



Sulfur isotopes, trace element, and textural analyses of pyrite, arsenopyrite and base metal sulfides associated with gold mineralization in the Pataz-Parcoy district, Peru: implication for paragenesis, fluid source, and gold deposition mechanisms

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Abstract

In the Pataz-Parcoy district, current mining activity is focused on the mesothermal quartz-carbonate-sulfide veins hosted by the Pataz batholith. Total gold production yielded approximately 8 Moz with grades in the mined ore shoots varying between 7 and 15 g/t Au, and locally reaching up to 120 g/t Au. High-grade ore shoots are extraordinarily enriched in sulfides, representing 10 to 20 modal vol% of the vein. Ore mineralogy is characterized by a complex paragenesis of pyrite, arsenopyrite, galena, sphalerite, chalcopyrite, and gold. Gold occurs mostly as electrum in equilibrium with base metals sulfides filling fractures of pyrite and arsenopyrite. A novel combination of secondary ion mass spectrometry, laser ablation inductively coupled plasma mass spectrometry, and electron probe microanalysis is used to track the compositional evolution of ore fluid(s) and to investigate the mineralization processes occurring in the Pataz-Parcoy district. Contrasting with the classical two-stage ore sequence previously proposed for the Pataz-Parcoy district, we suggest a revised paragenetic sequence, i.e., (1) deposition of pyrite core (PyI) with homogeneously distributed base metal sulfide inclusions, (2) progressive replacement of PyI by arsenian pyrite (PyII) and arsenopyrite associated with invisible gold deposition, and (3) deposition of sphalerite – galena ± chalcopyrite – electrum in fractured pyrite and arsenopyrite. We propose two models for the formation of base metal sulfide inclusions in PyI, i.e., (1) coprecipitation of base metal sulfide with PyI and later redistribution in cracks driven by partial As replacement of PyI to PyII and arsenopyrite and (2) preferential replacement of the PyI along crystallographic planes by percolation of the fluid responsible for base metal sulfide deposition in fractured pyrite and arsenopyrite.

Keywords Paragenetic sequence · Trace element · Arsenopyrite · Arsenian pyrite · Invisible gold · Sulfur isotopes

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Introduction

Batholith-hosted gold mineralization in the Pataz-Parcoy district exhibits spectacular sulfide-rich veins up to several meters wide and hundreds of meters long. Structural and geochemical features of the deposits are fairly uniform throughout the Pataz-Parcoy district with local mineralogical variations such as base metal sulfide (BMS; Schreiber et al. 1990; Haeberlin et al. 2004). However, the paragenetic sequence remains controversial. Previous workers have described a classical two-stage ore sequence composed of (1) early pyrite and arsenopyrite associated with coarse-grained euhedral quartz and (2) galena, sphalerite ± chalcopyrite, and native gold or electrum precipitated in pyrite fractures together with microgranular quartz (Schreiber et al. 1990; Haeberlin et al. 2004). More recently, Witt et al. (2016) proposed that gold

was introduced during deposition of an early, massive, fine-grained pyrite-arsenopyrite together with < 10 vol% clear, glassy quartz followed by the introduction of milky, white quartz-carbonate, and coarse-grained pyrite-arsenopyrite with up to 10 vol% galena and sphalerite. The discovery of a new, base metal-rich, gold-bearing vein system in the Santa Maria area, about 10 km south of the main mining center of Paraiso, illustrates the importance of understanding the relative timing of gold and base metal emplacement.

Interpretation of sulfide mineral textures and inclusion distribution is critical for assessing trace element and sulfur isotope data (Large et al. 2007; Cook et al. 2009; Large et al. 2009; Cook et al. 2013), especially to avoid over- or under-estimation of elemental concentrations. Inferences based on equilibrium partitioning of trace elements in sulfides (e.g., element in the parent fluid, the redox, pH, temperature, and f_{O_2} of fluid) can only be applied to elements (e.g., As, Au, and Cu) that are known to substitute into the crystal lattice of a sulfide mineral (Chouinard et al. 2005; Tanner et al. 2016). Trace element concentrations in pyrite associated with gold mineralization have been commonly used to evaluate the fluid evolution (e.g., element concentration in the parent fluid, the redox, pH, temperature, and f_{O_2} of fluid) in parallel with the paragenetic sequence of mineral deposition (Deditius et al. 2009; Reich et al. 2013).

Sulfur isotope fractionation in pyrite is well established and has been used to discuss the fluid source(s), interaction with wall rocks as well as with previously deposited minerals, and fluid mixing processes (Ohmoto and Rye 1979). Recent in situ coupled trace element and sulfur isotope analyses on sulfides in epigenetic, hydrothermal gold deposits (such as West Banshee and northern Carlin Trend Turquoise Ridge in northern Nevada) (Barker et al. 2009), Porgera in Papua New Guinea (Peterson and Mavrogenes 2014), and El Callao mining district in Venezuela (Velásquez et al. 2014) show clear covariation between $\delta^{34}S$ and trace elements values through the paragenetic sequence, possibly triggered by changes in oxidation state, pressure, temperature, and/or pH.

Arsenic-rich sulfides, such as arsenian pyrite and arsenopyrite, can carry gold in their crystal structure (Mumin et al. 1994; Fleet and Mumin 1997; Palenik et al. 2004; Reich et al. 2005; Barker et al. 2009; Deditius et al. 2014; Fougereuse et al. 2016). Many different mineral systems are known to contain invisible gold in arsenopyrite and arsenian pyrite including Carlin-type Au, porphyry Cu, Cu–Au, epithermal Au, orogenic Au, volcanogenic massive sulfides (VMS), and iron oxide Cu–Au (IOCG) (Deditius et al. 2014). A maximum Au content of 0.64 wt% was obtained from synthetic arsenian pyrite, whereas gold values up to 3.0 wt% Au have been reported in synthetic arsenopyrite from the Carlin-type deposits in Nevada (Fleet and Mumin 1997). It has been established that gold can be present as structurally bound cations (Au^{1+} or Au^{3+}) or as nanoparticles of native metal (Au^0)

(Simon et al. 1999). In arsenian pyrite, invisible gold has been described to be spatially associated with local As enrichment, which highlights a possible substitution of anionic or cationic As (As^{1-} or As^{3+}) into the pyrite structure, which in turn enhances the incorporation of Au (Reich et al. 2005; Deditius et al. 2008).

In this study, trace element and sulfur isotope geochemistry of individual growth bands of pyrite, arsenopyrite, and BMS are used to track the evolution of the ore fluid(s) composition and the processes responsible for gold deposition. We also highlight the presence and proportion of invisible gold which occurs together with pyrite and arsenopyrite. Finally, we re-examine the paragenetic sequence in the Pataz-Parcoy district using in situ micro-analytical methods, including scanning electron microscope (SEM), electron probe microanalysis (EPMA), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and secondary ion mass spectrometry (SIMS and NanoSIMS), and present a new, alternative model for sulfide and gold deposition, which contrasts with the two-stage ore sequence previously established in the Pataz-Parcoy district.

Geological settings of the Pataz-Parcoy district

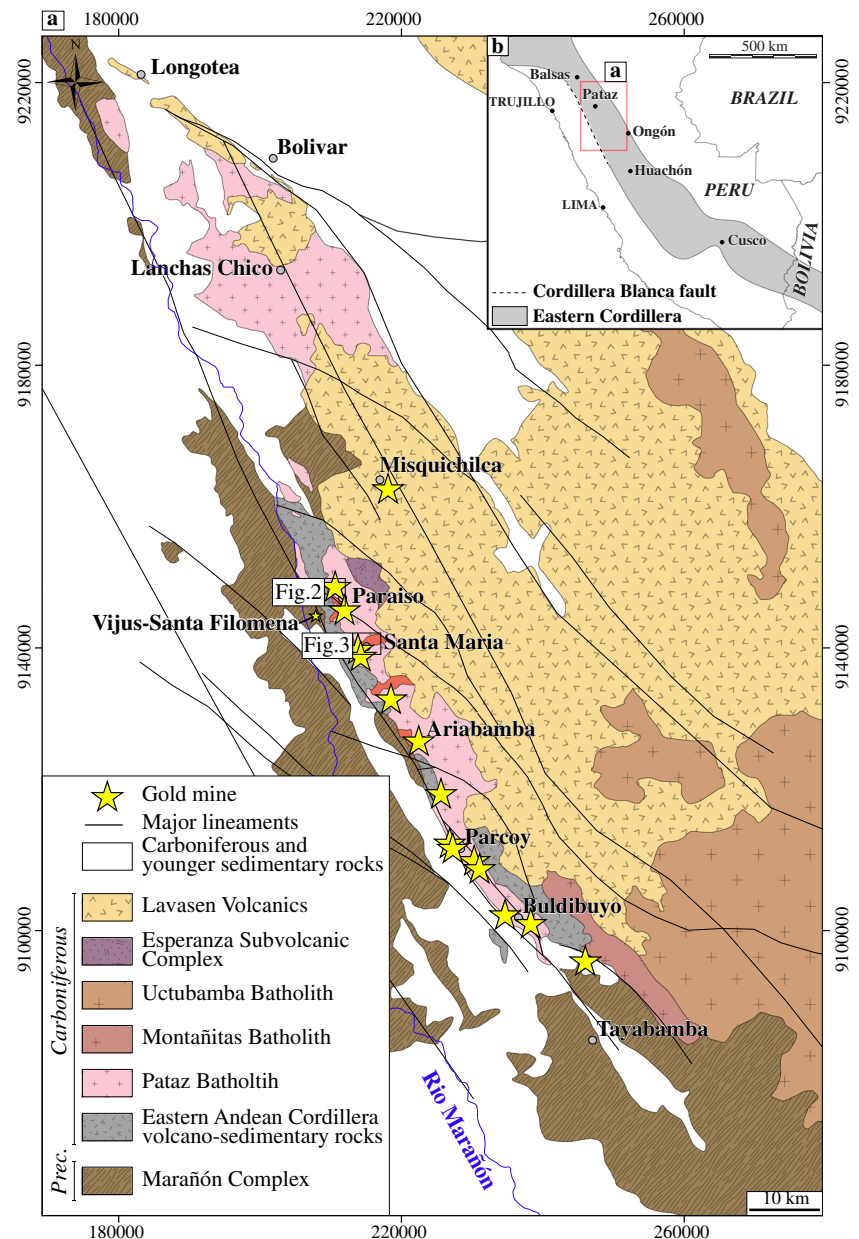
Regional structure framework

The Pataz-Parcoy district is located along the major 400-km long regional Cordillera Blanca fault (Fig. 1; Petford and Atherton 1992; Witt et al. 2013b) which separates the western from the eastern Andean Cordillera of northern Peru (Mégard 1984; Schreiber et al. 1990). Contrasting with the north-northwest striking regional Cordillera Blanca fault, the north-striking orientation of the Pataz-Parcoy district is interpreted as a transtensional jog (Witt et al. 2013b). The Pataz-Parcoy district essentially consists of a rift and graben terrane superimposed on a continental margin sequence. The structural framework is dominated by northwest- to north-northwest-steep reverse faults forming boundaries of graben and horsts and northeast- to east-northeast-striking lineaments of uncertain timing.

Lithostratigraphy

The oldest rocks of the Pataz-Parcoy district are found in the Neoproterozoic to Cambrian basement, referred to as the Marañón Complex (Fig. 1). The Marañón Complex comprises deformed paraschists and paragneisses metamorphosed from greenschist to lower amphibolite facies during the Terreneuvian to Cambrian Epoch 2 (Haeblerlin et al. 2004; Cawood 2005). During the Cambrian and Ordovician, the volcano-sedimentary succession forming

Fig. 1 Geology of the Pataz-Parcoy district. **a** Geological map of the Pataz-Parcoy district with location of main gold mines. **b** Location and regional geological map of Peru. Modified after Schreiber et al. (1990), Haeberlin et al. (2004), Witt et al. (2013b), and Sánchez Fernández (1995)



the eastern Andean Cordillera was deposited unconformably on the Marañón Complex (Fig. 1) (Schreiber et al. 1990; Haeberlin et al. 2004). The volcano-sedimentary sequence is composed (from bottom to top) of (1) poorly bedded, felsic volcanic sandstone of the Vijus Formation; (2) metamorphosed, siliciclastic sandstone, siltstone, and shale, with a minor component of felsic volcanoclastic sandstone of the Contaya Formation; and (3) felsic volcanic sandstone of the Atahualpa Formation (Witt et al. 2013b). Both the Marañón Complex and overlying volcano-sedimentary rocks were deformed and metamorphosed during the Early Ordovician Famatinian orogeny, at ca 480 Ma (Bahlburg and Hervé 1997; Chew et al. 2007).

In the Pataz-Parcoy district, Mississippian magmatism began with the emplacement of the calc-alkaline (I-type) Pataz batholith (Fig. 1). Early stage Pataz batholith consisted of a small volume of diorite attributed to tholeiitic magmas formed by melting of undepleted, metasomatized asthenosphere and assimilation of variable amounts of continental crust (Witt et al. 2013a). Some of the diorite magmas reached the surface and erupted as mafic to intermediate volcanoclastic rocks associated with minor microdiorite to diorite porphyry intrusions (Vista Florida Group; Witt et al. 2013a). Towards the end of diorite magmatism, a large volume of granodiorite and granite intruded as a sill complex within the moderately NE-dipping sequence of the eastern Andean Cordillera.

Granodiorite magmas were generated by partial melting of calc-alkaline diorite and andesitic lower crust (Witt et al. 2013a). Coeval with rifting and uplift of the Pataz batholith, K-rich (A-type) magmas formed by melting of a mid-crustal tonalitic source yielded the upper crustal emplacement of the Esperanza Subvolcanic Complex (ESC) and the Lavasen Volcanics (Fig. 1; Witt et al. 2013a). The Lavasen Volcanics consist mainly of a ~2000-m-thick succession of latite to rhyolitic pyroclastic and volcano-sedimentary rocks. The ESC is a shallow level bimodal subvolcanic complex dominated by latitic rocks, intruded by gabbro dikes. Directly southeast of the Pataz-Parcoy district, the Mississippian Montañas igneous system consists of two felsic igneous suites, i.e., (1) an older southern granodiorite – granite – dacite – quartz-phyric dacite suite and (2) a slightly younger northwestern monzogranite – (rhyo-) dacite/rhyolite – quartz-phyric (rhyo-) dacite suite (Angerer et al. 2018).

