and sulfide-rich polymetallic mineralization types, it is difficult to establish their relative timing. However, in the eastern flank of the volcanic complex, thin sphalerite–galena veins encased by argillic to phyllic alteration haloes cut the external mostly propylitic alteration zones peripheral to the vuggy silica-hosted Au–(Ag) bodies. This perhaps represents the best field relationship whereby it can be suggested that sulfide-rich polymetallic ores were emplaced subsequent to the Au–(Ag) epithermal mineralization. Other observations in the northern flank of the volcanic complex are consistent with this view, specifically quartz–alunite selvages of the massive pyrite–enargite bodies overprint and spatially, at deposit scale, overlap the external argillic to phyllic to propylitic alteration zones related to the Au–(Ag) mineralization.



◀ **Fig. 2** Distribution of the principal mineralization types and alteration assemblages of the Colquijirca district as defined during this study mainly by surface mapping and drill hole logging. Location of dated samples is given

Dated samples

In order to obtain quantitative data on the age of igneous activity in the Colquijirca district as well as the timing of the formation of the two mineralization types recognized from field observations, we conducted a $^{40}\text{Ar}/^{39}\text{Ar}$ study of three biotite samples taken from fresh dacitic porphyry domes and seven representative alunite-bearing ore samples. Three of the alunite-bearing samples correspond to the Au–(Ag) epithermal bodies (Marcapunta) and four to the sulfide-rich polymetallic replacements (Smelter and Colquijirca). Because of the extremely fine-grained habit of alunite at San Gregorio (less than 20 μm in length) attempts to concentrate sufficient coarse-grained alunite grains for geochronology were unsuccessful.

The three biotite samples correspond to three unmineralized dacitic domes: PBR-148, PBR-215 and PBR-216, and are located 1 km north, 0.7 km west and 2.5 km northwest (Huacchuacaja) of the diatreme vent, respectively (Figs. 2, 3). Rocks in these domes have a porphyritic texture similar to those observed in the altered ones, with large sanidine phenocrysts, smaller plagioclase, resorbed quartz, minor biotite, and hornblende. The microcrystalline groundmass is composed of quartz, potassic feldspar, and plagioclase. An electron microprobe analysis of biotite grains from sample PBR-215 yields Fe/(Fe + Mg) molar ratios ranging from 0.28 to 0.33.

In contrast to samples PBR-148 and PBR-215, which apparently correspond to individual domes, sample PBR-214 (Huacchuacaja, Fig. 2) comes from a fissure-controlled northwest-aligned multiple-dome intrusion complex 1.3 \times 0.25 km in horizontal dimensions with individual domes measuring less than 100 m in diameter. Thin sections from samples PBR-148 and PBR-215 show biotite grains which are slightly chloritized on the margins, although no more than 2 and 5 volume %, respectively. In addition, biotite grains in PBR-215 encapsulate euhedral quartz representing up to 4% of the total volume.

The three alunite samples from the Au–(Ag) high-sulfidation epithermal bodies (PBR-198 and PBR-214 from central Marcapunta and PBR-213 from 2 km south; Fig. 3) were extracted from altered rocks that consist predominately of quartz–alunite with minor zunyite, pyrite, and oxides such as goethite and hematite (Fig. 4A). As is typical for this mineralization type, dated alunite grains are pink, euhedral, and dominantly potassic (8.3–8.7 wt% K_2O , Table 1).

Three of the four alunite-bearing samples from the sulfide-rich polymetallic ores (samples PBR-131, PBR-137 from Smelter and PBR-218 from Colquijirca) cor-

respond to zone I (Fig. 2), and the fourth (sample PBR-108 from Colquijirca) is from zone III. Alunite concentrates from zone I are virtually free of inclusions. In accordance with the general composition of alunite from this zone throughout the northern part of the district, microprobe analyses reveal that dated alunite samples from Smelter (PBR-131, PBR-137) and Colquijirca (PBR-218) are more potassic (9.0–10.5% K_2O , Table 1) than alunite samples from the Au–(Ag) epithermal ores. Alunite from the base metal ores is, in general, paragenetically earlier than pyrite and enargite, although some alunite formed after pyrite and enargite. This reversed crystallization sequence and the intimate intergrowths of alunite and sulfides suggest that both are essentially coeval (Fig. 4B, C).

In zone III, alunite and sulfides occur in intricate intergrowth textures, and this is also evident in the alunite–sphalerite–galena-bearing sample (PBR-108) selected for dating (Fig. 4D). Alunite from this sample is colorless, euhedral and microscopically pure. Microprobe analyses indicate that alunite from zone III at Colquijirca ranges from 9.0 and 10.5 wt% K_2O . In comparison with alunites from zone I, the PBR-108 alunite grains have in general considerably higher F content and are slightly less sodic (Table 1).

Analytic procedure

Alunite and biotite grains were carefully handpicked from previously crushed and washed samples. Only grains of microscopically high purity (<2 vol% of quartz–opaque contaminants) were selected. The grain separates were additionally treated by ultrasonic cleaning. Additional details of the biotite and alunite samples, such as UTM coordinates, average grain sizes, and sample amounts are provided in Appendix 1 (see Electronic Supplementary Material).

The irradiation of mineral separates for $^{40}\text{Ar}/^{39}\text{Ar}$ analysis was carried out in the Triga reactor at Oregon State University, USA. All mineral samples were irradiated for 12 h with the Fish Canyon sanidine standard of 28.02 Ma (Renne et al. 1998).

