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ARTICLE

New $^{40}\text{Ar}/^{39}\text{Ar}$ alunite ages from the Colquijirca district, Peru: evidence of a long period of magmatic SO_2 degassing during formation of epithermal Au–Ag and Cordilleran polymetallic ores

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Abstract We present $^{40}\text{Ar}/^{39}\text{Ar}$ data acquired by infra-red (CO_2) laser step-heating of alunite crystals from the large Miocene Colquijirca district in central Peru. Combined with previously published data, our results show that a long (at least 1.3 My) and complex period of magmatic-hydrothermal activity associated with epithermal Au–(Ag) mineralization and base metal, Cordilleran ores took place at Colquijirca. The new data indicate that incursion of magmatic SO_2 -bearing vapor into the Colquijirca epithermal system began at least as early as ~ 11.9 Ma and lasted until ~ 10.6 Ma. Four alunite samples associated with high-sulfidation epithermal Au–(Ag) ore gave $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages between ~ 11.9 and ~ 11.1 Ma (compared to the previously documented ~ 11.6 to ~ 11.3 Ma). By combining individually these new ages with

crosscutting relationships, the duration of the Au–(Ag) deposition period can be estimated to at least 0.4 My. Three new $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages on alunite associated with the base-metal Cordilleran ores are consistent with previously obtained ages, all of them between 10.83 ± 0.06 and 10.56 ± 0.06 Ma, suggesting that most of the sulfide-rich polymetallic deposits of Smelter and Colquijirca formed during this short period. The recognition of consecutive alunite-bearing and alunite-free mineral assemblages within both the Au–(Ag) and the base-metal Cordilleran ores may suggest that SO_2 -bearing magmatic vapor entered the epithermal environment as multiple discontinuous pulses, a number of which was not necessarily associated in time with ore fluids. It is likely that a period of SO_2 -bearing vapor degassing longer than 11.9 to 10.6 Ma may be recognized with further more detailed work.

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Introduction

Hydrothermal systems with life spans over 1 My have been documented for several major porphyry-related systems, including Chuquicamata, El Teniente, Butte, La Escondida, and Cerro de Pasco (Ossandón et al. 2001; Gustafson et al. 2001; Pécskey and Molnár 2002; Heather et al. 2003; Maksaev et al. 2003; Baumgartner et al. 2006; Baumgartner 2007). Several studies propose that long hydrothermal life spans are the result of multiple pulses related to each one of the single intrusions and which should not exceed durations on the order of 50–100 ky (e.g., Marsh et al. 1997; Henry

et al. 1997; Muntean and Einaudi 2001; Seedorff et al. 2005). This paper is an attempt to identify such various pulses in a porphyry-related epithermal environment comprising disseminated high-sulfidation Au–(Ag) mineralization and Cordilleran polymetallic replacement deposits. The study has been carried out in the well-exposed Miocene Colquijirca district and includes infra-red (CO_2) laser $^{40}\text{Ar}/^{39}\text{Ar}$ Ar analysis of alunite, as well as K/Ar analysis for samples in which $^{40}\text{Ar}/^{39}\text{Ar}$ Ar dating was not suitable. Crosscutting relationships at Colquijirca indicate that alunite, which was derived

from magmatic SO_2 -bearing vapors (see below), is pre-, syn-, and post-Au–(Ag) and Cordilleran mineralization, providing a good opportunity to combine these relative ages with a highly resolved geochronological data base.

The Colquijirca district

The Colquijirca district, located 12 km south of the Cerro de Pasco district in central Peru (Fig. 1), contains two types of

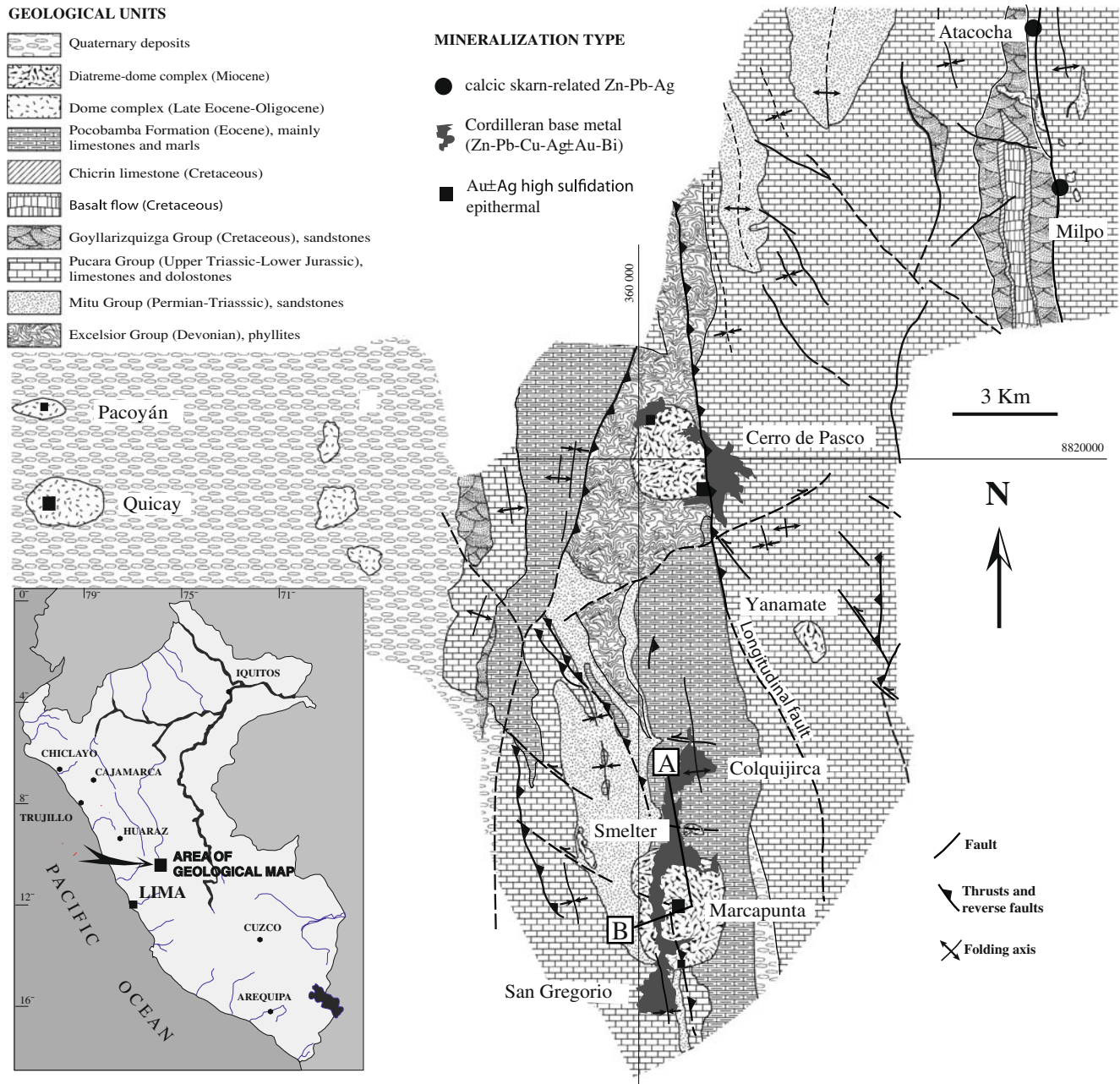


Fig. 1 General geology and main mining centers in the Cerro de Pasco sector, central Peruvian Andes. Geology compiled from Johnson et al. (1955), Angeles (1993), Sociedad Minera El Brocal S. A. staff, and this study

epithermal mineralization: a disseminated high-sulfidation Au–(Ag) prospect (Oro Marcapunta) and Cordilleran polymetallic deposits (Colquijirca, Smelter, Marcapunta Oeste, San Gregorio). We use the term Cordilleran polymetallic deposits to underline that these deposits are sulfide rich, contain Zn–Pb–Ag ores, and generally crosscut other styles of porphyry-related epithermal mineralization.