Geochronology

The SHRIMP U–Pb age of 338 ± 3 Ma on zircon from an albitite dike that intruded the Pataz batholith is interpreted as the minimum age for the Pataz batholith crystallization (Witt et al. 2013b). Schaltegger et al. (2006) dated the emplacement of the Pataz batholith at 336.4 ± 0.6 Ma (U–Pb ID-TIMS on zircons). With a closure temperature around 300 °C, $^{40}\text{Ar}/^{39}\text{Ar}$ dates of igneous biotite (329.2 ± 1.4 Ma and 328.1 ± 1.2 Ma, Haeberlin et al. 2004) reflect most likely the cooling of the batholith.

The age of auriferous, batholith-hosted, mineralized veins near Pataz is constrained by (1) maximum age of intrusion (336.4 ± 0.6 Ma) for the granodiorite host rock (Schaltegger et al. 2006) and (2) minimum age of 312.1 ± 0.8 Ma by $^{40}\text{Ar}/^{39}\text{Ar}$ of hydrothermal white micas (Haeberlin et al. 2004). Further south, near Parcoy (Fig. 1), Re–Os geochronology of molybdenite from an early quartz-arsenopyrite-molybdenite vein returned an age of 331.9 ± 1.7 Ma (Szappaposne-Vago et al. 2010). In the absence of a clear equilibrium assemblage and/or crosscutting relationship, this result likely represents dating of molybdenite deposition but may not reflect the timing of gold mineralization.

Hydrothermal alteration and gold mineralization types

The Pataz-Parcoy district hosts three main sites of hydrothermal activity, i.e., (1) batholith-hosted, mesothermal gold-bearing veins and related alteration halos, (2) basement-hosted veins and related alteration emplaced at shallow to intermediate depth in the Vijus-Santa Filomena area, and (3) hydrothermal alteration associated with near-surface gold mineralization hosted by the Esperanza Subvolcanic Complex and Lavasen Volcanics (Witt et al. 2016).

Current mining activity in the Pataz-Parcoy district (Fig. 1) is focused on the mesothermal quartz-carbonate-sulfide-gold veins hosted in the Pataz batholith with a total production of 8 Moz Au (Witt et al. 2016). Resources are estimated at >40 Moz Au for the 160-km-long Pataz-Marañón Valley Au belt (Haeberlin et al. 2004). Grades in the mined ore shoots vary between 7 and 15 g/t Au and locally reach about 120 g/t Au. Ore mineralogy is characterized by Fe- and base metal-rich sulfide assemblages. Despite a diversity of mineralization styles at the vein scale, ore mineralogy of the batholith-hosted mineralization is consistent throughout the 50-km-long Pataz-Parcoy gold belt, from Paraiso to Buldibuyo (Fig. 1).

Quartz-carbonate-sulfide veins are also hosted in basement rocks and volcano-sedimentary units of the eastern Andean Cordillera in the Vijus-Santa Filomena area (Fig. 1). Comb quartz, cryptocrystalline silica textures, with siderite, and barite argue for a shallower level of formation for basement-hosted veins relative to the mesothermal veins hosted by the batholith (Witt et al. 2016). Hydrothermal alteration in the Lavasen graben formed in a near-surface environment (Witt et al. 2016), an interpretation supported by the association of gold mineralization with volcanic features, including the Lavasen Volcanic-hosted Misquichilca phreatomagmatic breccia dike (Witt et al. 2016). The present juxtaposition of the near-surface epithermal mineralization against the mesothermal Pataz batholith mineralization is the result of syn- to post-mineralization differential uplift and formation of the Lavasen graben (Witt et al. 2016). Due to limited access to mineralized samples from basement-hosted and epithermal mineralization and because of their limited economical interest, this study is focused on veins hosted by the Pataz batholith.

Gold mineralization in the Pataz batholith

Lithostratigraphy with emphasis on the Pataz batholith

Gold mineralization in the Pataz-Parcoy district is mainly hosted in granodiorite, the volumetrically dominant component of the Pataz batholith and the focus of the mining activity around the Paraiso area (Fig. 2). The granodiorite exhibits a relatively uniform, massive texture and is medium- to coarse-grained with a mineralogy dominated by quartz, feldspar, biotite, and minor hornblende (Witt et al. 2013a). Gold-bearing vein systems are also hosted by diorite especially in the Santa Maria area (Fig. 3), with veins extending into a hornfels contact aureole affecting adjacent metasedimentary rocks. The diorite is medium- to coarse-grained with hornblende dominant over biotite (Witt et al. 2013a). Locally, gold-bearing veins are also observed in monzogranite, tonalite, and aplitic to andesitic dykes that have intruded the granodiorite.

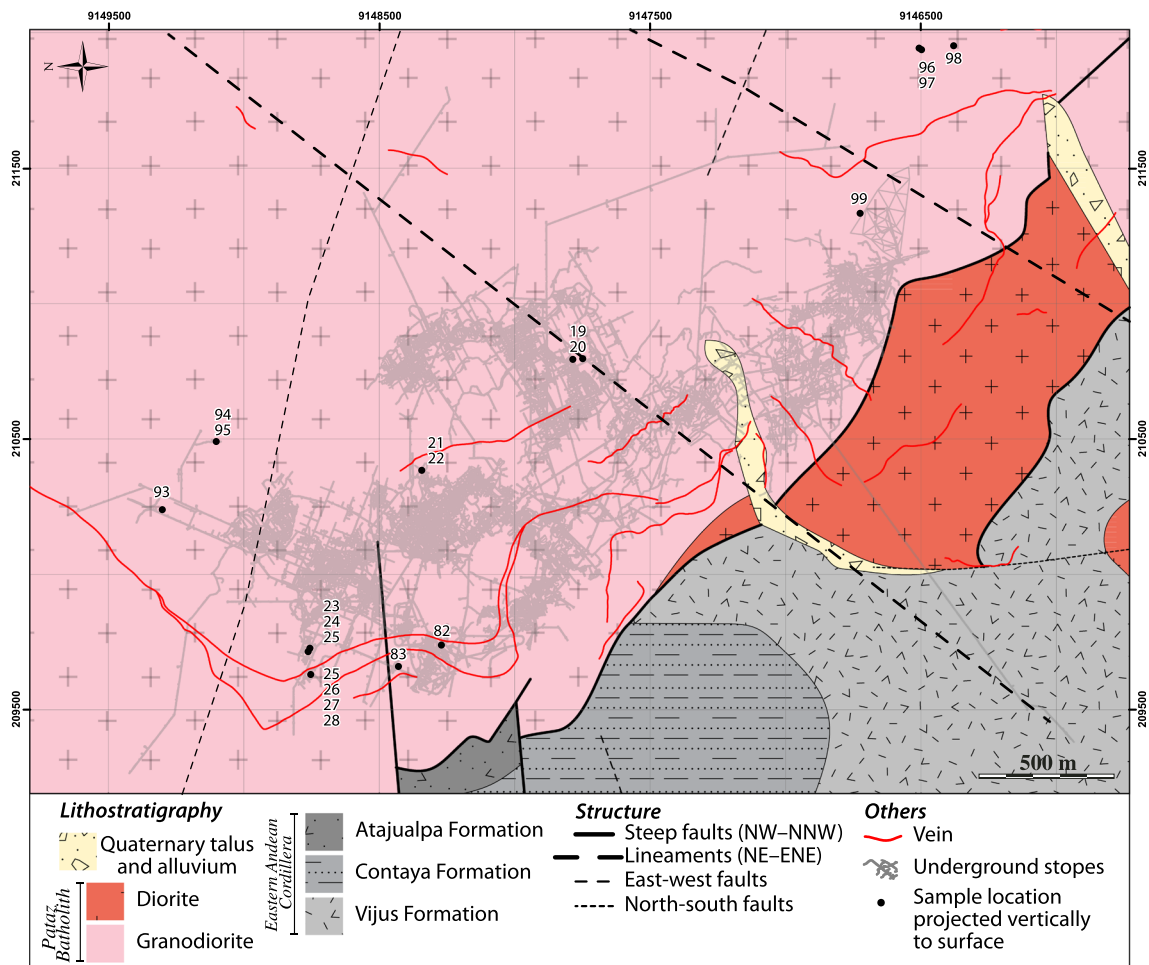


Fig. 2 Detailed geology of the Paraiso mine camp and associated batholith-hosted quartz-carbonate-sulfide veins. Note that the map is rotated anti-clockwise by 90°

Structural setting

Two principal structural settings have been distinguished in the Paraiso and Santa Maria areas (Figs. 2 and 3), i.e., (1) “flat” or subhorizontal, east-west-striking extensional veins dipping < 30° to the NE and (2) “steep” or north- to northwest-striking veins dipping 30° to 60° to the east and east-north-east (Schreiber et al. 1990; Witt et al. 2013a). Both flat and steep veins share similar morphology and textures, which suggests that they are genetically related. No consistent relationship between gold grade and vein orientation has been established in the Pataz-Parcoy district (Schreiber et al. 1990; Haeberlin et al. 2004; Witt et al. 2013a). The extensive gold-bearing vein system in the Santa Maria area (Fig. 3) is dominated by the same “flat” and “steep” veins.

Hydrothermal alteration

Hydrothermal alteration is characterized by bleaching of the granodiorite wall rock, forming a centimeter to meter wide

halo surrounding the veins. The hydrothermal alteration assemblage consists of white micas ± chlorite ± carbonate ± biotite and disseminated pyrite (± arsenopyrite). This hydrothermal alteration assemblage is typical for “mid-greenschist” facies settings with estimated temperatures of up to 400 °C and pressures up to 3 kbars (Mueller and Groves 1991; Hagemann and Cassidy 2000). Wall rock and wall rock clasts, in brecciated parts of the vein, are intensively altered but remain undeformed (Witt et al. 2016).

Vein morphology

Batholith-hosted, quartz-carbonate-sulfide veins of the Pataz-Parcoy district display a large range of morphologies and textures (Fig. 4a–e). Hydrothermal alteration of the wall rocks is dominated by white mica and disseminated euhedral pyrite and arsenopyrite (Fig. 4e), whereas internal portion of the vein is composed of massive sulfide (Fig. 4d) with local laminated to brecciated edges. The significant textural heterogeneities suggest repetitive hydrothermal fluid pulses ascending the

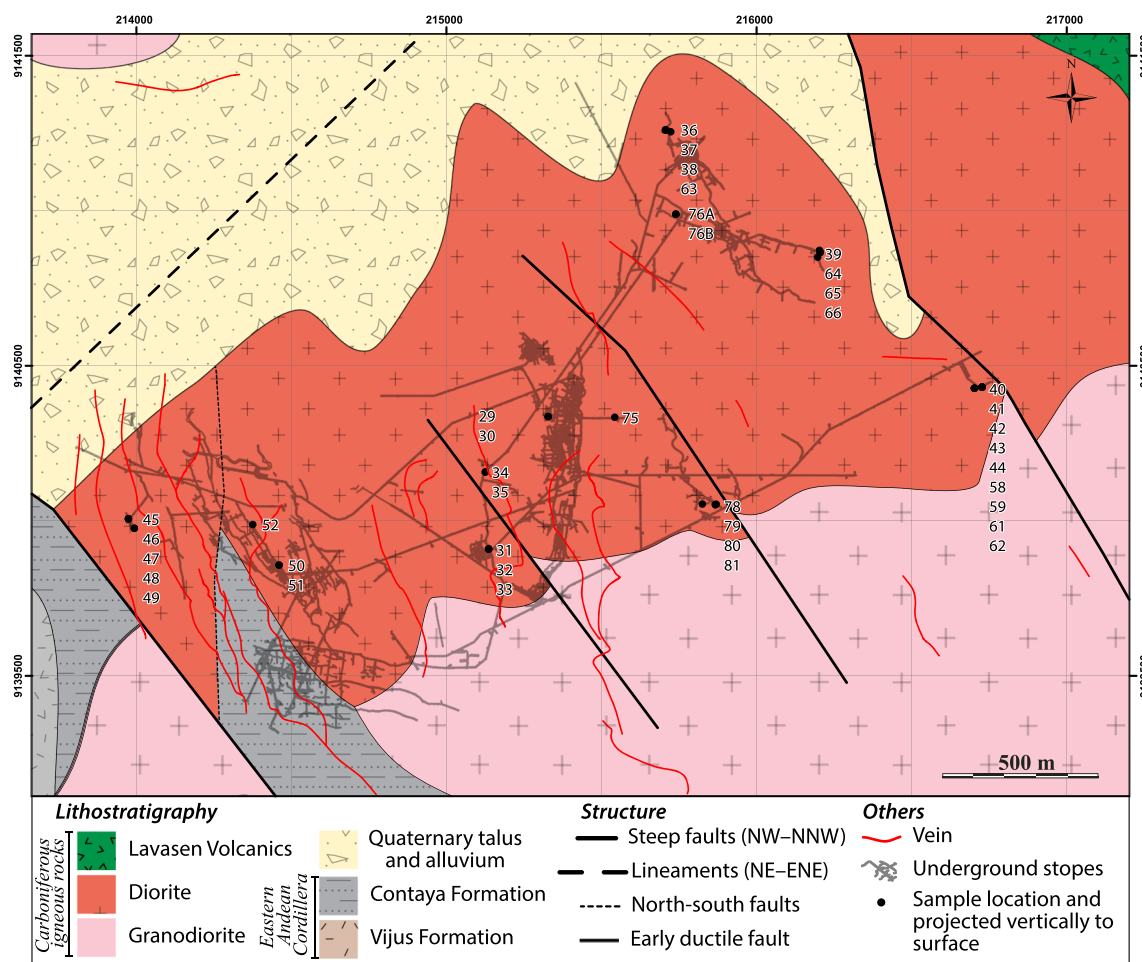


Fig. 3 Detailed geology of the Santa Maria mine and associated batholith-hosted quartz-carbonate-sulfide veins

fault system. Fault gouge at the margins of the veins (Fig. 4a) postdate mineralization and is interpreted by Witt et al. (2013b) as evidence for episodes of fault reactivation and development. Locally, displacement generated by vein reactivation across internal fractures produced structural thickening of the veins (Witt et al. 2013b).