The $^{40}\text{Ar}/^{39}\text{Ar}$ analyses were done at the University of Lausanne, Switzerland, using a low-blank double-vacuum resistance furnace and metal extraction line connected to a MAP 215-50 mass spectrometer using an electron multiplier. The incrementally heated gas was expanded and purified using activated Zr/Ti/Al getters and a metal cold finger maintained at a liquid nitrogen temperature. Time zero regressions were fitted to data collected from eight scans over the mass range of 40 to 36. Peak heights above backgrounds were corrected for mass discrimination, isotopic decay and interfering nucleogenic Ca-, K- and Cl-derived isotopes of Ar. Blanks were measured for all temperature steps and subtracted from the sample signal. For mass 40, blank values ranged from 4×10^{-15} mol below 1,350 $^\circ\text{C}$ to 9×10^{-15} mol at 1,650 $^\circ\text{C}$. Blank values for masses 36–39 were below

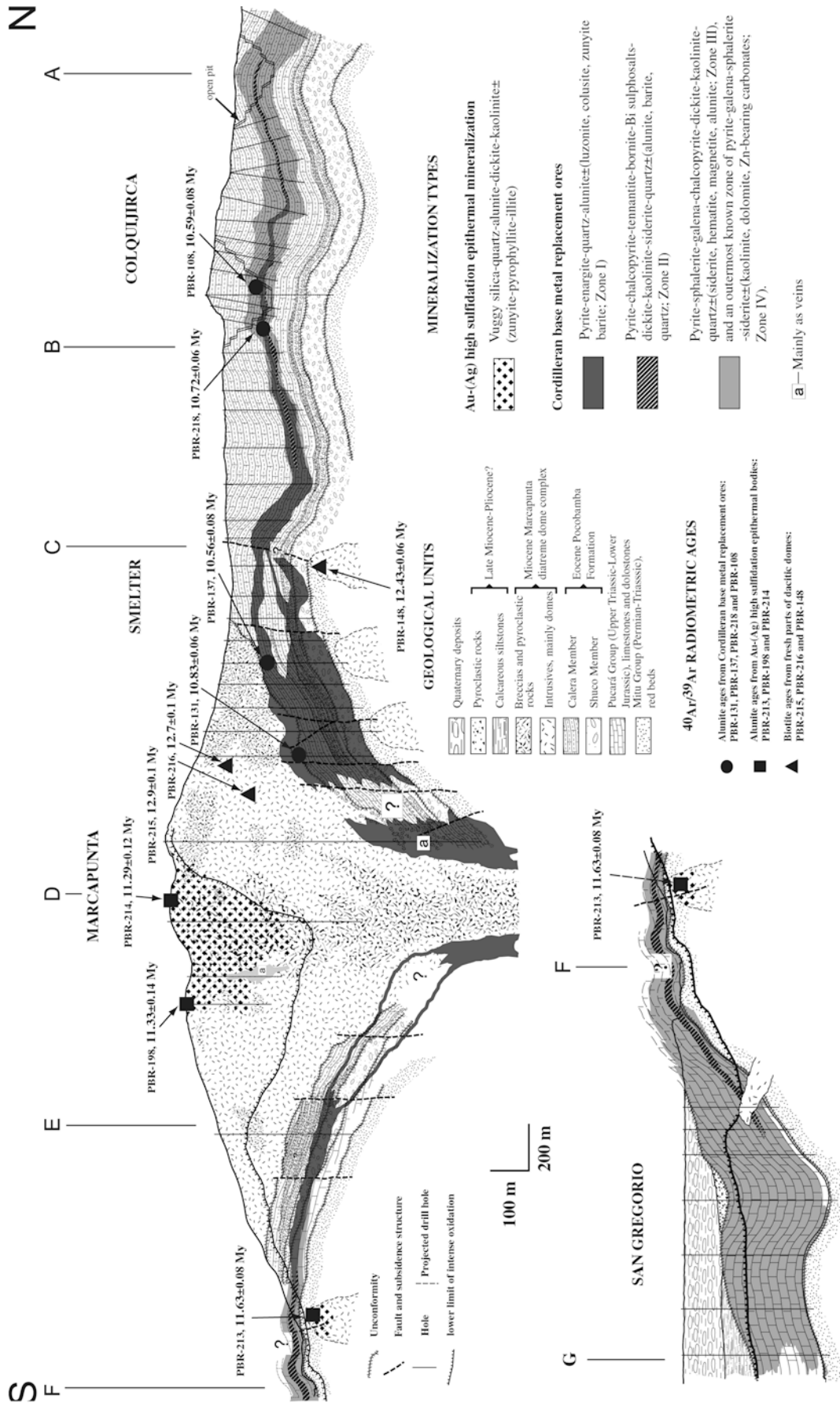


Fig. 3 North–south longitudinal section of the Colquijirca district following the main recognized ore bodies (ABCDEFGH section in Fig. 2). The section shows the main ore types, alteration assemblages, and location of samples with $^{40}\text{Ar}/^{39}\text{Ar}$ ages

2×10^{-17} mol for all temperatures. Isotopic production ratios for the Triga reactor were determined from analysis of irradiated CaF_2 and K_2SO_4 and the following values were used in the calculations: $^{36}\text{Ar}/^{37}\text{Ar}(\text{Ca}) = 0.0002640 \pm 0.0000017$, $^{39}\text{Ar}/^{37}\text{Ar}(\text{Ca}) = 0.0006730 \pm 0.0000037$, and $^{40}\text{Ar}/^{39}\text{Ar}(\text{K}) = 0.00086 \pm 0.00023$. A mass discrimination correction of 1.008 amu was determined by online measurement of air and was applied to the data. For this investigation, an uncertainty on the neutron flux (J) was determined with a precision of 0.5%, and this uncertainty has been propagated throughout the uncertainties on the reported ages. All ages and regressions in this paper are reported with a 95% level of confidence.