The term Cordilleran deposit was introduced by Sawkins (1972) and was subsequently used by Einaudi (1982), Guilbert and Park (1985), Bartos (1987), Macfarlane and Petersen (1990), Hemley and Hunt (1992), BendeZú and Fontboté (2002), BendeZú et al. (2003), and BendeZú (2007) and Baumgartner (2007). Main features of Cordilleran base-metal deposits can be summarized as follows (modified from Sawkins 1972 and Einaudi 1982): (1) close association in time and space with calc-alkaline igneous activity, i.e., same environment as most porphyry Cu and high-sulfidation epithermal Au–Ag deposits; (2) deposition “late” in the evolution of the porphyry system (as seen from abundant cross-cutting relationships and sparse geochronological data later than porphyry Cu, skarn, and high sulfidation Au (–Ag) deposits). (3) deposition mostly under epithermal conditions at shallow levels beneath the paleo-surface; (4) Cu–Zn–Pb–(Ag–Au–Bi) metal suites, very rich in sulfides (up to more than 50 wt.% total sulfides); (5) frequently, but not always, well-developed zoning of ore and alteration minerals, cores may show up to high-sulfidation and, though commonly this is not the case (see below) advanced argillic alteration assemblages; (6) frequent early pyrite–quartz stages with low sulfidation assemblages containing pyrrhotite–(arsenopyrite) that can be extensive and form large bodies zoned outward to Zn–Pb ores; (7) mainly occurrence as open-space fillings (veins, breccia bodies) in silicate host rocks and as replacement in carbonate rocks. Another feature pointed out below for Colquijirca is that Cordilleran ores display notably higher Ag/Au ratios than high sulfidation epithermal Au–(Ag) mineralization. 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). We prefer the classical term Cordilleran for this base metal mineralization related to porphyry systems because not always the zoning is well developed, as it depends of the host rock (better developed in carbonate rocks) and of the sulfidation state of the fluid. Cordilleran base-metal deposits have been historically an important source of Cu and Zn–Pb–Ag in the North American Cordillera (hence the name) and Peru. Currently, Cordilleran ores represent the main source of zinc and lead of Peru, which ranks within the top five producers worldwide in these two metals.

The disseminated high-sulfidation Au–(Ag) prospect and the Cordilleran polymetallic deposits of the Colquijirca district are spatially and temporally linked to a Miocene

diatreme–dome complex (Ahlfeld 1932; Lindgren 1935; McKinstry 1936; Yaringaño et al. 1997; Vidal et al. 1997; BendeZú 1997; Fontboté and BendeZú 1999, 2001; BendeZú and Fontboté 2002; BendeZú et al. 2003; BendeZú 2007).

The Marcapunta diatreme–dome complex, exposed in the center of the Colquijirca district (Sillitoe 2000; BendeZú et al. 2003; Sarmiento 2004), is one of a series of Miocene volcanic edifices, including Cerro de Pasco and Yanamate (Fig. 1), which consist of multiple dome-lava intrusions of mainly dacitic composition. Injection and explosion breccias and pyroclastic layers, typical of diatreme conduits, are extensively recognized at depth (Fig. 2). Inward-dipping normal fault–located in peripheral areas suggest that the entire edifice collapsed, likely prior to the main episodes of mineralization (Fig. 3 in BendeZú et al. 2003).

As in large sectors of Central Peru, the district is characterized by extensive exposures of carbonate rocks. A 400-m-thick sequence of limestone and dolostone of the Upper Triassic–Lower Jurassic Pucará Group occupies the southern and western sector of the Colquijirca district. The Eocene Pocobamba Fm., with a thickness of up to 450 m and mainly composed of continental marls and limestones (Angeles 1993), covers most of the northern and eastern sector of the Colquijirca district (Fig. 1).

The mining district was affected by Tertiary folding (NNE fold axes), which predates the emplacement of the Marcapunta volcanic complex (Angeles 1993). The major N–S trending, Longitudinal Fault (reverse fault), which has possibly been active since the Jurassic (Angeles 1993), defines the eastern border of the Colquijirca district and dissects the Cerro de Pasco district to the north (Fig. 1). Other fracture systems recognized in the Colquijirca district follow NW–SE and NE–SW trends (Fig. 1). The Longitudinal Fault appears to control the emplacement of the Miocene intrusive rocks, whereas NW–SE- and NE–SW-oriented fractures probably played a significant role in channeling the ore fluids in much of the district (Fig. 2). More details on the structural context of the district are given in BendeZú (2007).

The district hosts two main types of epithermal mineralization: (1) disseminated high-sulfidation Au–(Ag) mineralization, hosted by volcanic rocks from the Marcapunta complex, and (2) sulfide-rich Cordilleran polymetallic deposits hosted in the carbonate rocks of both the Pucará Group and the Pocobamba Formation.

High-sulfidation epithermal Au–(Ag) mineralization consists of oxide veinlets and disseminations hosted in vuggy silica ledges. The vuggy silica ledges are zoned outward to quartz–alunite and to argillic alteration assemblages, which affect most of the Marcapunta volcanic rocks. Typical gold and silver concentrations in the vuggy silica ledges are on the order of 0.2–3 and 10–70 g/t, respectively (Vidal et al. 1997) and Ag/Au ratios ranging from 10 to 30. The Au–(Ag)-bearing ledges display vertical dimensions of up to 100 m