Paragenetic sequence

Schreiber et al. (1990) and Haerberlin et al. (2004) described a simple and uniform paragenetic sequence composed of two main sulfide stages, i.e., (1) early pyrite and arsenopyrite associated with coarse-grained euhedral quartz and (2) galena, sphalerite $\pm$ chalcopyrite, and native gold or electrum precipitated in pyrite fractures together with microgranular quartz. More recently, Witt et al. (2016) proposed a new paragenetic sequence, i.e., (1) massive, fine-grained pyrite-arsenopyrite with gold and < 10 vol% clear, glassy quartz, followed by (2) milky, white quartz-carbonate and coarse-grained pyrite-arsenopyrite with up to 10 vol% galena and sphalerite, (3) fractured, coarse-grained sulfides with fractures locally filled

by fine-grained carbonate and sericite, and finally (4) a subordinate post-sulfide fracture filling stage where fractures filled by calcite, siderite, quartz, and chlorite.

Analytical methods and sampling

Sampling

A total of 41 mineralized samples were collected from batholith-hosted mineralization in the Pataz-Parcoy district. Owing to underground access authorization, representative sampling of mineralization was conducted with emphasis on the Santa Maria and Paraiso areas (Figs. 2 and 3). Sampling criteria included elevation, host rock, vein orientation, mineralization texture, mineral assemblage, and sulfide content. A selection of 29 samples was mounted in epoxy discs and polished down to 3 μ m for LA-ICP-MS analyses. Two representative samples of the ore body from Santa Maria (FVSM041 and FVSM044) were selected for in situ sulfur isotopes study. Sample preparation is detailed in LaFlamme

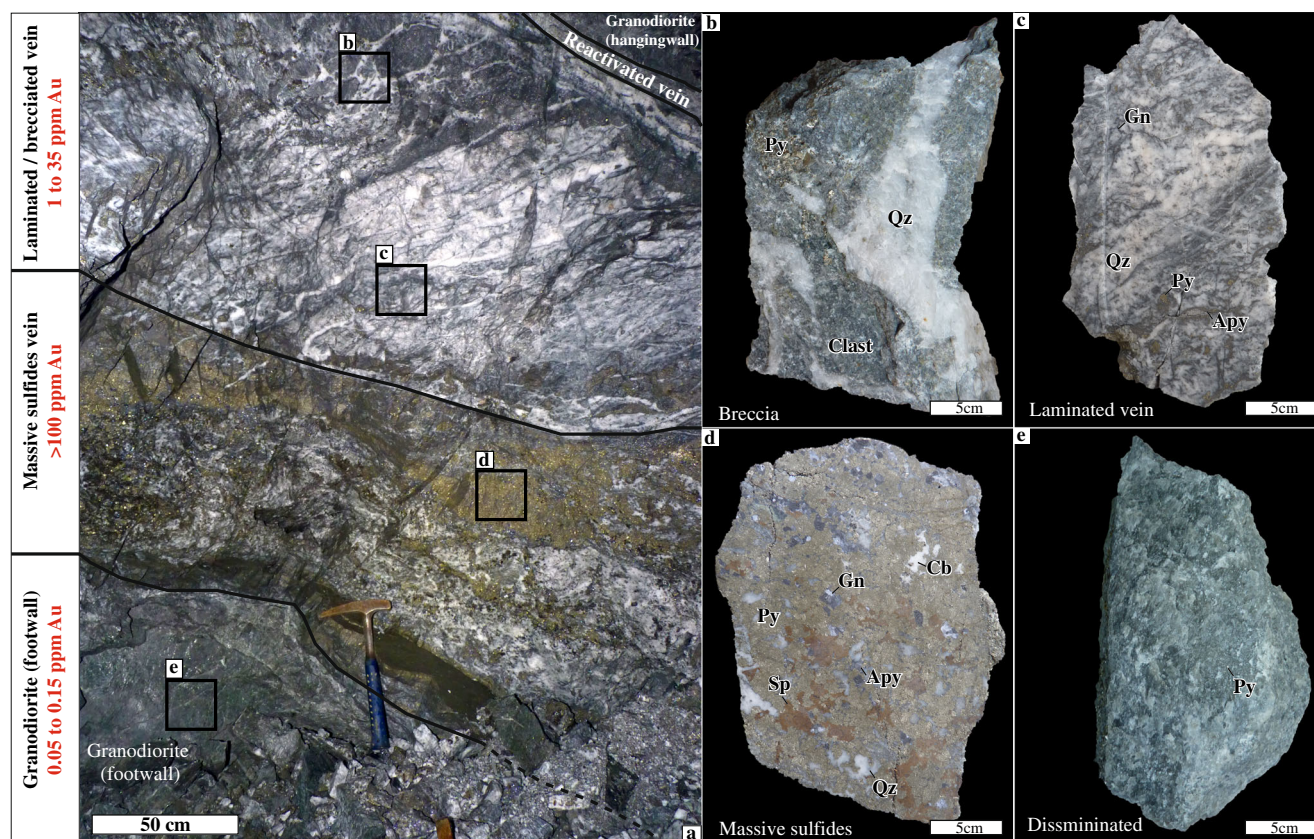


Fig. 4 Mineralization styles in the Patáz-Parcoy district. **a** Photograph from underground stope of sulfide-rich Julie vein (Santa Maria, level 2410) hosted in diorite. White quartz postdates massive sulfides and fills open-spaces leading to the disaggregation of massive sulfides band and formation of laminated and breccia-like textures. Late structural reactivation of the vein led to formation of fault gouge on hanging wall margin, internal oblique fractures with minor displacement of lamellae, and sub-parallel fracture on the footwall vein margin. **b** Photograph of brecciated hand specimen with undeformed altered diorite clasts

containing euhedral pyrite. **c** Polished slab of laminated vein style hand specimen with fine grain pyrite and arsenopyrite lamination and host rock clasts. **d** Massive sulfides specimen dominated by pyrite, sphalerite, galena, and minor chalcopyrite with late white quartz and carbonate infill. **e** Disseminated fine-grained euhedral pyrite in muscovite + chlorite + carbonate + quartz + pyrite altered diorite host rock. Py pyrite, Gn galena, Apy arsenopyrite, Sp sphalerite, El electrum, Qz quartz, Cb carbonate

et al. (2016). Sample FVSM044 consists of a ~2-cm laminated pyrite-arsenopyrite and gold vein located at the edge of a massive sulfide vein (Appendix 1). Sample FVSM041 was collected from a vein that contains massive pyrite and minor chalcopyrite (Appendix 2).

Scanning electron microscope

High-resolution electron backscattered (BSE) images were collected on a field-emission scanning electron microscope (SEM) (FEI Verios) at the Center for Microscopy, Characterization and Analysis (CMCA), University of Western Australia (UWA). The instrument was operated at 20 kV and at a current of 13 nA.

The electron probe microanalysis

Electron probe microanalysis (EPMA) analyses were performed, using a JEOL 8530F at the CMCA, UWA. Sulfur,

As, Sb, V, Fe, Ti, Se, Au, Te, Cu, Pb, Ni, Zn, Co, Ag, Cd, and Bi were analyzed in pyrite grains and S, As, Fe, Au, Ag, Sb, Pb, and Bi in arsenopyrite grains. Detection limits are summarized in Appendices 3 and 4. A pyrite blank correction has been used, and reproducible quantitative WDS analyses were obtained. A focused beam (~1 μm) was used to avoid small inclusions within the pyrite and arsenopyrite. Peak count times for elements were analyzed at 160 s per element per spectrometer with analytical conditions at 20 kV accelerating voltage, 50 nA probe current, and a point beam.

Laser ablation inductively coupled plasma mass spectrometry

Analysis of sulfides (in polished resin mount) was accrued utilizing a RESolution M-50A-LR incorporating a Compex 102 excimer laser, coupled to an Agilent 7700 s quadrupole ICP-MS at the GeoHistory Facility, John de Laeter Centre,

Curtin University. Following a 20-s period of background analysis, samples were spot ablated for 40 s at a 7-Hz repetition rate, using a 50- μm beam and laser energy of 2.5 J cm^{-2} . Oxide polyatomic interferences were minimized by tuning flow rates for a ThO/Th of $<0.5\%$. The sample cell was flushed with ultrahigh purity He (0.68 L min^{-1}) and N_2 (2.8 mL min^{-1}), and high purity Ar was employed as the plasma carrier gas. International glass standard GSD-1G was used as the primary reference material to calculate elemental concentrations and to correct for instrument drift on all elements except Au. Internal standards were determined by EPMA and include (1) ^{57}Fe as the element for pyrite, chalcopyrite, and arsenopyrite and (2) ^{34}S as the element for sphalerite. Certified sulfide standard Laflamme Po726 (synthetic pyrrhotite doped with platinum group elements and Au) was utilized as the primary standard for Au calculation. Standard blocks were run every 15 unknowns. Precision is better than 5% for most elements based on repeated analyses of secondary internal standards. The mass spectra were reduced using Iolite (Paton et al. 2011 and references therein). Data were collected on a total of 21 elements (^{107}Ag , ^{75}As , ^{197}Au , ^{137}Ba , ^{209}Bi , ^{59}Co , ^{52}Cr , ^{63}Cu , ^{55}Mn , ^{95}Mo , ^{60}Ni , ^{208}Pb , ^{121}Sb , ^{77}Se , ^{28}Si , ^{118}Sn , ^{47}Ti , ^{205}Tl , ^{51}V , ^{66}Zn , and ^{90}Zr). Dwell times were 0.1 ms except for Au and Ag which had 0.3 ms dwell times (Paton et al. 2011).

Secondary ion mass spectrometry

The secondary ion mass spectrometry (SIMS) data was collected using a CAMECA IMS1280 large-geometry ion probe at the CMCA, following LaFlamme et al. (2016), and specific analytical conditions are described below. Quadrupole sulfur isotope (^{32}S , ^{33}S , and ^{34}S) analysis was performed with the ion microprobe operating in multicollection mode using a 10 keV Cs⁺ primary beam ($\sim 3 \text{ nA}$; Gaussian mode) and a normal incidence electron flood gun for charge compensation during all analyses. Following a 30-s pre-sputter, secondary sulfur ions from the target sample were extracted at -10 kV and admitted to the mass spectrometer with a field magnification of 133, with automated centering of the secondary beam in the field aperture (both x and y ; aperture size $4000 \mu\text{m}$) and entrance slit (x direction only; slit width $60 \mu\text{m}$ or $90 \mu\text{m}$ in some cases). The NMR magnetic field controller locked the axial mass at the beginning of each session, and the mass spectrometer operated at a mass resolution ($M/\Delta M$) of about 2500 (exit slit width of $500 \mu\text{m}$ on the multicollector). The ^{32}S , ^{33}S , and ^{34}S were simultaneously detected by three Faraday cups using amplifiers with 1011Ω (L2) and 1010Ω resistors (L1 and H1). Count rates on ^{32}S varied from 5×10^8 to 3×10^9 cps on pyrite. Measurements of unknowns were interspersed with matrix-matched reference material including Sierra for pyrite analyses, Nifty-b for chalcopyrite analyses,

and Asp-200 for arsenopyrite analyses to calibrate isotope ratios and monitor internal precision.

High-resolution elemental mapping was carried out using the Cameca NanoSIMS 50 L at the CMCA, UWA. The samples were prepared as polished 1-in. resin mounts and carbon coated to provide conductivity. Measurements were performed with a Cs⁺ primary beam, with a spot size of approximately 100 nm , impact energy of 16 keV , and a beam current of 2 pA . The instrument was operated in multicollector mode, allowing the simultaneous detection of five ion species ($^{54}\text{Fe}^{32}\text{S}$, $^{75}\text{As}^{32}\text{S}$, $^{63}\text{Cu}^{32}\text{S}$, $^{66}\text{Zn}^{32}\text{S}$, $^{208}\text{Pb}^{32}\text{S}$, and ^{197}Au) from the same analysis region. Secondary ion images were obtained by rastering the primary ion beam across areas measuring $50 \times 50 \mu\text{m}$, at a resolution of 512×512 pixels (each pixel measuring approximately 97 nm), with dwell times of $21\text{--}40 \text{ ms}$ per pixel. Prior to imaging, the sample surface was presputtered with the primary ion beam (using 500-pA beam current) to $> 2 \times 10^{17} \text{ ions/cm}^2$, in order to remove surface contamination and implant Cs⁺ ions to reach a steady-state ion emission.

Results

Morphology and zoning of sulfides, oxides, and gold

Identification of mineral zoning and inclusion distribution is critical for the interpretation of in situ analytical results. Sulfide-bearing mineralogy is largely dominated by pyrite. Arsenopyrite is less abundant and occurs as a replacement of pyrite. Both minerals display multiple fractures. Fractures are filled by BMS including sphalerite, galena, and minor chalcopyrite. Electrum is in equilibrium with BMS or in pyrite and/or arsenopyrite fractures. A schematic diagram showing the paragenetic sequence is presented on Fig. 5, and individual mineral characteristics are discussed below.

Pyrite

Pyrite grains, observed in backscattered mode by SEM, show complex patchy zones (Fig. 6) with irregular cornered fragments of dark pyrite cores (PyI) engulfed by bright arsenian pyrite rims (PyII). Contacts between PyI and PyII are sharp profile.