Results

The $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra of the analyzed samples are presented in Fig. 4 and the results of the $^{40}\text{Ar}/^{39}\text{Ar}$ analyses are summarized in Fig. 5. Age plateaus were determined using the criteria of Dalrymple and Lamm (1971), specifying the presence of at least three contiguous incremental heating steps with statistically

indistinguishable ages and constituting more than 50% of the total ^{39}Ar released during the experiment.

$^{40}\text{Ar}/^{39}\text{Ar}$ data from magmatic biotite

Biotite sample PBR-148 provided a well-defined age plateau of 12.43 ± 0.06 Ma (2σ) (Fig. 4). Although it is within 2σ analytical uncertainties, the age is slightly older than the K/Ar age obtained previously on biotite from the upper part of Marcapunta at 11.9 ± 0.8 Ma, 2σ by Vidal et al. (1984). Sample PBR-216 from a Huachuacaja dome (Fig. 2) gave a slightly disturbed but generally flat apparent age spectrum whose initial steps may reflect partial radiogenic Ar loss. The inverse isochron age of sample PBR-216 at 12.7 ± 0.1 Ma, derived with an MSWD of 1.5, is consistent with the PBR-148 age plateau (Table 2). Sample PBR-215, the least pure of the three biotite samples (see above), does not show any interpretable plateau-like segments. Its inverse isochron age of 12.9 ± 0.1 Ma derived with an MSWD of 1.5 is, however, consistent with ages from the other magmatic biotites.

Alunite $^{40}\text{Ar}/^{39}\text{Ar}$ data from Au–(Ag) epithermal ores

All of the alunite samples related to the Au–(Ag) mineralization (PBR-198, PBR-213 and PBR-214) gave well-defined age plateaus between 11.29 ± 0.12 and

Fig. 4A–D Photomicrographs of some of the dated alunite-bearing ore samples showing their intergrown habits. Black scale bars represent 100 μm . **A** Backscattered electron image of sample PBR-198 (Au–(Ag) high sulfidation epithermal ores) showing tabular alunite intergrown with pyrite and quartz in a micro-cavity from vuggy silica. **B** Photomicrograph in transmitted light of sample PBR-131 (Cordilleran base metal ore from Smelter, zone I) showing the intimate association of alunite–enargite. **C** Photomicrograph in reflected light of sample PBR-137 (Cordilleran base metal ore from Smelter, zone I). **D** Polished section image in reflected light of sample PBR-108 (Cordilleran base metal ore from Colquijirca, zone III) revealing intricate intergrowth of alunite, galena and sphalerite

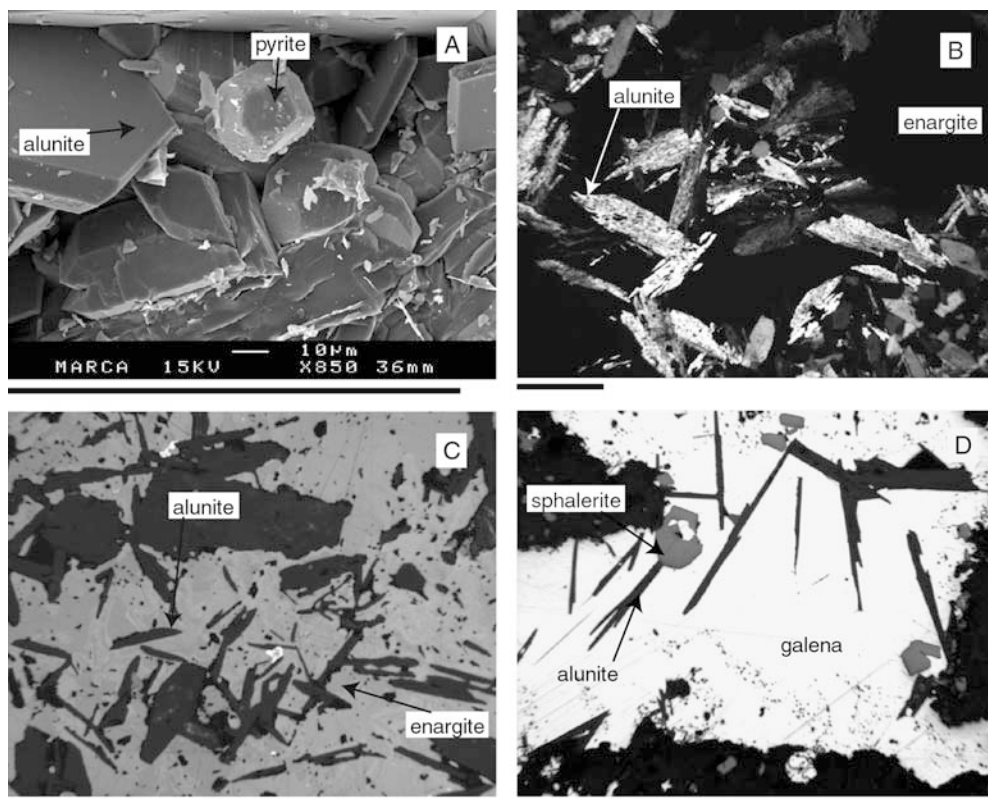


Table 1 Representative microprobe composition of alunite^a from Au–(Ag) and base metal mineralization in the Colquijirca district