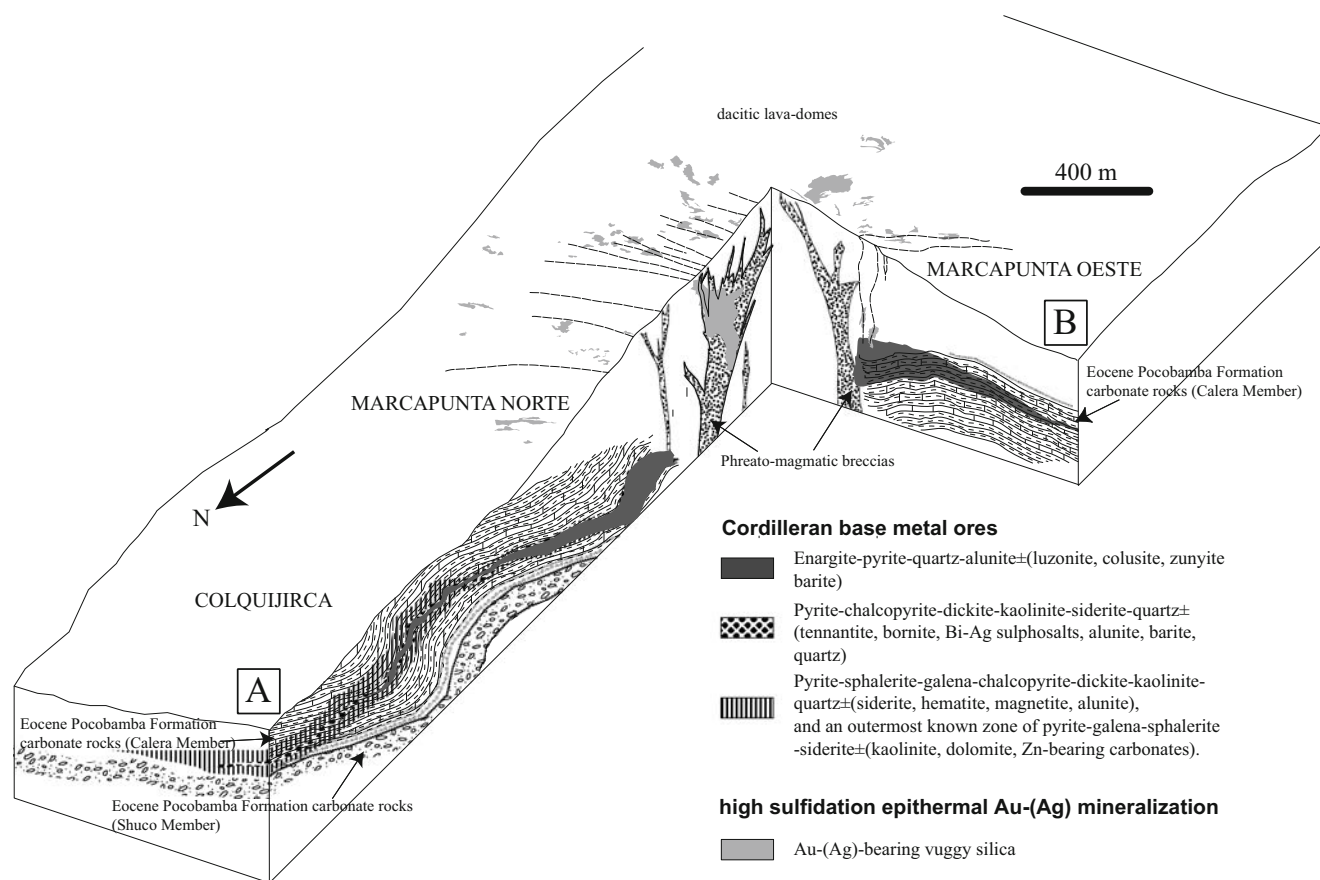


Fig. 2 Block diagram illustrating the spatial relationships between the high-sulfidation epithermal Au-(Ag) mineralization of Oro Marcapunta and the Cordilleran base-metal deposits of Marcapunta Oeste, Smelter and Colquijirca (following the AB profile of Fig. 1)

and have been mainly recognized in the central portion of the complex, associated with the diatreme breccia and pyroclastic infill, where their morphology is controlled by both lithological (phreatomagmatic breccias) and structural permeability (E-W fractures, Fig. 2). The deep portions of vuggy silica ledges contain unoxidized Au-(Ag) ores, which contain less than 5 vol.% of finely disseminated sulfides, and sulfide veinlets composed mainly of pyrite-enargite and very minor chalcocite, covellite, and sphalerite accompanied by clays, largely kaolinite, but also smectite and/or illite. Vuggy silica ledges and surrounding quartz-alunite zones, which are devoid of veinlets contain minor amounts of Au-(Ag), suggesting that most of the precious metals precipitated during veinlet formation. In several areas, quartz-alunite alteration is observed to postdate Au-(Ag)-bearing veinlets (see below), suggesting that several repeated episodes of vuggy silica-quartz-alunite alteration and Au-(Ag) deposition took place at Marcapunta.

Cordilleran epithermal deposits mainly consist of Cu-Zn-Pb-Ag±(Au-Bi)-zoned sulfide-rich replacements and represent the economically most important type of mineralization in the district. Cordilleran mineralization aggregates to a resource of at least 220 Mt, including ~130 Mt at

~2% Cu from the Smelter deposit (Marcapunta Norte) and the Marcapunta Oeste project and at least 90 Mt at ~6% Zn, ~2% Pb, and 3 oz/t Ag from the Colquijirca and San Gregorio deposits (Yaringaño et al. 1997; Vidal et al. 1997; Vidal and Ligarda 2004). The historical Zn-Pb-(Ag) Colquijirca mine is located further to the north and has been an important silver producer in Peru since pre-colonial times (Hutchinson 1920; Lindgren 1935; McKinstry 1936; BendeZú 2007). The San Gregorio deposit, located 3 km south of Marcapunta, was discovered during 1994–1995 and hosts at least 70 Mt at 7.3% Zn, 2.18% Pb, 0.57 oz/t Ag (Yaringaño et al. 1997), constituting the largest undeveloped Zn-Pb-(Ag) resource in the world. Mineralization at Colquijirca, Smelter, and Marcapunta Oeste is mainly hosted by the Pocobamba Fm., whereas the large San Gregorio deposit replaces Pucará Group rocks.

A significant feature of the Colquijirca Cordilleran deposits is the high total sulfide content, which fluctuates between an average of 30 and 50 vol.%. The most abundant minerals are pyrite, which crystallized during an Early silica-pyrite stage, followed in abundance by enargite-pyrite from the Main ore stage, and, finally, chalcocite from the Late ore stage (BendeZú 2007). Strongly oxidized