The pyrite core (PyI) is anhedral to sub-euhedral with a uniform internal texture and abundant sphalerite, galena and chalcopyrite, and minor electrum inclusions (Fig. 7). Inclusions are largely dominated by sphalerite showing circular and vermicular shapes (Fig. 8a–c). Inclusions are heterogeneous in size, ranging from 0.1 to $20 \mu\text{m}$. They are randomly dispersed or oriented within the crystallographic planes (Fig. 8b, c). Depletion of small inclusions around larger BMS blebs (e.g., $> 20 \mu\text{m}$) is common and can be defined as seriate distribution (Craig et al. 1981).

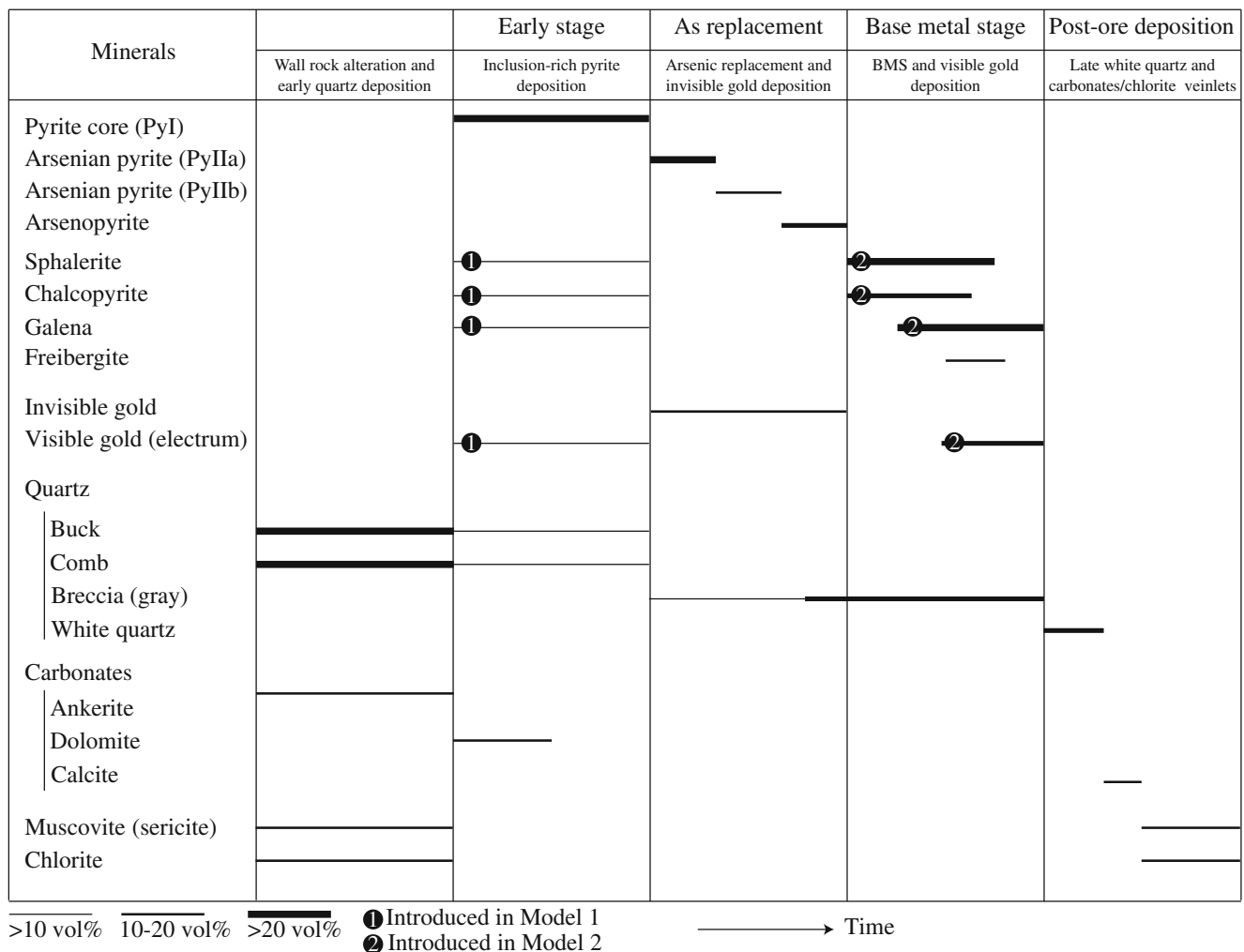


Fig. 5 Paragenetic sequence of ore and gangue minerals in the Pataz-Parcoy district. Modified after Haeberlin et al. (2004) and Schreiber et al. (1990)

PyII can be subdivided into two different generations, i.e., (1) a volumetrically dominant early arsenian pyrite (PyIIa) and (2) irregular later arsenian pyrite bands (PyIIb, Fig. 6). Early PyIIa shows complex internal oscillatory zoning (Fig. 7a–d) and fine-grained euhedral arsenopyrite inclusions (Fig. 7e). Later PyIIb is only observed in sample FVSM041 (Fig. 6). The internal texture of PyIIb is homogenous with rare oscillatory zoning (Fig. 7a).

Arsenopyrite

Arsenopyrite occurs mainly as a replacement of pyrite along fracture planes (Fig. 8d). Overgrowth of arsenopyrite is commonly observed around isolated pyrite grains in quartz (Fig. 9a). Rare 5 to 10 µm acicular arsenopyrites are present in PyII. Backscattered electron images reveal complex twinned arsenopyrite crystals with heterogeneous As content (Fig. 10) and locally light and dark nuclei, with the later depleted in As.

Base metal sulfide

Base metal sulfide (BMS) includes mainly sphalerite, galena, and minor chalcopyrite. Sphalerite commonly contains inclusions of chalcopyrite, galena, euhedral pyrite, and locally, electrum (Fig. 9e). Galena exhibits typical triangular cleavage pits and very rare BMS inclusions. Less abundant than sphalerite and galena, chalcopyrite is also observed in pyrite fractures together with sphalerite and electrum inclusions (Fig. 9f). Coexisting BMS phases commonly display 120° triple junction characteristic of co-crystallization under equilibrium condition (Fig. 9b; Craig et al. 1981; George et al. 2016).

Electrum

Electrum grains (5 to 100 µm) fill together with BMS, microfractures in the pyrite, and arsenopyrite (Fig. 9c–f). Electrum grains form inclusions in chalcopyrite (Fig. 9f) and sphalerite (Fig. 9e) and commonly display an equilibrium texture with galena (Fig. 9e).

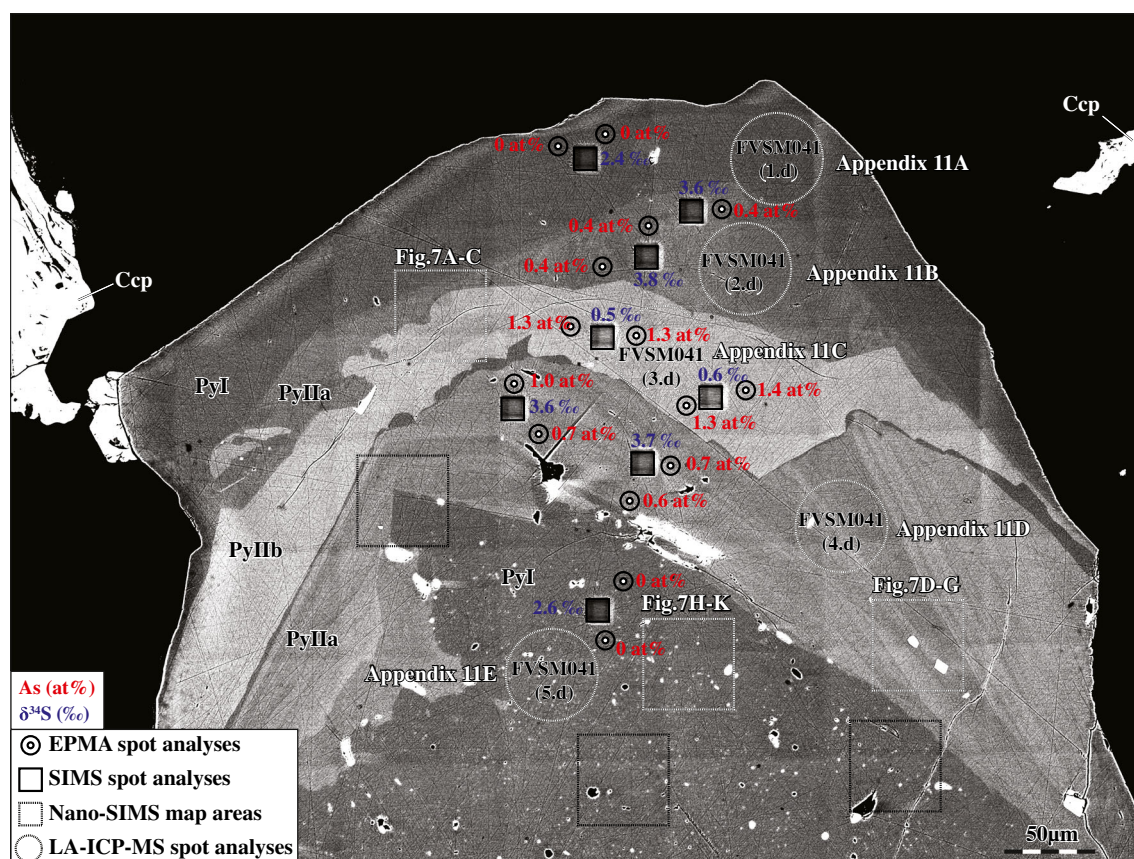


Fig. 6 Backscattered image of pyrite grain from sample FVSM041 with positions of in situ analyses. Lighter gray represents As-rich pyrite; darker gray As-poor pyrite. The corroded boundaries between different pyrite

generations suggest mineral dissolution processes. White minerals in backscattered image are base metal sulfides. Ccp chalcopyrite

Major and minor element chemistry of pyrite and arsenopyrite

Variation in major element chemical composition of pyrite and arsenopyrite is illustrated in the Fe-S-As diagram (Fig. 11). Pyrite core (PyI) analyses plot on the Fe-S axis because As is below EPMA detection limit. Variation of the Fe-S is most likely due to the abundance of BMS inclusions in PyI. Analyses of PyII fall along a dispersed trend that is approximately parallel to the As-S join (Fig. 11), indicating substitution of As in the S site. In PyII, the As content ranges from below detection limit to 2.4 at.%. Arsenopyrite analyses also show a trend parallel to the As-S join, indicating substitution of As for S. Compositions range from near stoichiometric arsenopyrite to non-stoichiometric arsenopyrite, depleted in As (27.82 at.% As, 38.77 at.% S, and 33.41 at.% Fe).

Trace element composition of sulfides

In situ laser ablation analyses have been conducted on 29 pyrite samples from various batholith-hosted ore bodies in the Pataz-Parcoy district with emphasis on the Santa Maria deposit (Fig. 3). All results are presented in Appendices 5 to 9 and summarized in Appendix 10.

Trace elements contained in PyI are largely dominated by Zn with values ranging from 1070 ppm to 2.2 wt% with a median value of 3830 ppm. The Au content in PyI ranges from below the detection limit (< 0.002 ppm) up to 55 ppm (median, 0.52 ppm). Laser ablation values of PyII return high arsenic content ranging from 0.1 wt% up to 4.1 wt% coherent with EPMA values (Fig. 11). Total trace element concentrations in PyII are low compared to PyI, and the gold content in PyII varies from 0.12 to 177 ppm (median, 8.1 ppm), whereas Ag values range from 0.05 to 94 ppm with a median value of 7.3 ppm. Gold values in arsenopyrite display a range from 0.13 to 195 ppm (median, 20.4 ppm). Antimony values range from 26.5 to 2890 ppm (median, 275 ppm). The LA-ICP-MS analyses show higher values of Au in arsenopyrite (Table 1) compared to PyII, with concentrations ranging from 3.9 to 195 ppm (median, 20.4 ppm). Silver contents in arsenopyrite vary from 0.09 to 158 ppm (median, 2.5 ppm), and Sb contents range from 51.4 to 1437 ppm (median, 275 ppm).