Sample	Au–(Ag) epithermal ores			Cordilleran base metal replacement bodies				
	PBR-214	PBR-335	PBR-338	Zone I PBR-130	Zone I PBR-131	Zone I PBR-218	Zone III PBR-108	Zone III PBR-253
K ₂ O	8.34	8.60	8.31	9.40	9.30	10.48	9.66	10.28
Na ₂ O	1.73	1.79	0.18	0.92	0.95	0.19	0.31	0.18
BaO	0.71	0.60	0.11	0.17	0.05	0.23	0.13	0.00
SrO	0.47	0.79	0.20	0.12	0.01	0.08	0.40	0.11
Al ₂ O ₃	36.29	35.35	37.38	37.26	37.35	36.81	36.04	37.26
SO ₃	39.88	39.93	38.63	39.90	40.15	38.35	39.28	39.53
P ₂ O ₅	0.39	0.43	0.54	0.06	0.12	0.00	0.38	0.26
H ₂ O ^b	14.17	14.77	11.20	13.68	13.61	11.96	11.89	12.49
F ⁻	0.33	0.21	2.15	0.36	0.63	0.97	2.48	1.31
Total	102.30	102.45	98.69	101.87	102.17	99.06	100.57	101.43
K	0.73	0.76	0.75	0.82	0.81	0.93	0.86	0.90
Na	0.23	0.24	0.02	0.12	0.12	0.03	0.04	0.02
Ba	0.02	0.02	0.00	0.00	0.00	0.01	0.00	0.00
Sr	0.02	0.03	0.01	0.00	0.00	0.00	0.02	0.00
∑ A site	1.00	1.04	0.79	0.95	0.93	0.96	0.92	0.93
Al	2.94	2.88	3.13	3.00	3.00	3.02	2.98	3.02
∑ R site	2.94	2.88	3.13	3.00	3.00	3.02	2.98	3.02
S	2.05	2.07	2.05	2.04	2.05	2.00	2.06	2.03
P	0.02	0.02	0.03	0.00	0.01	0.00	0.02	0.02

^aAlunites were analysed using a Cameca SX50 electron microprobe at the University of Lausanne. Instrumental conditions were: accelerating voltage of 12 kV, beam current of 10 nA, and spot size of 15 mm.
^bWeight% H₂O calculation based on observed values for sulfur, phosphorus, potassium, sodium, strontium, barium, and fluorine, and alunite stoichiometry using the formula AR₃(SO₄)₂(F, OH)₆, in which A refers to the large cations K⁺, Na⁺, Ba²⁺, and Sr²⁺, and R is Al³⁺.

11.63 ± 0.08 Ma (2σ) (Fig. 5). These ages range from slightly to significantly older than the 10.6 ± 0.6 Ma (2σ) K/Ar age obtained on an alunite sample from the upper part of the Marcapunta volcanic complex (Vidal et al. 1984). The age plateaus of 11.33 ± 0.14 and 11.29 ± 0.12 Ma derived from samples PBR-198 and PBR-214, respectively, are analytically indistinguishable at the 2σ confidence level. This may indicate that in this part of the diatreme complex close to the diatreme vent, a single pulse of hydrothermal activity generated the gold-bearing advanced argillic-altered rocks. Alunite sample PBR-213 collected 2 km south of the diatreme center (Figs. 2, 3) yielded a flat age spectrum of multiple contiguous steps defining an age plateau of 11.63 ± 0.08 Ma (2σ). This age is ~300,000 years older than the ⁴⁰Ar/³⁹Ar age plateaus of PBR-198 and PBR-214 (between 80,000 and 540,000 years, considering 2σ). Such a time gap indicates that high-sulfidation fluids in this southern part of the district were generated from a hydrothermal pulse prior to the pulse at 11.3 Ma.

Alunite ⁴⁰Ar/³⁹Ar data from the sulfide-rich polymetallic ores

As is the case for the Au–(Ag) epithermal ores, the four alunite samples from the sulfide-rich polymetallic ores yielded clear age plateaus ranging between 10.83 ± 0.06 and 10.56 ± 0.08 Ma (2σ). These new data are consistent with a previous K/Ar age reported by Vidal et al. (1984) on an alunite sample collected from massive enargite–pyrite ores in zone I (southern Smelter). No relation between position (ore zone I or III) and age plateau is recognized. Sample PBR-108 from Colquijirca (zone III) gave an age plateau of 10.59 ± 0.08 Ma (2σ), which is analytically identical to sample PBR-137 from Smelter

