Geology and Genesis of the Multistage High-Sulfidation Epithermal Pascua Au-Ag-Cu Deposit, Chile and Argentina

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Abstract

The giant Pascua epithermal Au-Ag-Cu deposit is located in the El Indio belt of north-central Chile and Argentina and was the product of a high-sulfidation hydrothermal system. The host rocks consist mainly of Triassic granite and heterolithic Miocene breccia pipes. Granitic rocks host ~60 percent of the mineralization (or >80% if granitic breccia fragments are included) but were not the cause of hydrothermal activity. The economic mineralization forms a large orebody centered on Brecha Central, the largest of the breccia pipes, and several smaller satellite bodies that are separated by zones of subeconomic mineralization.

Hydrothermal activity produced two main stages of advanced argillic and vuggy silica alteration. These were separated by an intermediate stage of argillic alteration, silicification and hypogene jarosite, which occurred penecontemporaneously with the emplacement of Brecha Central. Main-stage Au-Ag-Cu mineralization occurred toward the end of the second stage of alteration and involved precipitation of native gold with pyrite and enargite and incorporation of Au in the structure of these minerals. Four types of mineralization are recognized based on the occurrence of economic concentrations of Au in rocks containing significant amounts of the following minerals: (1) alunite, pyrite, and enargite; (2) pyrite; (3) pyrite and szomolnokite; and (4) native gold. Main-stage gold mineralization was followed by a sulfate stage represented by barite and anglesite at lower elevations and barite, anglesite, plus primary szomolnokite, the first reported occurrence of this phase as a hydrothermal ore mineral, at higher elevations. Late-stage silver mineralization, characterized by the occurrence of microscopic Cl-, I-, and Hg-bearing phases in voids and fractures, enriched the upper parts of the deposit, forming an extensive subhorizontal zone that overprints previous alteration and mineralization.

Advanced argillic alteration and high-sulfidation mineralization at Pascua are interpreted to have resulted from a high-level hydrothermal system developed above a porphyry stock located in Argentina. Extensive vuggy silica and advanced argillic alteration reflect interaction of the wall rocks with acidic magmatic vapors. Gold, copper, and arsenic are interpreted to have been transported by these vapors and to have deposited as a result of their cooling and subsequent condensation. Ore-forming hydrothermal activity terminated with silver enrichment in response to the condensation of residual magmatic vapors during the waning stages of the system.

Introduction

The Pascua Au-Ag-Cu deposit is one of several high-sulfidation epithermal deposits in the El Indio belt of north central Chile (Fig. 1). With estimated reserves of 17.6 million ounces (Moz) Au and 585 Moz Ag, or 27 Moz Au equiv (Barrick Gold Corporation, Annual Report, 2004), Pascua is the third largest gold-bearing high-sulfidation deposit in the world after Yanacocha (Peru) and Pueblo Viejo (Dominican Republic).

Typical high-sulfidation deposits form contemporaneously with volcanic activity in rocks that show the effects of interaction with extremely acid fluids, generally considered to be condensates from magmatic vapors containing elevated concentrations of HCl and H2SO4 produced by reaction of SO2 and H2O (Hedenquist et al., 1994). Alteration by these fluids leads to leaching of most elements including aluminum and, in the extreme, can produce rocks consisting dominantly of quartz, termed vuggy silica alteration by Stoffregen (1987). In general the alteration sequence in high-sulfidation systems is propylitic to argillic to advanced argillic and finally to vuggy silica alteration and is interpreted to reflect the progressive neutralization of the fluids by the wall rocks (Steven and Ratté, 1960). Precious metal and associated base metal mineralization typically postdates the bulk of the wall-rock alteration and is generally thought to have been deposited from

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mixtures of magmatic and meteoric aqueous liquids less acidic than those responsible for the alteration (Arribas, 1995).

In contrast to most high-sulfidation deposits, the Pascua deposit is hosted by granitic rocks, and there is little direct evidence of associated volcanic activity, except for the occurrence of biotite-bearing rhyodacitic porphyry dikes. Nevertheless, the host rocks were subject to multistage alteration and mineralization under unusually acidic conditions, even for a high-sulfidation deposit. In this paper, we describe the geologic and structural framework of the deposit and characterize the alteration and its relationship to mineralization. A detailed

Fig. 1. Simplified geology and location of the Pascua deposit and other major deposits in the El Indio belt of the Central Andes of Chile (modified after Martin et al., 1995, and Bissig et al., 2002).
paragenetic framework incorporating alteration, mineralization, and effects of weathering is used to establish a genetic model for the deposit, which attributes mineralization to the condensation of magmatic vapor.