Cadmium is the most abundant trace element in sphalerite, ranging from 2542 to 10,410 ppm (median, 4899 ppm). The trace element content of galena is dominated by Ag with values ranging from 171 to 1520 ppm (median, 741 ppm), and Sb with values from 197 to 1894 ppm (median, 819 ppm). Cadmium

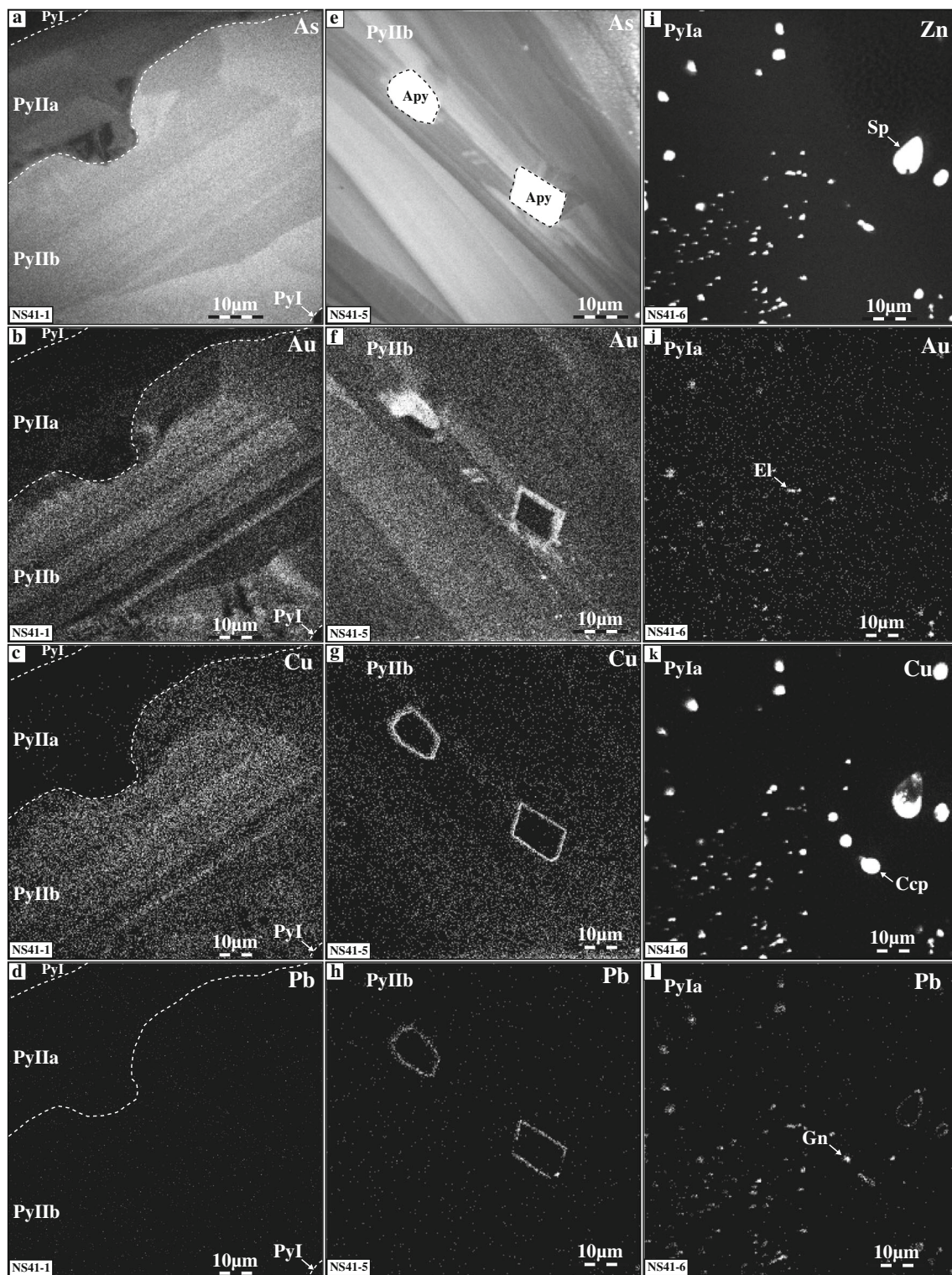


Fig. 7 NanoSIMS elementary maps of pyrite generations from sample FVSM041. **a–d** Correlated distribution of As, Au, and Cu in oscillatory zoned PyIb. **e–h** Correlated distribution of As and Au ($\pm$ Cu) in oscillatory zoned PyIb. Intergrowth arsenopyrite show a fine rim

enriched in Cu, Pb, and Au. **i–l** BMS inclusion distribution in PyIa. As, $^{75}\text{As}^{32}\text{S}$ distribution; Au, ^{197}Au distribution; Cu, $^{63}\text{Cu}^{32}\text{S}$ distribution; Pb, $^{208}\text{Pb}^{32}\text{S}$ distribution; Zn, $^{66}\text{Zn}^{32}\text{S}$ distribution; Sp, sphalerite; El, electrum; Ccp, chalcopyrite; Gn, galena

values in galena range from 28.4 to 83.8 (median, 50.9 ppm). Chalcopyrite contains only a few trace elements with relatively

low concentrations including Zn (94.7 to 454 ppm; median, 223 ppm) and Ag (1.3 to 65.0 ppm; median, 11.9 ppm).

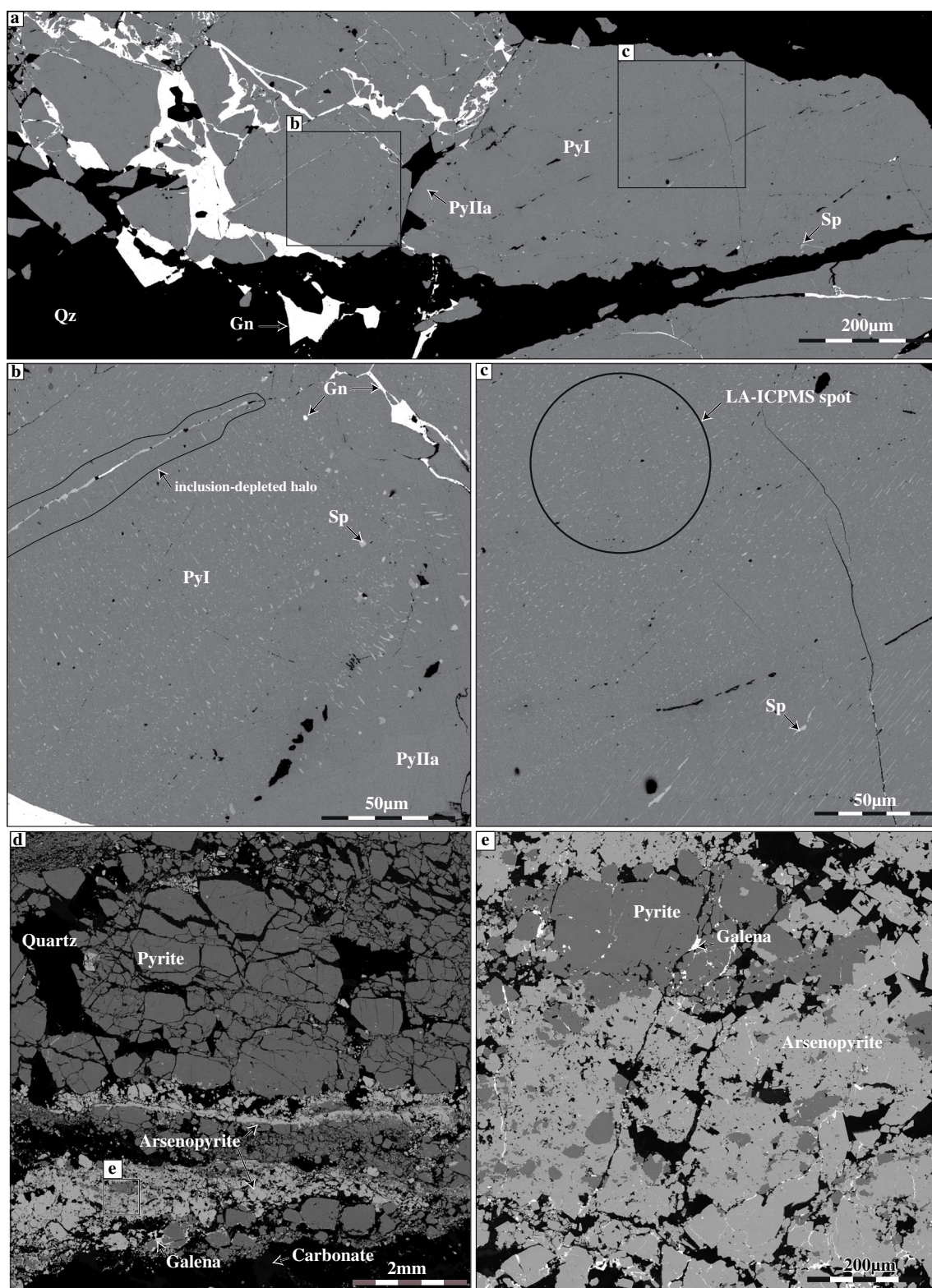


Fig. 8 Backscattered electron images showing base metal sulfide inclusions in pyrite. **a** Large coarse fragmented pyrite in quartz matrix, with base metal sulfides in pyrite fractures. Black squares represent inclusion location close-up **b** and **c**. **b** On the top left, inclusion-depleted halo around the crack shows redistribution of BMS inclusions out of the pyrite grain. On the bottom right, seriate distribution of inclusions in PyI close to areas replaced by arsenian pyrite. **c** Elongated inclusion of

sphalerite in PyI. Black circle represents LA-ICP-MS spot (75 μm in diameter) and shows the homogeneous distribution of inclusions in PyI. **d** Backscattered electron image of pyrite replaced by arsenopyrite along fracture planes. **e** Close-up on pyrite pseudomorphously replaced by arsenopyrite with sparse base metal sulfides filling fractures in pyrite and arsenopyrite

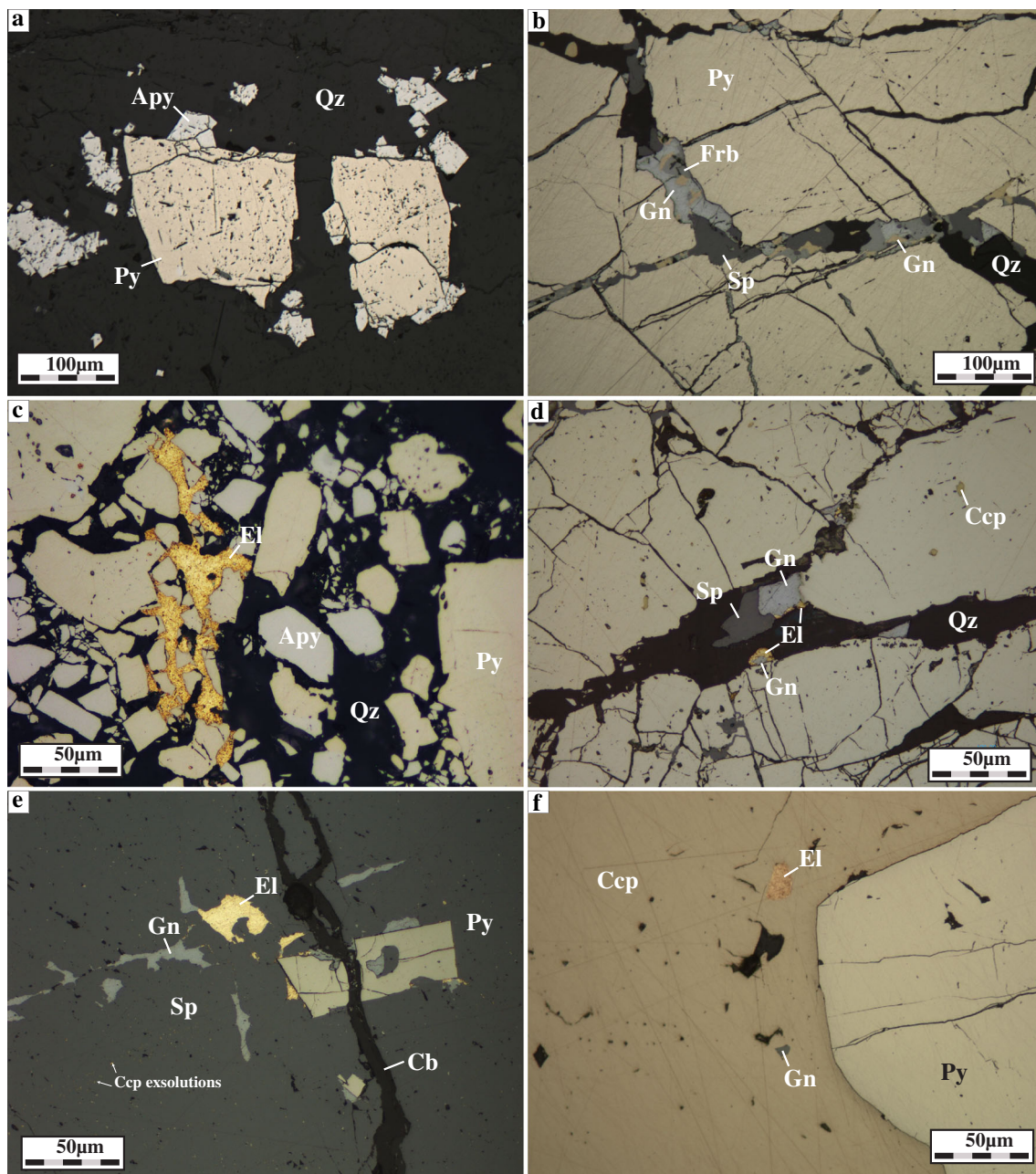


Fig. 9 Photomicrographs of gold and sulfide textural relationships in the Pataz-Parcoy district. **a** Pyrite and arsenopyrite in quartz vein from the sample FVSM062. **b** Base metal sulfide veinlet filling pyrite fractures. **c** Pyrite partially replaced by arsenopyrite with quartz in fractures and electrum occupying interstitial position. **d** Electrum in equilibrium texture with galena filling pyrite fracture. **e** Sphalerite showing classic

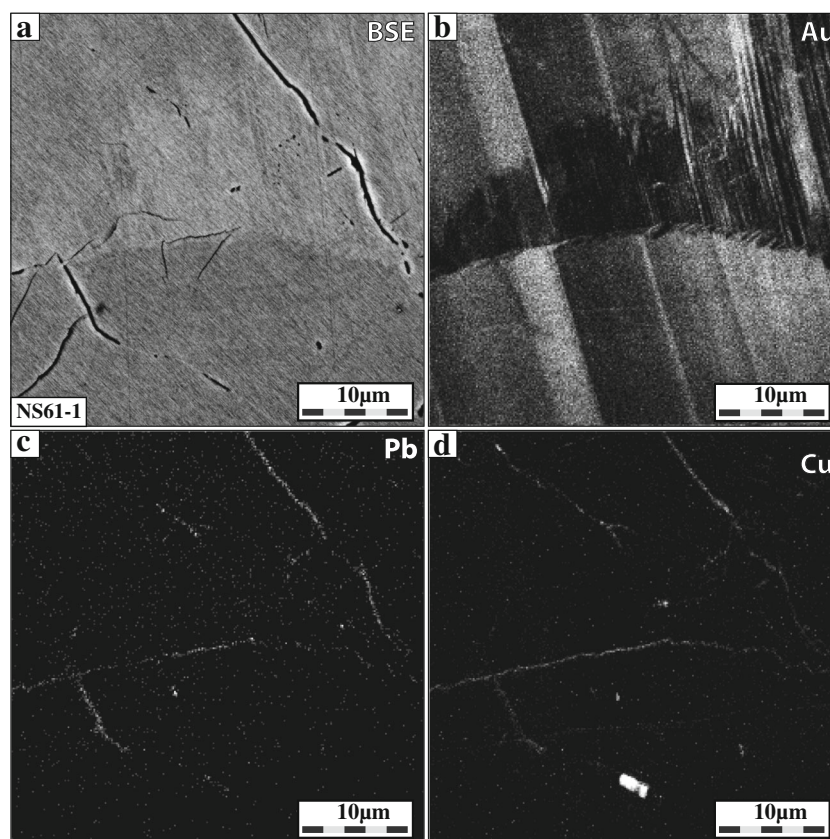
chalcopyrite exsolution with later precipitation of galena together with electrum. Pyrite isolated in sphalerite and partially replaced. **f** Galena and electrum inclusion in chalcopyrite. Py, pyrite; Apy, arsenopyrite; Gn, galena; Ccp, chalcopyrite; Sp, sphalerite; Frb, freibergite; Qz, quartz; Cb, carbonate

In situ sulfur isotope analysis of pyrite, arsenopyrite, and chalcopyrite

A total of 136 spots were analyzed in situ including 25 spots in PyI, 14 spots in PyII, and 15 spots in arsenopyrite on FVSM044. Analyses on sample FVSM041 included 22 spots in PyI, 31 spots in PyIIa, 14 spots in late PyIIb, and 25 spots in chalcopyrite.