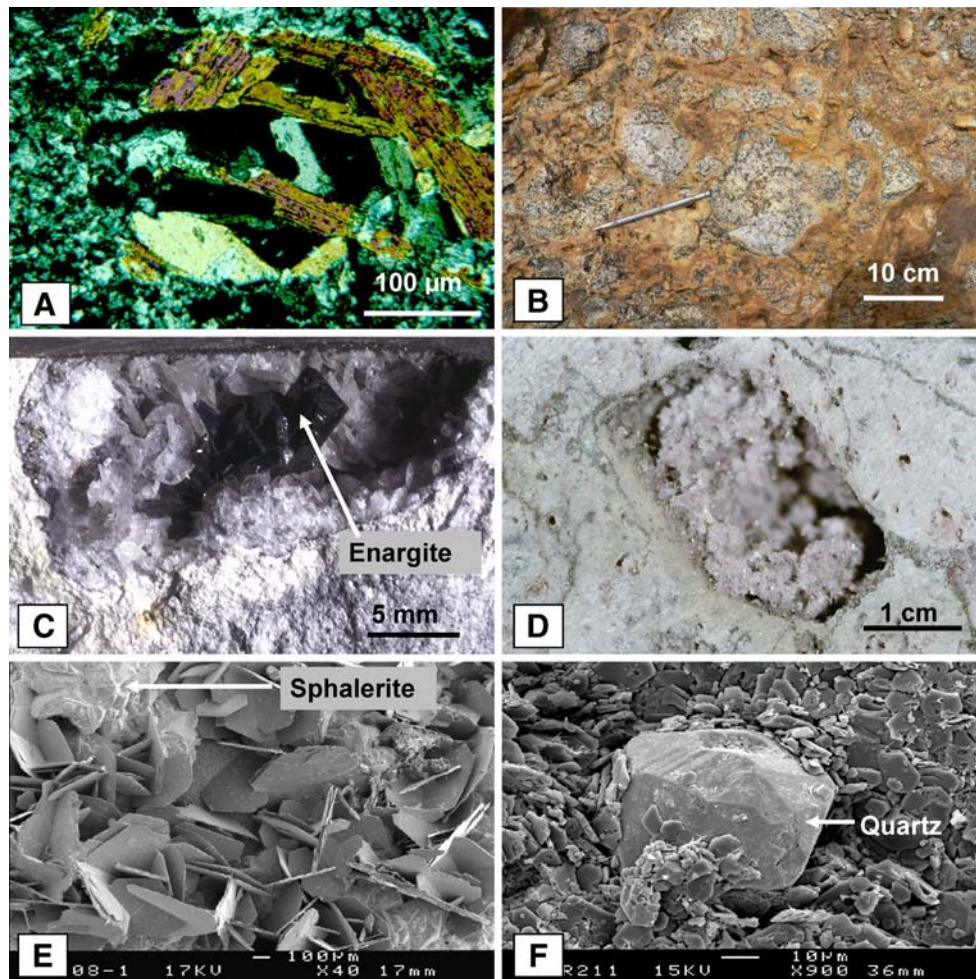


Fig. 3 Images of alunite samples dated in this study. **a** Photomicrograph in transmitted light of sample PBR-336 showing alunite from the high-sulfidation epithermal precious metal mineralization of Oro Marcapunta. Note that it is devoid of pseudocubic cores of the woodhouseite–svanvergitte end-member. **b** Photograph of an outcrop in southern Marcapunta in which plumose alunite (sample PBR-273) cements Au–(Ag) bearing rounded clasts (up to 2 ppm Au) of vuggy silica formed from the epithermal precious metal system. **c** Small geode displaying euhedral alunite intergrown with enargite plus minor amounts of pyrophyllite and pyrite, Smelter Cordilleran ore (sample

PBR-322). **d** Photograph showing the effect of Cordilleran mineralization on volcanic rocks. A void left by former sanidine is filled by platy euhedral alunite intergrown with quartz, pyrite, and enargite; these last two, in addition, are in the form of veinlets and as coatings in vugs. **e** Intimate intergrowth between alunite and sphalerite revealed by backscattered electron image of sample PBR-298 from the Cordilleran deposit of Colquijirca. **f** Backscattered electron image of sample PBR-208 showing the typical extremely fine-grained habit of alunite from the large Cordilleran deposit of San Gregorio

zones, originally composed of enargite–pyrite, display Ag/Au ratios ranging from 80 to 120, much higher than those found in the Oro Marcapunta disseminated Au–(Ag) ores (10 to 20). Another major feature of Cordilleran mineralization in the Colquijirca district is the distinct ore zoning, defined by (1) a Cu–(Au–Ag) nucleus dominated by enargite and usually accompanied by alunite-bearing assemblages; (2) an intermediate Cu–(Zn–Pb–Ag–Bi) zone where chalcopyrite, sphalerite, and galena predominate; and (3) an outer Zn–Pb–(Ag) envelope mainly composed of sphalerite and galena.

Cordilleran veins systematically cut the precious metal veinlets and veins in the easternmost portion of the

Marcapunta Oeste project. This is observed in drill holes CM3-444 and CM4-452, which encountered up to 350 m of vertical sections containing Au–(Ag) high-sulfidation epithermal ledges, which in the lowermost 50 m, are superimposed by Cordilleran ores (Bendezú 2007). The quartz–alunite zones developed during the high-sulfidation epithermal event contain Au–(Ag) veinlets, which were cut by centimeter-wide pyrite–(enargite)-rich veinlets and veins generated during the Cordilleran event. Furthermore, a majority of cavities within the vuggy silica contain intergranular fillings of Cordilleran stage enargite, which in part destroy earlier Au–(Ag) veinlets with quartz–alunite-bearing assemblages.

The sulfur isotope composition of alunite from the Colquijirca district indicates the alunite-bearing assemblages from the two epithermal mineralization types derived from SO₂-bearing magmatic vapors (Bendezú 2007). The $\delta^{34}\text{S}$ values for alunite from both the high-sulfidation Au–(Ag) and the Cordilleran mineralization (from 21.1‰ to 26.4‰) are typical of hydrothermal magmatic fluids in which sulfate has equilibrated with H₂S formed through disproportionation of SO₂ within a condensing vapor plume (e.g., Rye 1993).

Previous geochronologic data and scope of the present work

Previous ⁴⁰Ar/³⁹Ar dating in the Colquijirca district using furnace ⁴⁰Ar/³⁹Ar step-heating indicated that the Smelter and Colquijirca Cordilleran deposits were formed by a late hydrothermal event, subsequent to the high-sulfidation epithermal Au–(Ag) mineralization at Oro Marcapunta (Bendezú et al. 2003). Alunite samples related to the high-sulfidation Au–(Ag) system were dated at 11.6±0.08 to 11.3±0.06 Ma (2 σ) and those from the Cordilleran ores in the northern part of the district (Smelter and Colquijirca) at 10.8±0.08 to 10.6±0.06 Ma.

According to the same survey, magmatic biotite derived from flanking dacitic domes yielded ⁴⁰Ar/³⁹Ar ages ranging from 12.9±0.10 to 12.4±0.04 Ma, which is ~0.8 My older than the earliest recognized hydrothermal manifestation (e.g., alunite PBR-213 from the high-sulfidation epithermal Au–(Ag) event dated at 11.63±0.08 Ma). Baumgartner (2007) reports a slightly younger U–Pb age of 12.12±0.03 Ma for zircons from a dacitic dome from the western sector of the Marcapunta volcanic complex.

The relatively long time gap between the two epithermal events (0.5 My), interpreted by Bendezú et al. (2003) in terms of distinct hydrothermal events within the same magmatic cycle and the gap between the youngest dated magmatic dome and the oldest recognized hydrothermal manifestation (0.8 My) could be, in fact, an artifact due the low quantity of age data. This paper examines also these gaps on the basis of the new ⁴⁰Ar/³⁹Ar ages here presented.

Dated samples

Seven platy, coarse-grained alunite separates were selected for infra-red (CO₂) laser step-heating ⁴⁰Ar/³⁹Ar analysis. Four samples belong to the Oro Marcapunta high-sulfidation epithermal Au–(Ag) occurrence and three to the Cordilleran epithermal ores of the northern part of the district (Smelter and Colquijirca).

Three whole-rock samples from the San Gregorio Cordilleran deposit, in the southern part of the district, were dated using the K/Ar method.