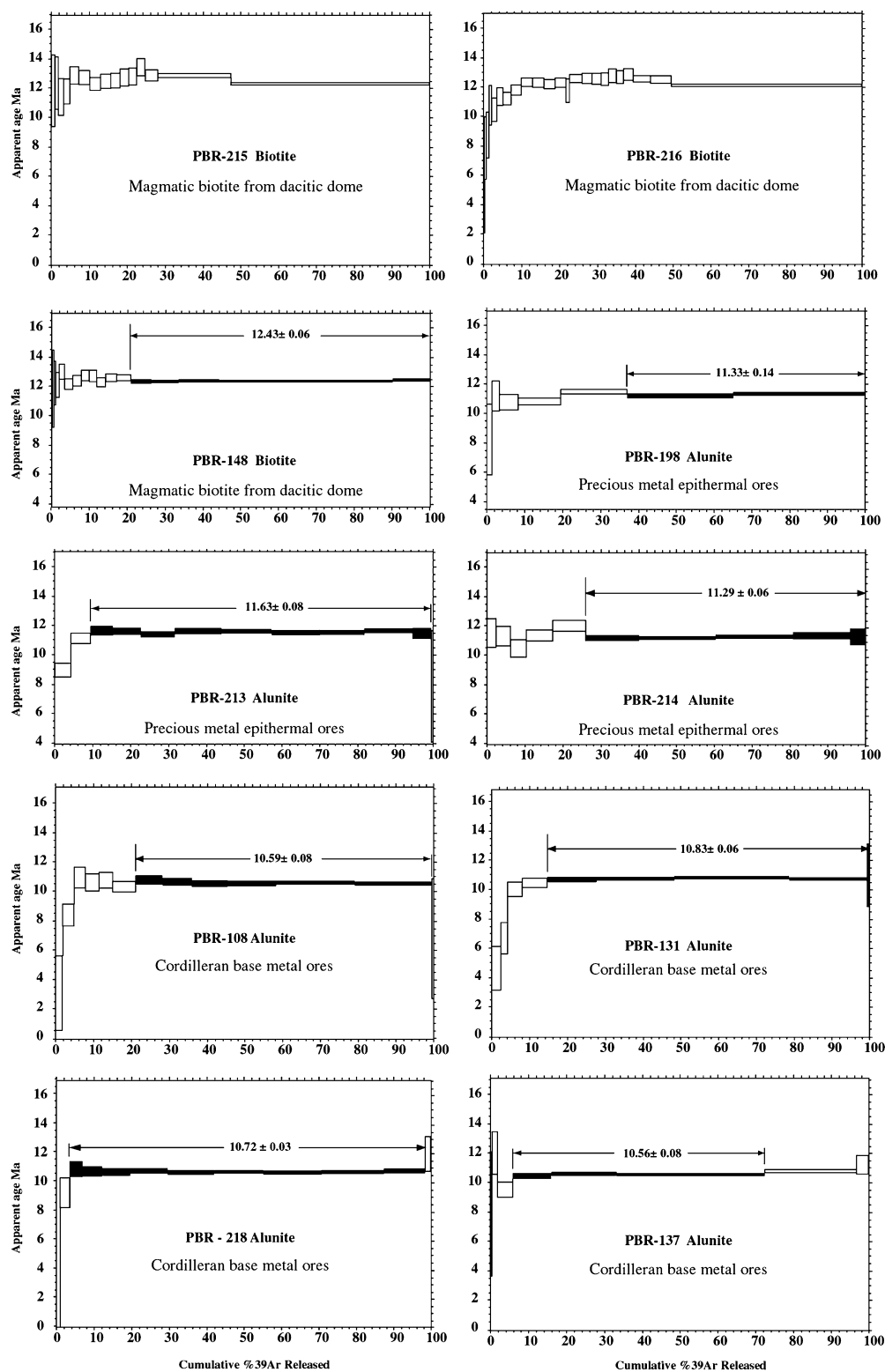
(zone I), at 10.56 ± 0.08 Ma (2σ). In zone I age plateaus have been obtained at 10.72 ± 0.06 Ma (sample PBR-218) and at 10.83 ± 0.06 Ma (sample PBR-131). These ages argue for a protracted history of hydrothermal activity that formed the Cordilleran base metal ores through one or more pulses. On the basis of the ⁴⁰Ar/³⁹Ar ages, the duration of this event can be estimated to be ~0.27 My (0.13 to as much as 0.41 My considering 2σ).

Discussions and conclusions

In the Colquijirca district, volcanic and hydrothermal activity between ~12.7 and 10.6 Ma, took place 2 million years later than at the Cerro de Pasco district (Fig. 6). At Cerro de Pasco, K/Ar ages obtained on biotite, sanidine, and plagioclase indicate that the volcanic and hydrothermal activity occurred between 14 to 15 ± (0.8–1.0) Ma at 2σ (Silberman and Noble 1977), which is similar to one whole rock K/Ar analysis from the nearby Yanamate diatreme-dome complex (Fig. 1) yielded an age of 15.2 ± 0.8 Ma at 2σ (Soler and Bonhomme 1988), which is more than 2 million years earlier than magmatic ages obtained in the Colquijirca district. On the basis of these available geochronological data it is concluded that Colquijirca represents the youngest expression of the Miocene magmatism in the region.

The ⁴⁰Ar/³⁹Ar determinations on mineralization in the Colquijirca district reveal that the two physically separate ore types, Au–(Ag) disseminated and the Cu–Zn–Pb–Ag–(Au–Bi) sulfide-rich ores (Figs. 2, 3), formed at different times with a difference in age of ~0.5 Ma (0.28–0.64 Ma at the 2σ level of confidence). Such a long time gap possibly indicates that both ore types were deposited from different hydrothermal events that, however, took place within the same magmatic cycle.

Fig. 5 $^{40}\text{Ar}/^{39}\text{Ar}$ age apparent age spectra from incremental heating analyses. Heating step segments from which plateau ages were calculated are shown in *filled boxes*



The older event is recognized through possibly two pulses of advanced argillic alteration formation at ~ 11.3 and ~ 11.6 Ma. Disseminated Au–(Ag) epithermal mineralization is related to this older event in areas affected by vuggy silica alteration in volcanic rocks of the Marcapunta diatreme-dome complex.