**Exploration History and Ore Reserves**

Following discovery of the El Indio deposit in 1977, St. Joe Minerals acquired an extensive land position in what is now called the El Indio belt. This included the Pascua area, where exploration was conducted mostly in the Esperanza area with joint-venture partners, notably Goldfields Corporation (1981–1982) and Anglo American Corporation (1982–1984). In 1987, Bond International Gold Corporation acquired St. Joe Minerals and started a major drilling campaign. Exploration continued through 1989, when Lac Minerals Ltd. acquired Bond International, and through 1994, when Barrick Gold Corporation acquired the property as a result of the purchase of Lac Minerals Ltd. Identified resources in 1994 were almost exclusively in the Esperanza area and were estimated at 1.8 Moz of Au. Barrick mounted another major drilling campaign in 1995 with the aim of substantially increasing the resource at Esperanza and testing peripheral targets for new mineralized zones (Barrick Gold Corp., unpub. report, 1996).

By 1996, the main high-grade core of the Pascua deposit, Brecha Central, had been discovered and was being delineated by surface drilling. In 1997, the deposit was explored to greater depth, mainly in the Alex exploration tunnel on the 4,680-m level (all elevations are reported as meters above sea level). The eastern portion of the Alex tunnel was extended into Argentina in April 1999, making it one of the first mining tunnels to cross an international border. At the end of 2001, reserves were estimated at 225 million tons (Mt) grading an average of 1.98 g/t Au, 66 g/t Ag, and 0.05 percent Cu, with approximately 80 percent of the mineralization in Chile. Potentially economic mineralization extends from an elevation of 4,550 to 4,950 m.

**Regional Geology**

The El Indio belt is part of the Main Cordillera of Chile, which was formed by plate convergence, interrupted by periods of regional extension (Jordan et al., 1993). During the Miocene, the region was dominated by the eastward-subducting Nazca plate, which gradually flattened from a ~35° dip to near horizontal (Pilger, 1984). Variations in the depth to the subducting plate and in the rate of plate convergence led to multiple episodes of compression, volcanism, and related hypabyssal intrusion and mineralization (Kay et al., 1999). All significant volcanic activity related to economic mineralization continued prior to flattening and eastward migration of the Nazca plate. Between the Eocene and Oligocene, igneous and sedimentary rocks of the Carboniferous-Triassic Pastos de Blancos Group underwent significant basement uplift and thrusting to form the Main Cordillera in the El Indio belt (Jordan et al., 1993).

The geology of the Pascua area has been described by Maksaev et al. (1984), Martin et al. (1995), Bissig (2001), and Bissig et al. (2001, 2002). The Paleozoic-Mesozoic basement in the El Indio belt comprises Permian to Early Jurassic rocks of the Pastos de Blancos Group (Fig. 1), which include (1) rhyolitic welded ash-flow tuffs of the Guanaco Sonso sequence (Permian), (2) intermediate to felsic granitoids of the Chollay unit (Permian to Triassic), (3) bimodal basaltic to rhyolitic volcanic and sedimentary rocks of the Los Tilos sequence (Middle Triassic to Early Jurassic), and (4) dioritic, granitic, and dacitic porphyries of the Colorado unit (Late Triassic to Early Jurassic). Igneous and sedimentary rocks of the Pastos de Blancos Group are locally covered by marine sediments of the early to middle Jurassic Laurato Formation. A major regional unconformity separates Pastos de Blancos rocks from volcaniclastic rocks of the overlying Cuartitos sequence (late Jurassic) and andesitic lava flows and associated volcaniclastic and sedimentary rocks of the Las Tolas sequence (Late Cretaceous to early Eocene).

Permian to early Eocene rocks were intruded by granodioritic and dioritic plutons and smaller bodies of the Bocatoma Unit, which are Eocene to Oligocene in age (avg age of 33 Ma: Martin et al., 1995; Bissig et al., 2001). Significant periods of volcanism occurred in the northern part of the El Indio belt between 27 and 18 Ma (Tilito dacite ash flows at 27–23 Ma and Escabroso andesite at 22–18 Ma) and between 16 and 11 Ma (Cerro de Las Tortolas I andesites at 16–15 Ma and Vacas Heladas andesite flows and tuffs at 13–11 Ma). Post-mineralization dacitic dikes of the Pascua Formation were emplaced between 7.5 and 8 Ma (Bissig et al., 2001). Silicic volcanism of the Vallecito Formation occurred at 6 to 5.5 Ma, and igneous activity in the region terminated with the emplacement of the Cerro de Vidrio rhyolite at ca. 2 Ma (Bissig et al., 2002).