Alunite samples from the high-sulfidation epithermal Au–(Ag) mineralization

Alunite samples PBR-336 and PBR-338 of the Oro Marcapunta high-sulfidation epithermal Au–(Ag) mineralization were collected from the southern flank of the southern topographic high of Marcapunta, approximately 400 m south of samples PBR-198 and PBR-214, which were previously dated using furnace ⁴⁰Ar/³⁹Ar step-heating (Bendezú et al. 2003). They represent internal parts of advanced argillic alteration zones (AAA zones), which immediately envelope leached vuggy silica cores. In these AAA zones, alunite is euhedral and dominantly accompanied by quartz (Fig. 3), though in some cases, pyrophyllite, diasporite, and zunyite are locally important (Bendezú 2007). Samples PBR-336 and PBR-338 are cut by Au-bearing veinlets composed mainly of oxides and minor jarosite and quartz, indicating that precious metal deposition postdated the advanced argillic alteration in the two points in which the samples were collected. The dated alunite grains are less than 1 mm long (Appendix 2), corresponding to the typical grain size of alunite in the internal part of the AAA zones. In contrast to alunite from the external parts of the AAA zones, the dated alunite from internal zones is homogeneous, and no pseudocubic cores of the woodhouseite–svanvergitite end-member were observed in thin section (Fig. 3). The dated samples display minor Na substitution by K (Na/K between 0.1 and 0.6, Table 1). The presented Na/K ratios indicate that dated alunite samples are compositionally close to the alunite end-member and that natroalunite, which is often macroscopically mistaken for alunite, was not recognized in this study.

The third Oro Marcapunta alunite separate (PBR-335) was extracted from a vuggy silica rock in which alunite occurs as thin coatings on cavities left by former sanidine phenocrysts (Fig. 3). Alunite grains are, in this sample, platy, euhedral, transparent, pinkish, and relatively coarse (up to 3 mm long). They are all compositionally homogeneous and close to stoichiometric alunite (Table 1).

Sample PBR-273 from Oro Marcapunta contains plumose alunite. Individual alunite grains, which typically occur in clusters within open-space fillings, are usually longer than 1 cm across. In this sample, plumose alunite cements a breccia, which contains rounded clasts of up to more than 10 cm of vuggy silica containing Au–(Ag)-bearing oxide veinlets (Fig. 3). Selective chemical analysis show that veinlets-bearing vuggy silica clasts are mineralized (up to 2 ppm Au), indicating that plumose alunite postdated a period of gold deposition, which in turn

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

Sample	High-sulfidation epithermal Au–(Ag) ores			Cordilleran base-metal ores		
	PBR-273	PBR-335	PBR-336	PBR-298	PBR-322	PBR-208
K ₂ O	9.89	9.78	8.22	10.04	8.85	9.21
Na ₂ O	0.82	0.81	1.78	0.24	2.04	0.42
BaO	0.43	0.38	0.25	0.26	0.16	0.08
SrO	0.82	0.32	0.02	0.02	0.51	0.16
PbO	0.00	0.02	0.01	0.01	0.01	1.32
Al ₂ O ₃	35.98	35.88	37.20	36.79	35.94	36.42
SO ₃	40.21	39.90	38.86	39.01	40.84	40.80
P ₂ O ₅	0.12	0.23	0.24	0.14	0.24	0.82
H ₂ O ^a	14.02	14.24	11.86	11.96	11.84	12.62
F ⁻	0.18	0.07	0.76	0.69	2.42	0.38
Total	102.47	101.63	99.20	99.16	102.85	102.23

Alunites were analyzed 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.

^a Weight percent H₂O calculated based on observed values of sulfur, phosphorous, potassium, sodium, strontium, barium, and fluorine, and alunite stoichiometry using the formula $AR_3(SO_4)_2(F, OH)_6$, in which *A* refers to the large cations K⁺, Na⁺, Ba²⁺, Pb²⁺, and Sr²⁺, and *R* is Al³⁺

postdated fine-grained quartz–alunite alteration. Minor quartz is the only accompanying phase and occurs as euhedral grains encapsulated within the clusters of alunite. An alunite grain from sample PBR-273 yielded compositions close to the alunite end-member, with an average Na/K below 0.1 (Table 1).

Alunite samples from the Cordilleran epithermal polymetallic deposits

Two of the three dated alunite samples extracted from the Cordilleran epithermal polymetallic deposits were collected from the internal parts of the Colquijirca deposit. Sample PBR-244 belongs to the Cu–(Au–Ag) zone of the Main stage, which is dominated by enargite and includes abundant alunite and quartz, along with minor zunyite (Fig. 3). Alunite is fine-grained (<500 μm; Appendix 2) and fills open spaces left by coeval pyrite, quartz, and enargite. In places, minute inclusions of enargite float within alunite masses. No microprobe data are available for these alunite grains.

Alunite blades from sample PBR-298 were separated from a rock belonging to the innermost portion of the Zn–Pb–(Ag) zone (i.e., the sphalerite–galena-rich part). This type of assemblage, composed of alunite–quartz–sphalerite–galena–pyrite ± (kaolinite–diaspore), is solely found in portions immediately adjacent to the Cu-bearing zones. The dated alunite occurs in open spaces intimately intergrown with sphalerite, galena, pyrite, and quartz (Fig. 3). Composition of alunite PBR-298 represents the virtually pure K-rich end-member (Table 1).

The third sample (PBR-322) from the Cordilleran ores was collected in the Smelter deposit where alunite occurs together with silica (mainly quartz), enargite, zunyite ± dickite. The dated alunite is intimately intergrown with enargite (Fig. 3c), which is indicative to have precipitated together from the Main ore stage (Bendezú 2007). Alunite of sample PBR-322 contains significantly more Na (up to 2.04 Na₂O wt.%) than samples PBR-244 and PBR-298 (Table 1).

Two alunite-rich concentrates from fine-grained material composed of sulfides sphalerite and subordinate galena and pyrite, kaolinite, quartz, and alunite of the San Gregorio Cordilleran deposit were prepared (PBR-208 and PBR-284a). The grain size for all components is in the order of several tens of microns, and alunite does not exceed 30 μm (Fig. 3; Appendix 2). Petrographic observation (Fig. 3) does not show evidence of reaction between alunite and sulfides and quartz. Furthermore, alunite appears encroached into the sulfides and quartz, and the reverse relationship is also recognized in other samples. These observations suggest that alunite, sulfides (including sphalerite–galena), and quartz precipitated coevally, presumably from the same ore fluids. The interpretation is supported by fluid inclusion data from sphalerite and quartz, which share similar homogenization temperatures and salinities (Bendezú 2007). Microprobe analyses of rare, large alunite grains (up to 100 μm) yielded bulk compositions close to stoichiometry, although in some cases, the A site is occupied by significant amounts of Pb (up to 1.32 wt.%, Table 1). Concentrate PBR-209 was obtained from a 50-cm-thick vein, which cuts oxidized

sulfide rock. Estimates of the composition of the three concentrates, made using an optical binocular microscope, are (in volume percent): PBR-208, 85% alunite, 10% kaolinite–quartz, 5% pyrite; PBR-209, 80% alunite, 10% kaolinite, 5% anatase, 5% quartz; PBR-284a, 75% alunite, 15% pyrite-sphalerite, 10% quartz–kaolinite.

Analytic procedure

Infra-red (CO₂) laser ⁴⁰Ar/³⁹Ar analysis

Step-heating ⁴⁰Ar/³⁹Ar analysis of alunite grains using a laser have been reported by Mote et al. (2001) and Vasconcelos and Conroy (2003). The significantly lower amount of material (between 3 and 5 mg) required for laser degassing of alunite, relative to conventional furnace heating, allows a more specific sampling.