During a second event (10.8–10.6 Ma), sulfide-rich polymetallic mineralization formed subhorizontal flat elongated tube-like lenses replacing Eocene carbonate beds from the northern border of the Marcapunta diatreme-dome complex for 4 km north. This mineralization has a definite zoning which—from internal to

Table 2 Summary of $^{40}\text{Ar}/^{39}\text{Ar}$ age data of the Colquijirca district

Sample	Location	Mineral	Plateau age (Ma \pm 2 s) ^a	Inverse isochron age (Ma \pm 2 s) ^b	Isochron-derived MSWD ^c	40/36 ratio of intercept (\pm 2 s)
Dacitic domes						
PBR-148	Northern Marcapunta	Biotite	12.43 \pm 0.06^d	12.4 \pm 0.1	0.85	322 \pm 22
PBR-215	Western Marcapunta	Biotite		12.9 \pm 0.1	1.50	290 \pm 2
PBR-216	Huachuacaja	Biotite		12.7 \pm 0.1	1.50	270 \pm 2
Precious metal high sulfidation epithermal ores						
PBR-198	Central Marcapunta	Alunite	11.33 \pm 0.14	11.4 \pm 0.1	4.60	282 \pm 3
PBR-213	Southern Marcapunta	Alunite	11.63 \pm 0.08	11.6 \pm 0.1	0.99	291 \pm 29
PBR-214	Central Marcapunta	Alunite	11.29 \pm 0.12	11.3 \pm 0.1	2.40	319 \pm 40
Cordilleran base metal lode and replacement bodies						
PBR-108	Colquijirca	Alunite	10.59 \pm 0.08	10.6 \pm 0.1	1.20	289 \pm 37
PBR-131	Smelter	Alunite	10.83 \pm 0.06	10.9 \pm 0.1	0.84	291 \pm 10
PBR-137	Smelter	Alunite	10.56 \pm 0.08	10.6 \pm 0.1	0.55	287 \pm 24
PBR-218	Colquijirca	Alunite	10.72 \pm 0.06	10.7 \pm 0.1	0.19	307 \pm 13

^aPlateau age calculated according to the criteria of Dalrymple and Lamphere (1971)

^bAge estimated by representing the temperature steps from the plateau or plateau-like segment on a $^{36}\text{Ar}/^{40}\text{Ar}$ versus $^{39}\text{Ar}/^{40}\text{Ar}$ plot

^cMSWD: mean square of weighted deviates. It can be calculated only for three or more points

^dAges in boldface type were selected for the interpretation discussed in the text

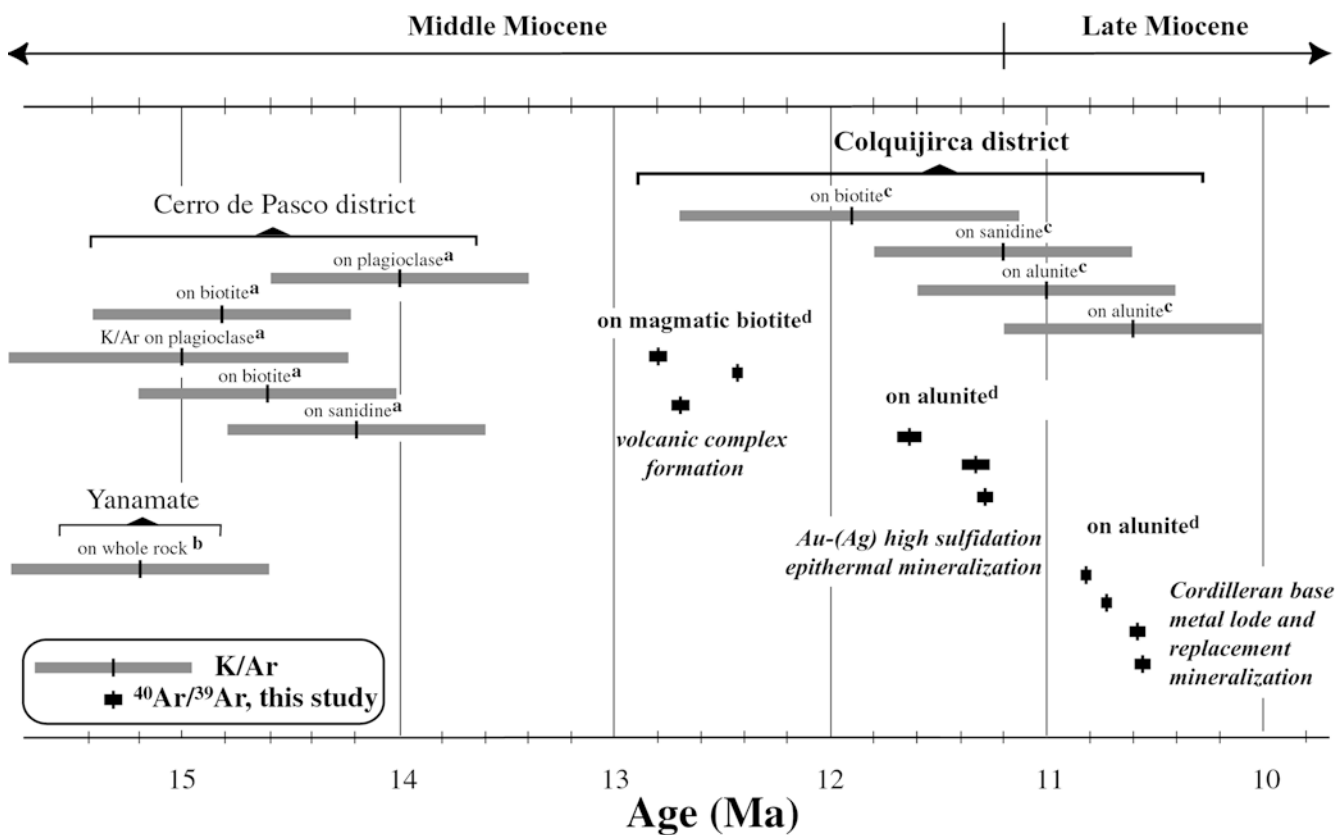


Fig. 6 Summary diagram of available geochronological data (K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$) from the Colquijirca and Cerro de Pasco districts: *a* from Silberman and Noble (1977) at 2σ , *b* from Soler and Bonhomme (1988) at 2σ , *c* from Vidal et al. (1984) at 2σ , *d* Bendezi et al. (this study) at 2σ level of confidence

external parts— displays the three following general main associations:

- Cu–(Au) in enargite–pyrite ores, with alunite, zunyite and/or dickite–kaolinite (zone I)

- Cu–(Ag–Bi) as chalcopyrite \pm (tennantite–bornite–Bi sulfosalts) with alunite–dickite–kaolinite (zone II)
- Zn–Pb–(Ag) as sphalerite–galena with kaolinite \pm alunite, siderite (zone III)

The alunite $^{40}\text{Ar}/^{39}\text{Ar}$ ages from zones I and III show that the sulfide-rich base metal ore types are contemporaneous within errors. The geochronologic data confirm the geometric observations suggesting that the

massive pyrite–enargite Cu–(Au) ores of Smelter and the Colquijirca (mainly Zn–Pb–(Ag) deposits) are parts of a continuous replacement (Figs. 2, 3).

The recognized features of the sulfide-rich polymetallic replacement ores, including mineral zoning, the high sulfidation and oxidation states of the sulfide assemblages in the internal parts, associated advanced argillic alteration, and the late timing of formation, characterize them as Cordilleran lode and replacement deposits in the sense of Einaudi (1982, 1994).

The Pucará-hosted San Gregorio deposit, for which age determinations are not yet available, is considered to be a low-temperature and more acidic and oxidizing equivalent of the sphalerite–galena-bearing zones encountered in the northern part of the district (Fontboté and BendeZú 2001).

From the current knowledge of the lifespan of a single intrusion-related hydrothermal system (e.g., <50,000 years, Marsh et al. 1997; Henry et al. 1997; Muntean and Einaudi 2001), the period of activity of the two mineralization events, Au–(Ag) (~340,000 years) and sulfide-rich polymetallic (~270,000 years) are apparently representative of relatively long-lived hydrothermal processes.

Multiple pulses of shallow intrusions are identified at Colquijirca where several swarms of porphyritic dome intrusions, several a few hundred meters long, are present around the diatreme neck at Marcapunta. Everything which has been dated in this study is several hundred thousand years older than recognized hydrothermal processes.

If we consider that dome intrusions occurred as early as 12.7 Ma and that the hydrothermal system deposited ores as late as ~10.6 Ma (PBR-137), the simplest conclusion is to assume that magmatic–hydrothermal activity was active for a minimum period of 2 Ma. Intermediate ages within this interval such as the earliest recognized hydrothermal pulse at ~11.6 Ma from the vuggy silica formation in southern Marcapunta, and the earliest dated dome at ~12.4 Ma (PBR-148) argue for this possibility. Two million years of inferred magmatic activity represents an interval of time long enough for the development of a complex evolutionary history involving several thermal and/or magmato-volcanic episodes related to a single, fairly large magma chamber. Considering the present results, the most plausible scenario for the Colquijirca district is that the two recognized hydrothermal events were linked to at least two major thermal episodes within the same magmatic cycle (BendeZú and Fontboté 2002c).

In the Colquijirca district, the relative sequence of events and the absolute ages obtained establish for the first time that Cordilleran base metal lode and replacement ores which are mainly epithermal and formed at high-sulfidation and oxidations states, were emplaced considerably later (~460,000 years) than the Au–(Ag) high-sulfidation epithermal mineralization.

Acknowledgements The present investigation was carried out with the support of the Sociedad Minera El Brocal S.A. and the Swiss National Science Foundation (FN 2000-062000.00). We also would like to acknowledge the generous help provided, especially in the early period of this investigation, by the El Brocal staff, and in particular: Juan Proaño, Isaac Cruz, Carlos Yacila, Ivan Montegudo, Máximo Yaringaño, and Lucio Canchis. Thanks are also extended to Lewis Gustafson and John Dilles for the constructive reviews and comments, as well as to an anonymous reviewer who significantly improved the manuscript. We would also like to thank Richard Goldfarb for the editorial support and, lastly, Larry Meinert, who contributed additional helpful comments and suggestions.