The range of $\delta^{34}\text{S}$ for all sulfides examined in this study varies from -1.9 to $+4.4\text{‰}$ (Fig. 12). All of the data plot on the mass-dependent fractionation line ($\delta^{33}\text{S} = 0.504 \times \delta^{34}\text{S}$; Hulston and Thode 1965). Analyses of PyI range between $+1.8$ and $+3.0\text{‰}$. Arsenian pyrite rims (PyIIa) display a larger dispersion of values ranging from $+1.8$ to $+4.4\text{‰}$. The $\delta^{34}\text{S}$ values of late-stage PyIIb vary from -0.1 to $+1.3\text{‰}$.

Fig. 10 NanoSIMS elementary maps of arsenopyrite from sample FVSM061. **a** Backscattered image of arsenopyrite area analyzed by NanoSIMS lighter gray represents As-rich arsenopyrite and darker gray As-poor arsenopyrite. **b** Homogeneous ^{197}Au distribution in micron-scale oscillatory zoned arsenopyrite. **c** Micro fractures infilled by galena. **d** Micro fractures infilled by chalcopyrite



Arsenopyrite grains yield values between -0.1 and -1.4‰ . The $\delta^{34}\text{S}$ values of chalcopyrite range from $+1.5$ to $+2.9\text{‰}$, overlapping with values for PyI.

NanoSIMS maps

High-resolution NanoSIMS elemental maps of $50 \times 50 \mu\text{m}$ areas allowed investigation of selected trace element (As,

Au, Ag, Pb, Zn, and Cu) distribution in finely zoned pyrite and arsenopyrite (Fig. 7). NanoSIMS images of PyI (Fig. 7i–l) reveal the presence of 100 nm to 10 μm rounded inclusions of BMS and electrum. Arsenian pyrite rims (PyII) show oscillatory zoning textures defined by correlated variation of As, Au, and Cu (Fig. 7a–c). Arsenopyrite inclusions, intergrown with PyII, are rimmed by Au, Cu, and Pb (Fig. 7e–h). The As-depleted areas of arsenopyrite exhibit fine oscillatory zoning

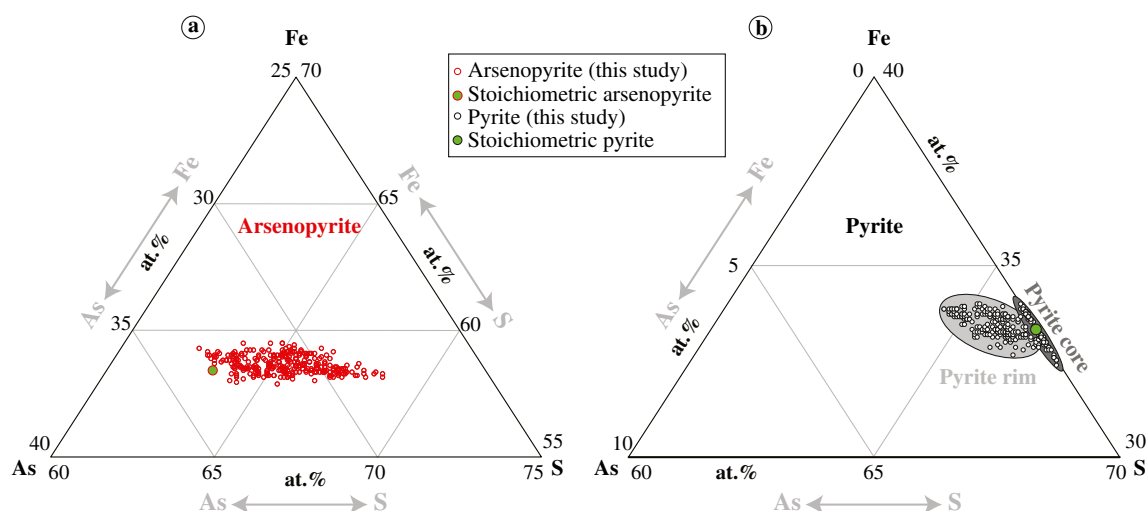
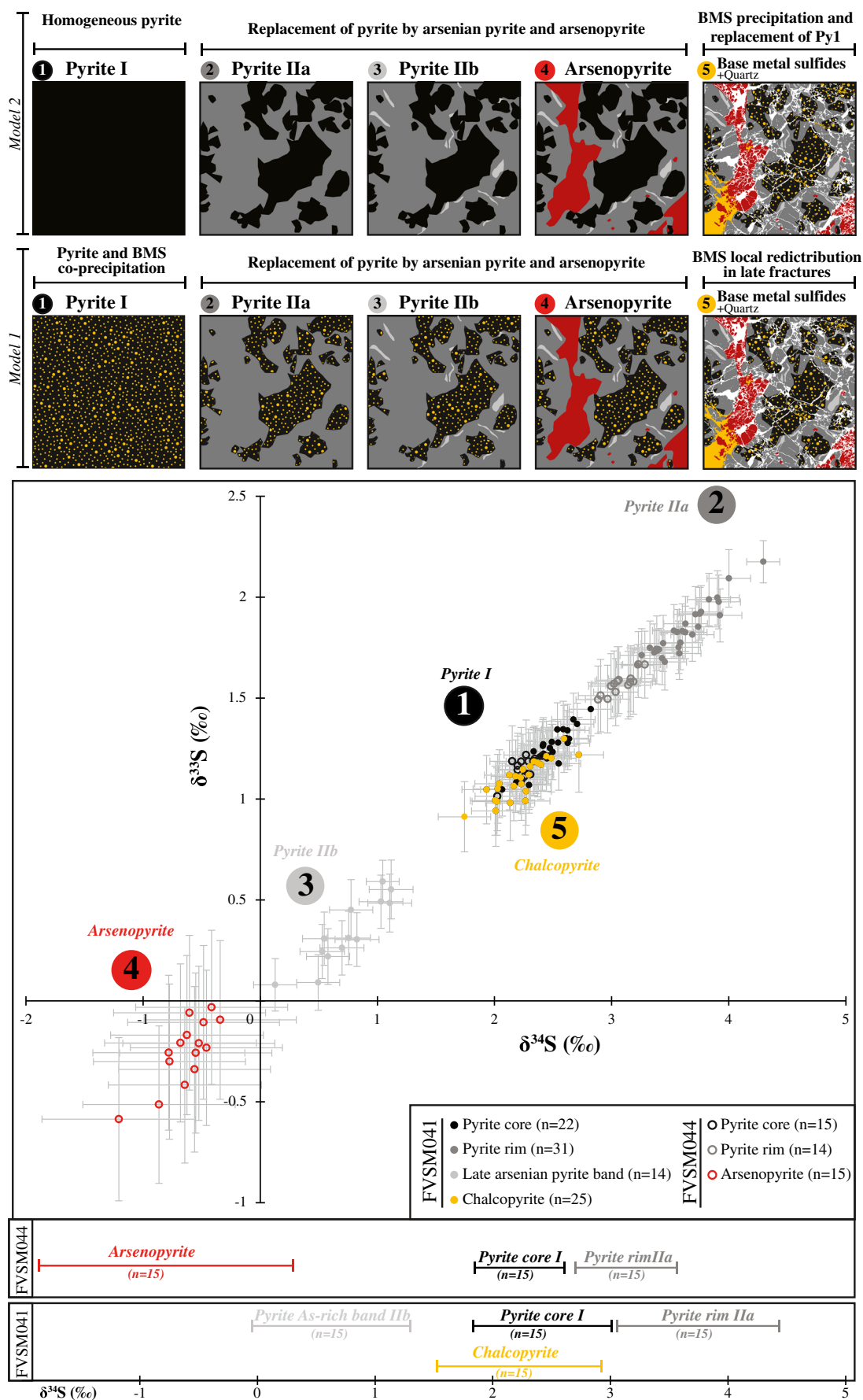


Fig. 11 As–Fe–S ternary diagram for pyrite and arsenopyrite from Patáz-Parcoy district ore deposits

Table 1 Summary of trace element concentrations (in ppm) in pyrite, arsenopyrite, sphalerite, galena and chalcopyrite determined by LA-ICP-MS spot analysis. All data below 2 sigma uncertainty are below detection limit

		Ag_ppm	As_ppm	Au_ppm	Bi_ppm	Cd_ppm	Co_ppm	Cu_ppm	Ni_ppm	Pb_ppm	Sb_ppm	Sn_ppm	Zn_ppm
Pyrite_core PyI n = 205	Min	2.0	0.9	<0.1	<0.1	7.4	<0.1	9.7	<0.1	2.5	0.6	<0.1	1070.0
	Max	198.4	910.0	55.0	257.0	259.8	346.0	13,000.0	58.9	47,000.0	282.0	645.0	22,970.0
	Mean	25.6	115.7	1.3	4.9	55.9	8.7	516.9	2.0	1931.8	18.7	49.7	5476.3
	Median	17.8	47.7	0.5	<0.1	34.9	<0.1	187.0	<0.1	83.0	10.3	20.7	3830.0
Pyrite_rim PyIIa and b n = 160	Min	<0.1	1020.0	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	0.1
	Max	445.0	41,000.0	176.7	44.0	9.4	1643.0	2860.0	1690.0	66,000.0	1058.0	184.0	970.0
	Mean	10.6	8881.6	14.8	4.2	1.1	61.1	95.3	39.5	2462.9	23.3	2.9	77.1
	Median	2.7	7660.0	8.1	0.8	0.2	1.7	15.2	0.8	83.2	6.4	<0.1	0.6
Arsenopyrite n = 89	Min	<0.1	460,100	0.1	<0.1	<0.1	<0.1	0.6	<0.1	1.0	26.5	<0.1	<0.1
	Max	400.0	460,100	195.0	25.7	24.4	427.0	1210.0	110.0	26,700.0	2890.0	6.2	6.2
	Mean	25.8	460,100	27.4	1.9	1.1	22.5	34.4	12.0	2756.4	346.9	0.5	0.5
	Median	2.6	460,100	20.4	0.2	<0.1	1.2	6.7	1.0	120.5	275.0	0.1	0.1
Sphalerite n = 53	Min	3.4	<0.1	<0.1	<0.1	1119.0	<0.1	7.7	<0.1	3.5	0.9	0.1	0.1
	Max	241.2	22.0	2.9	2.0	10,410.0	0.4	20,300.0	1.2	140,000.0	266.0	44.4	44.4
	Mean	58.9	2.3	0.2	0.4	5117.5	<0.1	1471.5	0.2	8893.9	43.1	6.4	6.4
	Median	33.7	0.2	<0.1	<0.1	4899.0	<0.1	387.0	<0.1	49.8	17.2	2.7	2.7
Galena n = 53	Min	170.8	1.4	<0.1	1.4	28.4	<0.1	0.1	<0.1	134,000	196.6	241.0	241.0
	Max	1520.0	12.6	1.9	2271.0	294.0	<0.1	92.0	<0.1	134,000	1894.0	154,000.0	154,000.0
	Mean	735.7	2.1	<0.1	131.3	62.3	<0.1	8.3	<0.1	134,000	860.3	34,593.7	34,593.7
	Median	741.0	1.8	<0.1	15.2	50.9	<0.1	1.1	<0.1	134,000	819.0	16,460.0	16,460.0
Chalcopyrite n = 20	Min	1.3	40.2	<0.1	<0.1	1.1	<0.1	346,300	<0.1	0.6	0.5	9.3	9.3
	Max	65.0	86.0	1.0	4.9	11.1	8.0	346,300	0.4	147.0	29.1	88.5	88.5
	Mean	16.9	50.1	0.3	1.4	3.6	3.9	346,300	0.2	23.7	8.3	49.1	49.1
	Median	11.9	43.1	0.2	1.2	3.3	3.8	346,300	0.1	5.4	4.8	49.1	49.1



◀ **Fig. 12** Schematic diagram of the five steps sulfide paragenesis (*Model 1* and *Model 2*) and associated sulfur evolution. *Model 1* exposes a co-precipitation of BMS with PyI and later redistribution in cracks driven by partial replacement of PyI to PyII and arsenopyrite. *Model 2* proposes a preferential replacement of PyI along crystallographic planes by percolation of the fluid responsible for BMS deposition in fractured pyrite and arsenopyrite. Sulfur isotope values collected during the five paragenetic steps on pyrite, arsenopyrite, and chalcopyrite are presented in a three-isotope plot with 2σ errors

defined by gold concentration (Fig. 10a–d), whereas the late replacement by stoichiometric arsenopyrite is depleted in Au. Narrow cracks and boundaries between As-depleted arsenopyrite and later stoichiometric arsenopyrite show enrichment in Cu and Pb.