Alunite grains were individually handpicked from crushed and washed samples following the procedure adopted for the furnace ⁴⁰Ar/³⁹Ar analysis (Bendezú et al. 2003). Only grains of microscopically high purity (<2 vol.% of quartz and opaque contaminants) were selected, obtaining for each alunite separate between nearly 50 to several hundred grains, depending on the granulometry of the quartz–alunite as-

semblage. The grain separates were subsequently cleaned for 10 min in deionized water in an ultrasonic bath. Further details of the alunite samples, including UTM coordinates and sample amounts, are provided in Table 2. Alunite grains selected for ⁴⁰Ar/³⁹Ar analysis were irradiated with the FCT sanidine standard (28.02±0.16 Ma; Renne et al. 1998) for 8 h in the 1 MW, Cd-lined CLICIT facility at the University of Oregon. The alunites and monitors were analyzed at the ⁴⁰Ar/³⁹Ar laboratory of the University of Lund, Sweden. The laboratory consists of a Micromass 5400 mass spectrometer, equipped with a Faraday and an electron multiplier. The stainless steel extraction line includes two SAES C50-ST101 Zr–Al getters, and extracted gas was cooled to ~–150°C by a Polycold P100 cryogenic refrigeration unit mounted over a cold finger. Single grains of alunite were step-heated using a defocused 50-W CO₂ laser rastered over the samples to provide even-heating of the grains. Samples were measured on the electron multiplier, and time-zero regressions were fitted to data collected from ten scans over the *m/e* range of 40–36. Peak heights and backgrounds were corrected for mass discrimination, isotopic decay of ³⁹Ar and ³⁷Ar, and interfering nucleogenic Ca-, K-, and Cl-derived isotopes. The total decay constant for ⁴⁰K is that calculated by Stegger and Jaeger (1977) at 5.543E–10/a. The reactor irradiation correction values are: (³⁶Ar/³⁷Ar)_{Ca}, 2.69E–4; (³⁹Ar/³⁷Ar)_{Ca},

Table 2 Summary of the dating results of the Colquijirca district

Sample	Location	Dating results, error (Ma±2σ)	
		Plateau age ^a	Inverse isochron age
Dacitic domes			
PBR-148 ^b	Northern Marcapunta	12.43±0.06	12.4±0.1
PBR-215 ^b	Western Marcapunta		12.9±0.1
PBR-216 ^b	Huacchuacaja		12.7±0.1
High-sulfidation epithermal Au–(Ag) ores			
PBR-273 ^c	Southern Marcapunta	11.51±0.06	11.44±0.13
PBR-338 ^c	Central Marcapunta	11.10±0.06	11.15±0.07
PBR-335 ^c	Central Marcapunta	11.69±0.06	11.73±0.07
PBR-336 ^c	Central Marcapunta	11.90±0.07	11.79±0.07
PBR-198 ^b	Central Marcapunta	11.33±0.14	11.4±0.1
PBR-213 ^b	Southern Marcapunta	11.63±0.08	11.6±0.1
PBR-214 ^b	Central Marcapunta	11.29±0.12	11.3±0.1
Cordilleran base-metal ores			
PBR-322 ^c	Smelter	10.64±0.06	
PBR-298 ^c	Colquijirca	10.76±0.06	10.75±0.07
PBR-244 ^c	Colquijirca	10.75±0.06	10.60±0.08
PBR-108 ^b	Colquijirca	10.59±0.08	10.6±0.1
PBR-131 ^b	Smelter	10.83±0.06	10.9±0.1
PBR-137 ^b	Smelter	10.56±0.08	10.6±0.1
PBR-218 ^b	Colquijirca	10.72±0.06	10.7±0.1

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

^b This study

^c Bendezú et al. 2003

7.09E–4; and $(^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}}$, 16E–4). ^{40}Ar blanks were calculated before every new sample and after every three heating steps. ^{40}Ar blanks were between 4.0 and 2.0E–16 mol. Blank values for m/e 39 to 36 were all less than 7E–18 mol. Age plateaus were determined using the criteria of Dalrymple and Lamphere (1971), which specify the presence of at least three contiguous incremental heating steps with concordant ages that constitute >50% of the total ^{39}Ar released during the step-heating experiment. In addition, ages have also been calculated with the inverse isochron method (McDougall and Harrison 1999). Inverse isochron diagrams allow to test the assumption made in the plateau ages where any trapped non-radiogenic Ar has an atmospheric composition ($^{40}\text{Ar}/^{36}\text{Ar}=295.5$). The entire analytical process is automated and utilizes a software modified specifically for this laboratory and originally developed at the Berkeley Geochronology Center by Al Deino. $^{40}\text{Ar}/^{39}\text{Ar}$ step-heating data, including heating schedules, are presented in Appendix 1.

K/Ar analysis

As indicated above, the fine-grained nature of the material from San Gregorio prevented handpicking and $^{40}\text{Ar}/^{39}\text{Ar}$ analysis. Therefore, alunite concentrates from San Gregorio were prepared for K/Ar analysis. Concentrates were achieved by centrifuging a crushed material immersed within distilled water. Denser material rich in sulfide was removed. The remaining fraction was then ultrasonically cleaned, which additionally allowed separating part of the residual contaminants, particularly pyrite. Any additional treatment has not been carried out on the separates. As a consequence, the purity of the alunites is only approximately 75–85%. Mineralogical composition of the dated alunite separates is given in Appendix 2.

For measurement of potassium concentration in alunite, an aliquot of the final separate was grounded and reacted in a Teflon container with HNO_3 and HF at $\sim 120^\circ\text{C}$. After evaporation of the acids, the sample was diluted by HCl solution, and a Na buffer was added, and analyses have been made by flame photometry. The analytical precision was 2% at the 1-sigma confidence level.

For gas extraction, tantalum crucible was used, heated by high frequency. Before degassing, ^{38}Ar spike was added for isotope dilution analysis. Purification was carried out in a low-blank metallic line using titanium and SAES 707 getters and cold trap.

Argon isotopic analyses were performed on-line in a 15-cm radius sector type mass spectrometer equipped with a single collector system. In all cases, mass discrimination factors for Ar isotopes were determined using sample of atmospheric Ar. Details of the instruments, the applied methods, and results of calibration have been described elsewhere (Balogh 1985).

Atomic constants suggested by Steiger and Jäger (1977) were used for calculating the ages. All analytical errors represent one standard deviation (i.e., 68% analytical confidence level). Since we base our analytical errors on the long-term stability of instruments and on the deviation of our results obtained on standard samples from the interlaboratory mean, the analytical errors are likely to be overestimated.

Results

$^{40}\text{Ar}/^{39}\text{Ar}$ data and age spectra are shown in Table 2 and Fig. 4, respectively. Discussion is based on plateau ages. In six of the seven dated samples, plateau ages are indistinguishable from the inverse isochron ages (at $\pm 2\sigma$ analytical uncertainties, Table 2). The $^{40}\text{Ar}/^{39}\text{Ar}$ intercepts on the inverse isochrones suggest that the initial argon reservoirs in the alunite grains were atmospheric. Analytical data of conventional K/Ar dating are presented in Table 3, and errors are reported at the $\pm 2\sigma$ level.