References

- Ahlfeld F (1932) Die Silberlagerstätte Colquijirca, Perú. *Z Prakt Geol* 40:81–87
- Angeles C (1993) Geología de Colquijirca y alrededores. Informe privado Sociedad Minera El Brocal S.A., 39 pp
- Angeles C (1999) Los sedimentos cenozoicos de Cerro de Pasco: estratigrafía, sedimentación y tectónica. In: Sociedad Geológica del Perú, Volumen Jubilar No 5, pp 103–118
- Bartos PJ (1989) Prograde and retrograde base metal lode deposits and their relationship to underlying porphyry copper deposits. *Econ Geol* 84:1671–1683
- BendeZú R (1997) Características geológicas, mineralógicas y geoquímicas de los yacimientos de Zn–Pb–(±Ag) de San Gregorio y Colquijirca emplazados en unidades sedimentarias en los bordes del sistema epitermal de alta sulfuración de Marcapunta. Tesis Ing., Universidad Nacional de Ingeniería, Lima, 60 pp
- BendeZú R, Fontboté L (2002a) Au–(Ag) epithermal and “Cordilleran base metal lodes and replacement bodies”: two different high sulfidation mineralization types. Examples from the Colquijirca district, central Peru. XI Congreso Peruano de Geología, Lima, Resúmenes, pp 73–74
- BendeZú R, Fontboté L (2002b) Spatial and temporal relations between “Cordilleran base metal lodes and replacement bodies” and precious metal high sulfidation epithermal mineralization in the Colquijirca district, central Peru. In: Abstracts SEG Meeting Global exploration 2002 on integrated methods for discovery, Denver 14–16 April 2002, pp 63–64
- BendeZú R, Fontboté L (2002c) Late timing for high sulfidation Cordilleran base metal lode and replacement deposits in porphyry-related districts: the case of Colquijirca, central Peru. *SGA News*, vol 13, pp 1, 9–13. (also accessible under http://www.unige.ch/sciences/terre/mineral/ore/min_ore.htm)
- Bowditch SI (1935) The geology and ore deposits of Cerro de Pasco, Peru. Dissertation, Harvard University, Cambridge, Massachusetts, 160 pp
- Dalrymple GB, Lamphere MA (1971) $^{40}\text{Ar}/^{39}\text{Ar}$ technique of K–Ar dating: a comparison with the conventional technique. *Earth Planet Sci Lett* 12:300–308
- Einaudi MT (1977) Environment of ore deposition at Cerro de Pasco, Peru. *Econ Geol* 72:893–924
- Einaudi MT (1982) Description of skarns associated with porphyry copper plutons, southwestern North America. In: Titley S R (ed) *Advances in geology of the porphyry copper deposits, southwestern North America*. Univ Arizona Press, Tucson, pp 139–184
- Einaudi MT (1994) High sulfidation and low sulfidation porphyry copper/skarn systems: characteristics, continua, and causes. Society of Economic Geologists, International exchange lecture, WEB: <http://pangea.Stanford.edu/ODEX/marco-hilosulf.html>
- Fontboté L, BendeZú R (1999) The carbonate hosted Zn–Pb San Gregorio deposit, Colquijirca District, central Peru, as part of a high sulfidation epithermal system. In: Stanley et al (eds) *Fifth Biennial SGA Meeting, Mineral Deposits: processes to Processing*, vol 1, pp 495–498

- Fontboté L, Bendeziú R (2001) The carbonate-hosted San Gregorio and Colquijirca (Zn–Pb–Ag) deposits (central Peru) as products of an epithermal high sulfidation system. *Proexplor* 2001, Lima, Perú, Abril 2001, CD-ROM, doc. 18 pp
- Gray JE, Coolbaugh MF, Plumlee GS, Atkinson WW (1994) Environmental geology of the Summitville mine, Colorado. *Econ Geol* 89:2006–2014
- Guilbert JM, Park CF Jr (1986) The geology of ore deposits, 4th edn. WH Freeman, New York, 985 pp
- Hedenquist JW (1987) Mineralization associated with volcanic-related hydrothermal systems in the circum-Pacific basin. In: Horn MK (ed) Transactions, fourth Circum-Pacific Energy and Mineral Resources Conference, Singapore. American Association of Petroleum Geologists, Tulsa, Oklahoma, pp 513–524
- Hedenquist JW, Arribas A Jr, Reynolds TJ (1998) Evolution of an intrusion-centered hydrothermal system: Far Southeast-Lepanto porphyry and epithermal Cu–Au deposits, Philippines. *Econ Geol* 93:373–404
- Henry CD, Elson HB, McIntosh WC, Heizler MT, Castor SB (1997) Brief duration of hydrothermal activity at Round Mountain, Nevada determined from $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology. *Econ Geol* 92:807–826
- Lacy WC (1953) Differentiation of igneous rocks and its relation to ore deposition in central Peru, *Boletín de la Sociedad Geol Perú* 26:121–138
- Lindgren W (1935) The silver mine of Colquijirca, Perú. *Econ Geol* 30:331–346
- Marsh TM, Einaudi MT, McWilliams M (1997) $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of Cu–Au and Au–Ag mineralization in the Potrerillos district, Chile. *Econ Geol* 92:784–806
- Muntean JL, Einaudi MT (2001) Porphyry–epithermal transition: Maricunga belt, northern Chile, *Econ Geol* 96:743–772
- McKinstry HE (1936) Geology of the silver deposit at Colquijirca, Peru. *Econ Geol* 31:619–635
- Petersen U (1965) Regional geology and major ore deposits of central Peru. *Econ Geol* 30:407–476
- Renne PR, Swisher CC, Deino AL, Karner DB, Owens TL, DePaolo DJ (1998) Intercalibration of standards, absolute ages and uncertainties in $^{40}\text{Ar}/^{39}\text{Ar}$ dating. *Chem Geol* 145:117–152
- Silberman ML, Noble DC (1977) Age of igneous activity and mineralization, Cerro de Pasco, central Peru. *Econ Geol* 72:925–930
- Sillitoe R H (2000) Zinc exploration at Colquijirca, Central Peru. Private report for Compañía de Minas Buenaventura SA, 9 pp
- Soler P, Bonhomme MG (1988) Oligocene magmatic activity and associated mineralization in the polymetallic belt of central Peru. *Econ Geol* 83:657–663
- Stoffregen R (1987) Genesis of acid–sulfate alteration and Au–Cu–Ag mineralization at Summitville, Colorado. *Econ Geol* 82:1575–1591
- Vidal C, Mayta O, Noble DC, McKee EH (1984) Sobre la evolución de las soluciones hidrotermales dentro del centro volcánico Marcapunta en Colquijirca-Pasco. Volumen Jubilar Sociedad Geológica del Perú, 10, pp 1–14
- Vidal C, Proaño J, Noble N (1997) Geología y distribución hidrotermal de menas con Au, Cu, Zn, Pb y Ag en el Distrito Minero Colquijirca, Pasco: IX Congreso Peruano de Geología, pp 217–219
- Yarangaño M, Arias W, Panéz M (1997) Exploraciones y evaluación de los yacimientos del Distrito Minero de Colquijirca, Pasco: IX Congreso Peruano de Geología, pp 231–236