Discussion

Effect of nanoscale inclusions on the interpretation of mineral geochemistry

In sulfides, trace elements can be present as solid solution, nanoparticles, or as fine visible mineral inclusions. Genna and Gaboury (2015) have demonstrated the importance of using trace elements in solid solution or included as nanoparticles to discriminate between different pyrite generations. The Tanner et al. (2016) study of pyrite crystals highlighted the limitations of equilibrium-based interpretations using trace element geochemistry when the trace element distribution is controlled by inclusions. Commonly, in the case of large inclusions (> 100 nm in size), spikes in the time-resolved, down-hole laser ablation profile can be used to identify the presence and nature of inclusions (Cook et al. 2016). On the other hand, several authors have suggested that “flat” laser ablation spectra are evidence that elements are present in the lattice of the sulfide or that inclusions are at the nanoscale (Large et al. 2007; Cook et al. 2013; Genna and Gaboury 2015). However, when inclusions are homogeneously distributed, the down-hole profile can be smooth, and therefore, recognition of inclusions versus solid solution and/or nano-inclusions is not possible (Cook et al. 2016). In this study, electronic microscopy together with NanoSIMS has revealed (1) the presence of numerous BMS inclusions in PyI, from 100 nm to 10 μ m in diameter and (2) narrow cracks (< 1 - μ m width), filled with BMS, cross cutting all pyrite and arsenopyrite generations. The relatively small size of BMS inclusions (< 5 μ m), compared to the laser beam diameter (75 μ m spots), as well as their homogeneous distribution (Fig. 8b, c) are suggested to be responsible for the relatively constant signal in the time-resolved laser ablation profile of PyI (Appendix 11).

Therefore, we propose that co-variation between elements can be used to discriminate elements related to the presence of

inclusions and elements present in the crystal lattice of sulfides (Table 2). For this purpose, the LA-ICP-MS data is used with analyses from all sulfides and spot analyses containing obvious inclusions and/or a mixture of minerals (e.g., PyI mixed with PyII and/or BMS). Pearson correlation coefficient between trace elements is summarized in Appendix 12.

Co-variation of trace elements

The Zn vs Cd diagram (Fig. 13b) shows a correlation of both elements in PyI, PyII, chalcopyrite, and arsenopyrite. Therefore, we argue that, for these sulfides, the Zn content reflects the proportion of sphalerite inclusions. An exception is made for galena, which contains Cd in its crystal lattice. Identification of galena inclusions is best observed in Pb vs Ag and Ag vs Sb diagrams (Fig. 13a, d). The co-variation of Pb and Ag in PyI and PyII, chalcopyrite, and sphalerite reflects the proportion of galena inclusions. The plot of Ag vs Sb also illustrates the proportion of galena inclusions in pyrite. However, Sb values in arsenopyrite are de-coupled with Ag (Fig. 13a). This may reflect the substitution of Sb in arsenopyrite solid solution and/or as metal nanoparticles. Chalcopyrite is depleted in trace elements (< 0.01 ppm).

Arsenopyrite and PyII analyses show de-coupled Au and Ag. Contrasting with values from other sulfides, this is interpreted as reflecting the presence of gold as metal nanoparticles (< 0.1 μ m) and/or as solid solution in the lattice of As-rich sulfides, instead of electrum inclusion. This interpretation is supported by the homogenous repartition of gold in arsenian pyrite and arsenopyrite using NanoSIMS mapping (Figs. 7 and 10). The As vs Au diagram (Fig. 13) displays a typical positive correlation as described by numerous authors (Mumin et al. 1994; Reich et al. 2005; Deditius et al. 2014) and consistent with the preferential precipitation of Au in the As-rich sulfides.

Visible gold in the Patáz-Parcoy district has only been observed as electrum. In Au vs Ag diagram (Fig. 13), data from PyI and chalcopyrite plot in the electrum Au–Ag ratio field. This is compatible with electrum inclusions observed in PyI, chalcopyrite, and sphalerite (Table 1). In Py II and arsenopyrite, Au concentration increases independently to Ag and, therefore, is not reflecting the presence of electrum inclusions. The elevated concentration of Ag (median, 741 ppm) in galena makes the Au–Ag correlation related to the presence of electrum inclusion impossible to distinguish.

Re-evaluation of trace element signatures

The trace element content in sulfides from the batholith-hosted quartz-carbonate-sulfide veins is largely controlled by the presence of discrete inclusions and/or narrow cracks infilled by BMS. Therefore, a re-evaluation of the so-called trace element signature is proposed and summarized in

Table 2 Re-evaluation of trace element signature for sulfides from the Pataz-Parcoy district

Mineral	Pyrite					Arsenopyrite	Sphalerite	Galena	Chalcopyrite
	PyIa		PyIIa		PyIIb				
Major element	Fe, S		Fe, S ± As		Fe, S ± As	Fe, S, As	Zn, S	Pb, S	Cu, Fe, S
Mineral inclusion	Ccp, Sp, Gn, El, Apy		Apy		Apy	Gn, Sp	Gn, Ccp, Py, El	Sp, Ccp, El	Gn, Sp, El
Trace element	Zn, Cu, Pb, Cd, Ag, Au, Cu, In, Mn, Pb, Sb, Sn, Zn		As, Au, Ti, Cu		Sb, Pb, Ag	Cu, Pb, Zn, Sn, Mn	Pb, Cu, Ag, Sb, Sn Cd, In, Au	Zn, Cu, Cd, Mn, In, Sn, Ag, Au	Zn, Pb, Cd, Mn, Ag, Sb, Sn, Au
Lattice-bound	Co, Ni		As, Au, Cu (± Co, Ni)		As, Au, Cu (± Co, Ni)	Sb, Au	Cd, Mn	Ag, Sb, Sn, Cd	In, Sn

Py, pyrite; *Apy*, arsenopyrite; *Gn*, galena; *Ccp*, chalcopyrite; *Sp*, sphalerite; *El*, electrum

Table 2. With the exclusion of trace elements related to BMS inclusions, Co and Ni are the only elements that are likely included within the crystal structure of the pyrite core (PyI). However, most of the Co and Ni analyses from all sulfides are below detection limit, and the correlation observed in Fig. 13 cannot be attributed to fine mineral texture variations. Arsenian pyrite rims (PyIIa and b) display rare inclusions (Fig. 7), but SEM and NanoSIMS imaging reveal narrow cracks (< 0.1-μm width) filled by BMS. Co-variation between trace elements (Fig. 13) and the distribution of elements illustrated using the nanoSIMS maps (Fig. 7) indicates that As, Au, and Cu partition homogeneous within the crystal structure of arsenian pyrites. Arsenopyrite grains contain only rare inclusions but are cut by narrow cracks infilled by BMS and electrum (Fig. 10). Once analyses affected by BMS inclusions are rejected from the dataset, the lattice-bound trace elements include Au and Sb. The NanoSIMS images show that Au is homogeneously distributed in alternating micron-scale bands (1- to 10-μm width) with sharp boundaries (Fig. 10), which suggests that Au is most likely lattice-bound.

Paragenesis and geochemical model(s) for sulfides and gold deposition

Based on ore mineral zoning and crosscutting relationships, a discrete As replacement event associated with deposition of invisible gold has been identified in the Pataz-Parcoy district (Fig. 5) and contrasts to the two-stage ore sequence described by previous authors (Schreiber et al. 1990; Haeberlin et al. 2004).

As discussed by Bortnikov et al. (1991), the interpretation of sulfide inclusion formation is important to clarify the crystallization sequence of minerals, and hence for understanding the history of ore deposit formation. In the Pataz-Parcoy district, inclusions in the pyrite core (PyI), including BMS and electrum, are similar to the mineral assemblage present pyrite and arsenopyrite cracks. Moreover, in situ LA-ICP-MS analyses reveal that the trace element signature of pyrite cores perfectly matches the signature from sulfides located in fractures of pyrite and arsenopyrite. However, pyrite textures clearly show that pyrite core formation and subsequent BMS deposition in brittle fracture networks are separated by As-rich fluid circulation responsible for the replacement of pyrite by arsenian pyrite and arsenopyrite. Therefore, two end-member models are discussed for the formation of pyrite core inclusions: (1) co-genetic formation resulting from rapid co-precipitation, where BMS were trapped during pyrite formation and (2) selective replacement along crystallographic planes. The interpretation of BMS inclusions in pyrite cores impacts on the interpretation of the paragenetic sequence and on the geochemical processes responsible for the deposition of sulfides and gold. Therefore, two depositional models for

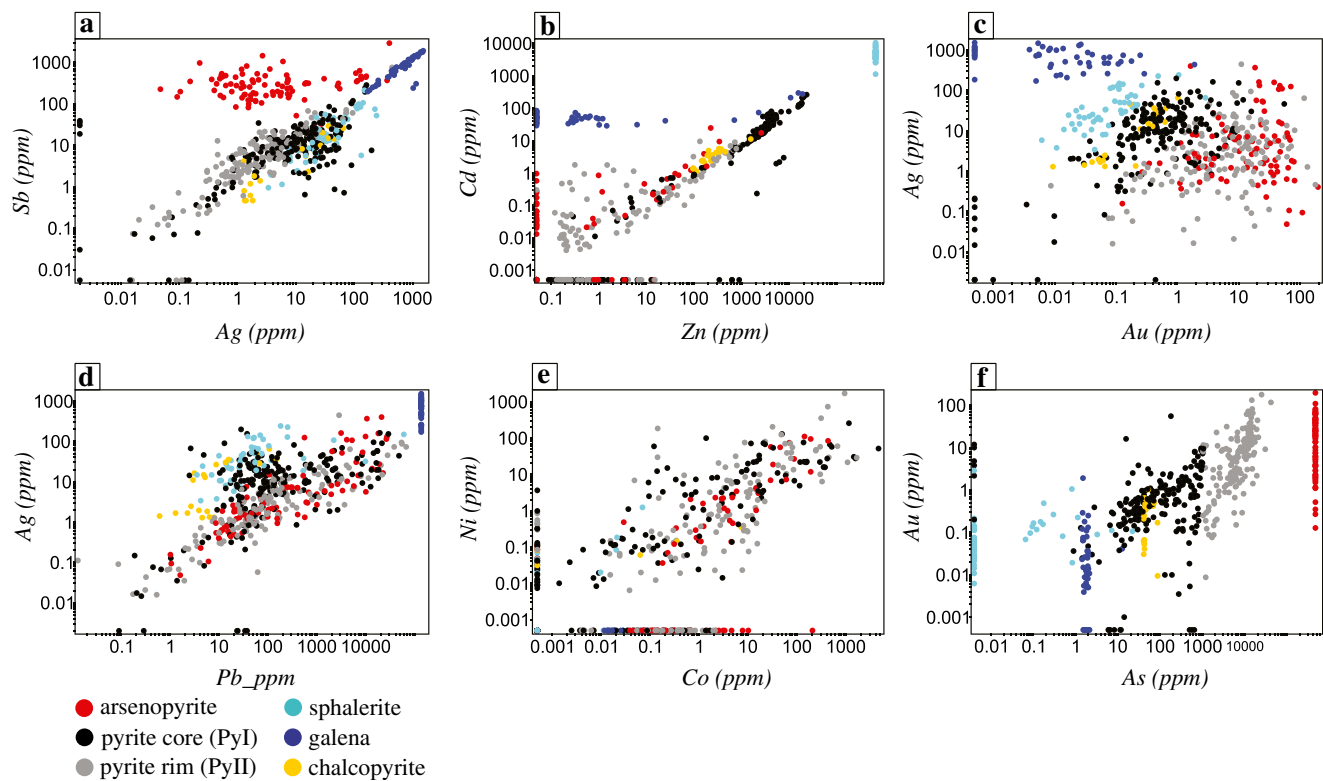


Fig. 13 Binary plots of selected trace elements (in ppm) for PyI, PyII, arsenopyrite, sphalerite, galena, and chalcopyrite from the Pataz-Parcoy district. **a** Sb vs Ag. **b** Cd vs Zn. **c** Ag vs Au. **d** Ag vs. Pb. **e** Ni vs Co. **f** Au vs As

batholith-hosted gold mineralization in the Pataz-Parcoy district are proposed.

Model 1: co-genetic formation of pyrite and BMS inclusions

The first model (Fig. 12) suggests that mineralization commenced with co-deposition of pyrite (PyI), BMS, and electrum. This was followed by the replacement of pyrite by arsenian pyrite (PyII and III) and arsenopyrite. The replacement process was responsible for the redistribution of pyrite BMS inclusions in the surrounding fractures. The rounded and elongated shapes of BMS inclusions (Fig. 8) have been interpreted as a co-precipitation or as a decomposition of a higher-temperature (FeS_2) solid solution (Tarassova et al. 2015). Similarly, in the Čoka Marin deposit, Pačevski et al. (2012) reported that rapid co-precipitation of metal sulfides would permit the trapping of minor BMS inclusions within pyrite. The seriate distribution of BMS has been previously described by Craig et al. (1981) as a distinctive texture for exsolution processes. Circulation of an As-rich fluid resulted in partial to complete replacement of pyrite cores by arsenian pyrite and arsenopyrite that incorporate invisible Au and Cu. Invisible Au precipitating with arsenian pyrite and arsenopyrite was either sourced from the As-rich fluid and/or scavenged from electrum inclusions contained in replaced pyrite

cores (Fig. 7i). The EPMA analyses reveal an antithetic relation between As and S and no relation between As and Fe in samples from the Pataz-Parcoy district (Fig. 11). This indicates substitution of As for S in the pyrite structure, as previously reported by Fleet and Mumin (1997) and Reich et al. (2005). The dissolution-precipitation process of pyrite during As-rich fluid circulation led to a reorganization of its crystal structure. As described by Velásquez et al. (2014) in the El Callao district (Venezuela), dissolution-precipitation can result in the redistribution of the BMS into pyrite and arsenopyrite cracks. Figure 8b provides direct evidence of such a process, where elongated inclusions are partially connected to the crack and surrounded by inclusion-free pyrite. The inclusion-depleted halo around the crack argues for a redistribution of BMS inclusions from the pyrite grain. This is also supported by the seriate distribution of inclusions in pyrite cores close to areas replaced by arsenian pyrite (Fig. 8b). The close spatial relationship between BMS and pyrite-arsenopyrite at the vein- and micro-scale supports a local redistribution in late fractures.