Alunite $^{40}\text{Ar}/^{39}\text{Ar}$ data from the Oro Marcapunta high-sulfidation epithermal Au–(Ag) mineralization

All four dated alunite samples related to the high-sulfidation epithermal Au–(Ag) mineralization yield age plateaus at 11.90 ± 0.07 (PBR-336), 11.69 ± 0.06 (PBR-335), 11.51 ± 0.06 (PBR-273), and 11.1 ± 0.06 Ma (PBR-338; Table 2, Fig. 4, Appendix 1). These ages extend previous estimates (11.29 ± 0.12 – 11.63 ± 0.08 Ma; Bendežú et al. 2003) of the duration of acid-sulfate hydrothermal activity at Oro Marcapunta by 0.5 My.

Alunite $^{40}\text{Ar}/^{39}\text{Ar}$ data from the Smelter and Colquijirca Cordilleran deposits

Three alunite samples from the Cordilleran deposits yield plateaus ages ranging between 10.64 ± 0.06 and 10.76 ± 0.06 Ma (PBR-244 from Colquijirca at 10.75 ± 0.06 Ma; PBR-298 from Colquijirca at 10.76 ± 0.06 Ma; and PBR-322 from Smelter at 10.64 ± 0.09 Ma; Fig. 4, Table 2). These new data are consistent with mineralization ages presented by Bendežú et al. (2003) for other samples from Smelter and Colquijirca (10.56 ± 0.08 Ma, sample PBR-137 to 10.83 ± 0.06 Ma, sample PBR-131).

Alunite K/Ar data from the San Gregorio Cordilleran deposit

Alunite concentrates PBR-208 and PBR-284a of the San Gregorio Cordilleran deposit yield similar K/Ar ages of $\sim 13.1 \pm 2.2$ (PBR-208) and 13.2 ± 2.2 Ma (PBR-284a; Table 3; Fig. 5). The third alunite concentrate (PBR-209), extracted

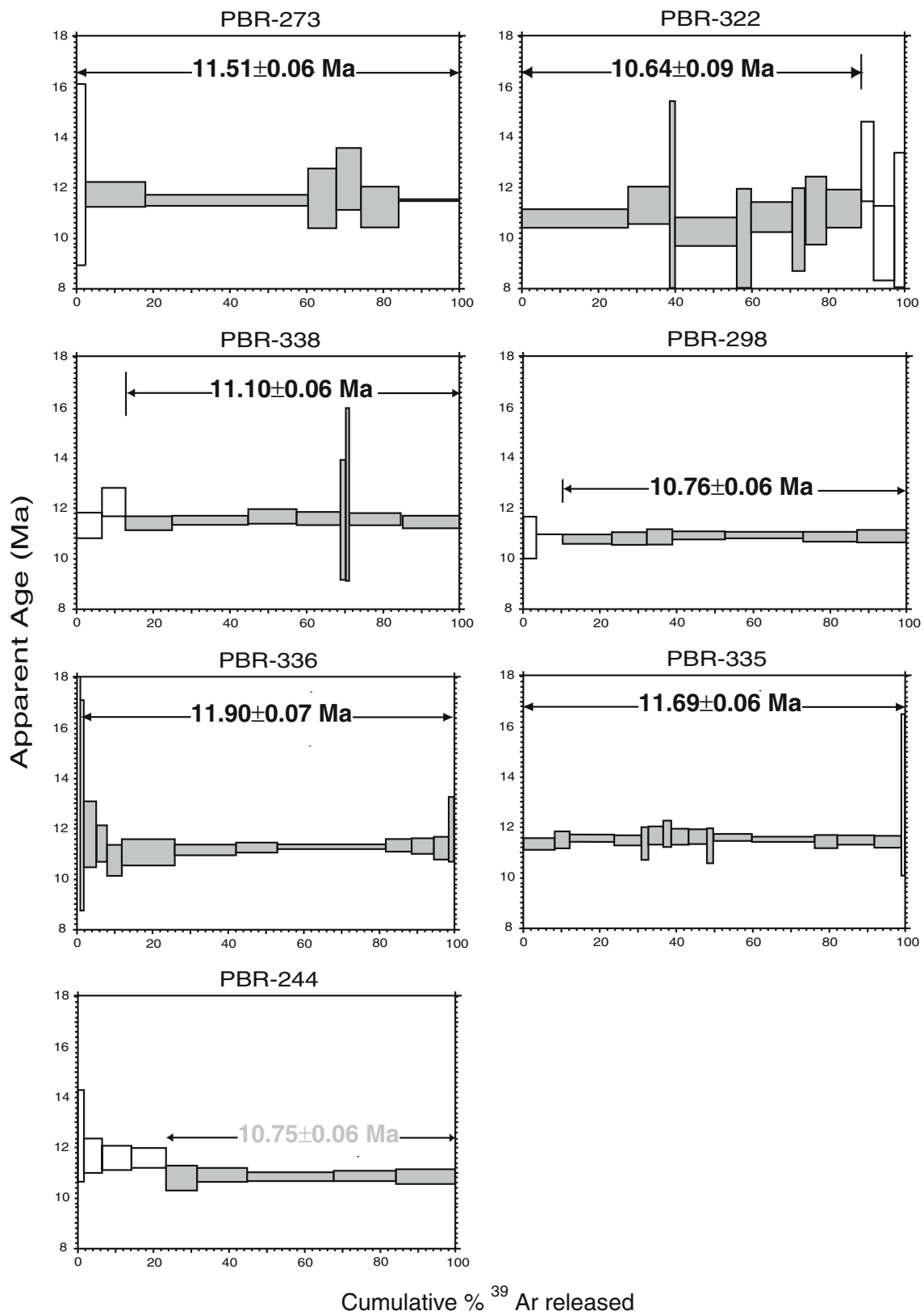


Fig. 4 $^{40}\text{Ar}/^{39}\text{Ar}$ apparent age spectra from analyses through laser degassing. Step segments from which plateau ages were calculated are shown in filled boxes