Model 2: selective replacement of pyrite by BMS

In the second model, the first hydrothermal fluid to circulate is responsible for deposition of inclusion-free pyrite. Similar to

Model 1, circulation of As-rich fluid caused partial to complete replacement of pyrite cores by arsenian pyrite and arsenopyrite associated with the deposition of invisible gold and Cu in pyrite lattice. A later, third fluid flux is then responsible for the introduction and deposition of BMS and electrum in pyrite and arsenopyrite cracks. Disequilibrium reactions between BMS, especially sphalerite, and previous zoned pyrite led to replacement of pyrite cores. Elongated BMS inclusions would most likely be due to fluid percolation along crystallographic planes. The absence of inclusions in arsenian pyrite and arsenopyrite could be the result of reorganization of the crystal structure, consequently to the substitution of As for S, which prohibits the percolation of the later hydrothermal fluid into arsenian pyrite.

Outstanding issues

The main concern about *Model 1* is the mineralogical mass balance between BMS inclusions and redistributed BMS in pyrite and arsenopyrite fractures. Average Au concentration in pyrite core is of the order of 1 ppm (Table 2), whereas Au fire assay grades of the sample are of the order of 100 ppm (Appendix 13). The removal of electrum inclusions, originally contained in pyrite core, cannot explain the concentration of gold grade obtained by fire assay analyses. This mass balance issue implies that a second pulse of gold is necessary. Moreover, the proportion of sphalerite inclusions in PyI is one to two orders of magnitude larger than galena, whereas at the mine scale, the proportion between the two sulfides is approximately equal.

The major concern about *Model 2* is the presence of BMS inclusions in the PyI but the absence of inclusions in surrounding PyII and arsenopyrite. In the case of dissolution-reprecipitation process, the product, in this case arsenian pyrite and arsenopyrite, should show abundant porosity (Putnis 2009). However, the complete reorganization of the crystal lattice of the minerals could have destroyed porosity (Harlov et al. 2011).

Evolution of the hydrothermal fluid during sulfide deposition

A study by Tanner et al. (2016) raised the limitations of equilibrium-based interpretations on the trace element geochemistry in the case where their distribution is controlled by inclusions in pyrite crystals. In this case, inferences based on equilibrium partitioning of trace elements in pyrite such as temperature, pressure, and redox estimates cannot be applied. In this study, we demonstrate that a majority of trace elements contained in pyrite are controlled by inclusions, whereas some

elements (e.g., Au, Cu, and Sb) are most likely structurally bound. The structurally bound elements As, Au, and Cu are used below to constrain the evolution of the hydrothermal fluids during pyrite crystallization.

The similar range of $\delta^{34}\text{S}$ values (Fig. 12) for chalcopyrite and PyI and the morphology and distribution of the BSM inclusions, analogue to chalcopyrite disease in sphalerite, Bortnikov et al. (1991) suggests deposition from a common fluid and/or under the same physico-chemical conditions (e.g., f_{O_2} , pH, and temperature). It is well established that in arsenian pyrite, in a reducing environment, arsenic is negatively correlated with sulfur and substitutes as anionic As^{1-} (Fleet 1989). In more oxidized systems, arsenic can be negatively correlated with iron, and As^{3+} likely substitutes for Fe^{2+} as reported from Yanacocha (Deditius et al. 2008) and Pascua high-sulfidation epithermal gold deposits (Chouinard et al. 2005). Cations such as Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Hg^{2+} , and Pb^{2+} can also enter in the pyrite lattice by isovalent substitution for Fe^{2+} and can reach concentrations > 1 wt.% (Deditius et al. 2008). Another group of cations including Cu^+ , Au^{+3+} , Ag^+ , and As^{3+} have been proposed by Chouinard et al. (2005) to enter pyrite by a coupled heterovalent substitution for Fe^{2+} such as $\text{Au}^{3+} + \text{Cu}^+ \leftrightarrow 2\text{Fe}^{2+}$, and $\text{As}^{3+} + \text{Ag}^+ \leftrightarrow 2\text{Fe}^{2+}$.

In the Patatz-Parcoy district, negative correlation between As and S (Fig. 11b) suggests that arsenic occurs in anionic As^{1-} state in arsenian pyrite and substitutes for S^{1-} . Because of the relatively low content of lattice-bound Au and Cu (20 to 200 ppm) compared to Fe (~46 wt.%) in arsenian pyrite, it is not possible to illustrate a potential direct substitution of Au and/or Cu for Fe. The most accepted mechanism for Au incorporation into pyrite is a substitution of cationic Au for Fe in distorted octahedral sites by anionic As substitution for S (Fleet and Mumin 1997; Reich et al. 2005). A divalent oxidation state of Cu may have allowed direct substitution for Fe^{2+} . However, the co-variance of Au vs Cu (Fig. 14) and NanoSIMS maps (Fig. 7) reveals that Au and Cu are incorporated in the same proportion and in the same location into the lattice of arsenian pyrite. Therefore, a coupled heterovalent substitution for Fe^{2+} , such as $\text{Au}^{3+} + \text{Cu}^+ \leftrightarrow 2\text{Fe}^{2+}$, may be more likely instead, as discussed by Chouinard et al. (2005) for the Pascua gold deposit.

The dissolution texture in PyI and progressive replacement by PyIIa support the introduction of a second hydrothermal fluid (Fig. 12) with distinct physico-chemical characteristics, supported by a ~2‰ shift in $\delta^{34}\text{S}$ values from 2.5 to 4.5‰. The evolution of the As-rich fluid is characterized by a progressive decrease of $\delta^{34}\text{S}$ values, from ~4‰ in PyIIa to ~1‰ in PyIIb down to -1‰ in arsenopyrite. The common parameters which could explain this sulfur fractionation include (1) an increase of f_{O_2} , and/or (2) a decrease of temperature, and/or

(3) a decrease of the pH, and/or (4) fractionation of isotopes between co-precipitated sulfides (Seal 2006). However, sulfur isotope fractionation during dissolution-reprecipitation processes has never been investigated, and the As substitution for S may locally affect the $\delta^{34}\text{S}$ composition of newly formed As-bearing sulfides. As the fluid evolved from PyIIa to PyIIb, the correlated Au and Cu content increased from around 20 to 200 ppm. The coupled heterovalent substitution of Au and Cu for Fe^{2+} described above ($\text{Au}^{3+} + \text{Cu}^+ \leftrightarrow 2\text{Fe}^{2+}$) was proposed by Chouinard et al. (2005) as being consistent with oxidizing conditions. Therefore, the heterovalent substitution observed in the pyrites from the Patáz-Parcoy district (Fig. 14) suggests a progressive increase of f_{O_2} , i.e., progressive oxidation of the hydrothermal fluid during pyrite replacement. This interpretation is supported by the progressive decrease of $\delta^{34}\text{S}$ values during pyrite replacement. The evolution of the hydrothermal fluid towards more oxidized conditions may result from the injection of more oxidized magma potentially triggered by a regional or local switch of the tectonic regime.

Invisible precious metals in sulfides: implications for metallurgy

Invisible gold in As-rich pyrite and arsenopyrite

Gold is a trace element in several sulfides (e.g., arsenian pyrite and arsenopyrite) and is commonly called sub-microscopic or invisible gold (Mumin et al. 1994; Fleet and Mumin 1997; Palenik et al. 2004; Reich et al. 2005; Barker et al. 2009; Deditius et al. 2014; Fougere et al. 2016). Several studies

demonstrated that sub-microscopic gold can be bound into the crystal lattice of the sulfide (solid solution gold) or present as discrete inclusions (colloidal gold) (Cabri et al. 1989; Cathelineau et al. 1989). The metallurgical implications for the presence of invisible gold in sulfide can be significant as demonstrated in the Ashanti Gold Belt, Ghana, where 10% of sulfide in a gold ore averaging 100 ppm of invisible Au contributes 10 g/t to the overall grade of the gold deposit (Mumin et al. 1994).

In the Patáz-Parcoy district, PyII and arsenopyrite return an average Au concentration of 14.8 ppm and 27.4 ppm, respectively (Table 1). These absolute values are relatively low when compared with maximum Au content from synthetic arsenian pyrite and arsenopyrite (gold contents of 0.64 wt% and 3.0 wt%, respectively; Fleet and Mumin 1997). However, ore bodies can contain 10 to 20 modal vol% sulfides (Fig. 4), largely dominated by PyII (~35 modal vol% of sulfides species) and arsenopyrite (~10 modal vol% of sulfides species). Therefore, it is estimated that invisible gold contributes 0.8 to 1.6 g/t to the overall grade of the gold deposit.

Historically, a total of 5.9 million tonnes of ore in the Paraiso-Santa Maria gold area (northern Patáz district) has been processed at the processing plant located in Vijus (*Planta Marañón*) with an average grade of 13.64 g/t resulting in gold production of 2.41 Moz. It is well established that invisible gold is refractory to conventional extraction methods (Cabri 1987), including direct cyanidation as used in the *Planta Marañón*. Therefore, with around 1 g/t of invisible gold compared to the historical 13.6 g/t overall gold grade of the Patáz-Parcoy district, approximately 7.4% of the gold is not being recovered by direct cyanidation. This result is very consistent with the 92% gold recovery from both the Vijus and Santa Maria plants, published by Cia. Minera Poderosa S.A. (<http://www.poderosa.com.pe>).

The recently discovered sulfide-rich veins in the lode gold system at Santa Maria contain up to 30 modal vol% sulfide; therefore, refractory gold could comprise up to 3 g/t and be responsible for a drop of the recovery down to around 85%. Therefore, in order to better recover gold encapsulated in arsenian pyrite and arsenopyrite, pre-treatments could be applied in order to break and/or alter the matrix of the sulfides using common techniques such as pre-aeration, roasting, high pressure oxidation, and biological oxidation (Chrysosoulis et al. 2005). However, additionally to the high investment costs for high pressure operations, pre-leaching processes face environmental disadvantages including the generation of SO_2 and As_2O_3 in roasting and technical issues with the extended time periods and

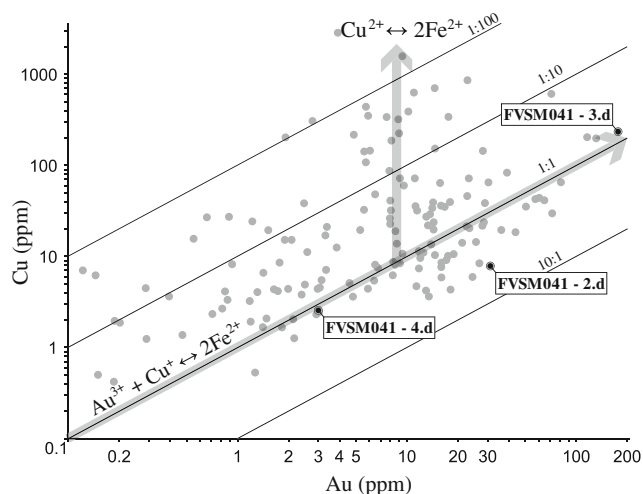


Fig. 14 Relation between Au and Cu in arsenian pyrite (PyIIa and PyIIb). Gray arrows show interpreted isovalent substitution of Cu for Fe^{2+} and heterovalent substitution of Au and Cu for Fe^{2+}

bacterial growth inhibition in the presence of arsenic (Iglesias and Carranza 1996; Leng et al. 2009).

Conclusions

Detailed mapping, recording of crosscutting relationships at the macro-scale (underground stopes and diamond drill core), and micro-scale (i.e., petrographic) and a variety of micro-chemical analyses were used to propose a new paragenetic sequence including (1) deposition of PyI with BMS inclusions, (2) progressive replacement of PyI by PyII and arsenopyrite and associated invisible gold deposition, and (3) deposition of sphalerite – galena ± chalcopyrite ± electrum in fractured pyrite and arsenopyrite. Two hypotheses are proposed for the formation of BMS inclusions in early PyI, i.e., (1) a co-precipitation of BMS with PyI and later redistribution in cracks driven by partial replacement of PyI to PyII and arsenopyrite and (2) a preferential replacement of PyI along crystallographic planes by percolation of the fluid responsible for BMS deposition in fractured pyrite and arsenopyrite.

The progressive increase of f_{O_2} during PyI replacement by PyII and arsenopyrite is proposed to be responsible for the progressive decrease of $\delta^{34}S$ from ~4‰ in PyIIa to ~–1‰ in arsenopyrite. Co-variation of trace elements, such as Ag vs Sb, Zn vs Cd, Au vs Ag, Pb vs Ag, As vs Au, and Co vs Ni in combination with NanoSIMS imaging of As, Au, Zn, Pb, and Cu was used to discriminate elements related to the presence of inclusions and elements present in the crystal lattice of sulfides. Based on the identification of trace elements related to inclusions, we propose the following trace element are bound in the lattice: (1) Co and Ni for PyI, (2) As, Au, and Cu for PyII, (3) Sb and Au for arsenopyrite, (4) Cd and Mn for sphalerite, (5) Ag, Sb, Sn, and Cd for galena, and (6) In and Sn for chalcopyrite.

This study reports the presence of invisible gold in the Patáz-Parcoy district and emphasizes the potentially refractory behavior of the sulfide-rich batholith-hosted mineralization. Furthermore, LA-ICP-MS analysis was used to quantify, for the first time, invisible gold contained in PyII (~15 ppm Au) and arsenopyrite (~30 ppm Au), thus highlighting the significance of detailed mineralogy investigations to solve gold recovery problems.

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