Table 3 K/Ar data obtained on alunite separates

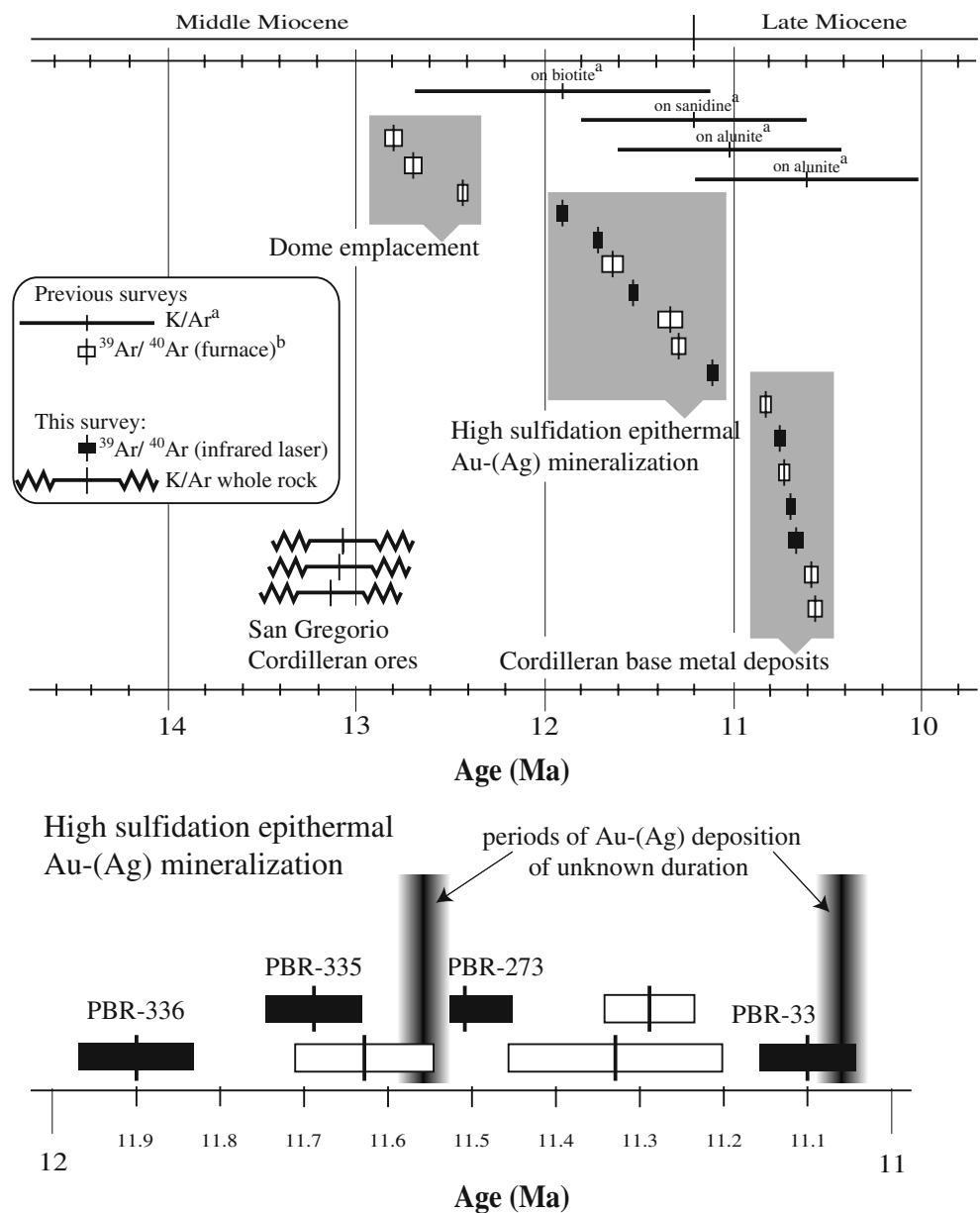
No. of K/Ar	Sample	K (%)	⁴⁰ Ar rad (%)	⁴⁰ Ar rad (ccSTP/g)	K/Ar age (Ma)
6,092	PBR-208.	7.76	18.1	3.975×10^{-6}	13.1±1.1
6,095	PBR-284a	5.24	18.4	2.696×10^{-6}	13.2±1.1
6,093	PBR-209.	6.27	9.5	3.453×10^{-6}	14.1±2.1
			10	3.404×10^{-6}	13.9±2.0

from a crosscutting vein, yielded in a first batch an age of 13.9±4.0 Ma ($\pm 2\sigma$). In order to confirm this apparent older age, a duplicate analysis was made (14.1±4.2, no 6094). On the basis of the mineralogical composition (Table 3), we can exclude the presence of significant excess/inherited argon caused by some detrital mica in this alunite concentrate.

Discussion

According to the new infra-red (CO₂) laser analysis of alunite combined with the previously published data, a long (at least ~1.3 My) and complex period of magmatic-hydrothermal activity associated with Au-(Ag) and Cordilleran ores took

Fig. 5 Summary diagram of available geochronological data (K/Ar and ⁴⁰Ar/³⁹Ar) from the Colquijirca district, at 2σ level of confidence: (a) from Vidal et al. (1984); (b) Bendezú et al. (2003)



place at Colquijirca. The new data indicate that incursion of magmatic SO₂-bearing vapor into the Colquijirca epithermal system began at least as early as ~11.9 Ma, i.e., ~0.3 My earlier than the previously oldest recorded age at ~11.6 Ma and lasted until ~10.6 Ma.

The four alunite samples associated with the high-sulfidation epithermal Au–(Ag) ores gave ⁴⁰Ar/³⁹Ar plateau ages between ~11.9 and ~11.1 Ma (compared to the previously documented ~11.6 to ~11.3 Ma). Within this period of alunite precipitation, two discrete pulses of Au–(Ag) deposition can be distinguished by combining individual ⁴⁰Ar/³⁹Ar ages with crosscutting relationships. Since PBR-273 plumose alunite cements clasts of vuggy silica which, in turn, are cut by alunite-free Au–(Ag)-bearing oxide veinlets, an early Au–(Ag) deposition pulse must have predated the plumose alunite precipitation at 11.51±0.06 Ma. A younger period of Au–(Ag) deposition postdated the 11.1±0.06 Ma age of PBR-338 alunite sample as the rock containing this alunite is cut by Au–(Ag)-bearing oxide veinlets. As far as known to the authors, this is the first time that several Au–(Ag) deposition pulses have been discriminated in a high-sulfidation epithermal Au–(Ag) system. These two pulses suggest a minimum duration of the Au–(Ag) deposition of at least around 0.4 My.

The recurrent acid sulfate–Au–(Ag) deposition events distinguished in the Oro Marcapunta high-sulfidation epithermal environment may represent shallow manifestations of repeated alteration–mineralization events as recognized deeper in the porphyry environment elsewhere (e.g., Muntean and Einaudi 2001; Seedorff et al. 2005).

Generation of magmatic–hydrothermal acidic fluids continued in the Colquijirca system between 10.83±0.06 and 10.56±0.06 Ma as recorded by the three ⁴⁰Ar/³⁹Ar plateau ages obtained on alunite related to the Cordilleran polymetallic ores. Because of the consistency of the ages yielded by the seven analyzed alunite samples, which postdate and are coeval with Cordilleran ores, it can be suggested that probably most of the polymetallic deposition occurred during the 10.83-to-10.56-Ma period.

The recognition of consecutive alunite-bearing and alunite-free mineral assemblages within both in the Au–(Ag) and in the Cordilleran ores may suggest that SO₂-bearing magmatic vapor entered the epithermal environment as multiple discontinuous pulses, a number of which was not necessarily associated in time with ore fluids. It is likely that a period of SO₂-bearing vapor degassing longer than 11.9 to 10.6 Ma would be recognized if a more detailed work was carried out.

Despite the large errors, the concordance of two of the three K–Ar ages at 13.1±2.0 Ma obtained for the large San Gregorio deposit in the southern part of the district opens the possibility that the San Gregorio ore formation predates the other known high-sulfidation systems in the Colquijirca

district, including those of the Au–(Ag) epithermal system at Oro Marcapunta and the Cordilleran deposits of Smelter and Colquijirca. According to this possibility, mineralization at San Gregorio may have been contemporaneous with one or more of the episodes of dacitic doming such as that dated at 12.9±0.1 Ma in the western flank of the Marcapunta complex (biotite ⁴⁰Ar/³⁹Ar, sample PBR-215, BendeZú et al. 2003).

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