The regional structure in the El Indio belt is dominated by northerly trending high-angle reverse and normal faults and similarly trending folds (Martin et al., 1999). These structures developed in response to periods of crustal shortening and relaxation related to eastward-directed subduction of the Nazca plate (Kay et al., 1999). A subordinate structural trend is defined by west-northwest faults (e.g., Pascua fault system) and may reflect the fabric of the Precambrian basement rocks (Davidson and Mpodozis, 1991).

The Pascua deposit occurs near the center of a graben, which is bounded 10 km to the west by the east-verging high-angle Chollay reverse fault and about 16 km to the east by the west-verging high-angle El Indio reverse fault zone.

**Deposit Geology**

**Paleozoic rocks**

The oldest basement rocks exposed in the Pascua area are rhyolitic to dacitic ash-flow tuffs and minor lava flows of the Guanaco Sonso sequence of the Pastos de Blancos Group (Martin et al., 1995; J. Hamilton, unpub. report for Barrick Gold Corp., 1998, Fig. 2). Three rock units comprise the sequence: a basal dacitic crystal to crystal-lithic ash-flow tuff, a middle rhyolitic quartz-sandine-plagioclase ash-flow tuff, and an upper rhyodacitic quartz-K-feldspar-lithic ash-flow tuff. The basal unit hosts most of the mineralization in the Esperanza sector. All units except for the uppermost 200 m of the sequence are cut out by an underlying granite intrusion.

In the southeast part of the Alex tunnel (4,680-m level) and in drill holes at higher levels, diorite is exposed that was intruded by Late Triassic granite of the Colorado unit (Figs. 3 and 4).
FIG. 2. Surface geology of the Pascua area. The lines CA-00 and AN-00 show the locations of the corresponding cross sections and long sections presented in later figures. Grid in UTM.
Based on this crosscutting relationship, the diorite is interpreted to be part of the Paleozoic basement. Xenoliths of diorite in the granite have been variably metasomatized, and the intruding granite was contaminated by assimilation of diorite, so that rocks in this area now range from diorite to granite in composition.

Mesozoic rocks

Early Mesozoic granitic rocks contain approximately 60 percent (80% including clasts in breccia bodies) of the Au-Ag reserves at Pascua. All granitic units are Late Triassic in age and have been dated at 191 to 193 Ma using ⁴₀Ar/³⁹Ar methods (K.A. Foland, unpub. report for Barrick Gold Corp., 1999; Bissig et al., 2001). Therefore, they are slightly younger than rocks of the Colorado unit (219–221 Ma; Martin et al., 1995) and are informally referred to as the “Pascua-Lama intrusive complex” (K. Heather, unpub. report for Barrick Corp., 2000).

All of the granitic rocks are similar in composition but subunits can be defined on the basis of texture. Granite C is a porphyritic granite and Granite A, with an average grain size of <0.5 mm, is a fine-grained variety of Granite C, whereas Granite B is a crowded porphyry. The different types of granite all have gradational or mutually crosscutting contacts, indicating that they are part of a single, multiphase intrusion.

The three granite types are irregularly layered and dip moderately to steeply west-southwest. Granite A forms the top of the intrusion and is underlain in turn by Granites B and C, with the latter comprising the local basement. The eastern contact of Granite A is adjacent to the western margin of Brecha Central (Fig. 3), from which it extends ~1,200 m northwest to intrude an overlying roof pendant of the Guanaco Sonso volcanic rocks. The contact with Granite B is irregular and dips west-southwest at ~65° to 80°. Granite B is bound to the west by Granite A and to the east by Granite C. The irregular west-southwest–dipping contact of granite C with granite B is exposed underground but generally displays a steeper angle than that between Granites A and B (Fig. 3).

Tertiary rocks

Bodies of leucocratic Bocatoma diorite (~33 Ma; Martin et al., 1995) occur as small cylindrical to irregular stocks and dikes in the Pascua area. These include the Diorita Este stock immediately east and south of the Esperanza deposit and the larger Cerro Negro stock east and north of the Penélope sector.

Several generations of rhyodacitic to lamprophyric dikes occur throughout the property. Of particular importance for the geologic history are the Tertiary rhyodacitic quartz-feldspar-biotite porphyry dikes belonging to the Pascua Formation, dated at ~7.85 Ma (Bissig et al., 2001). These dikes are known only from underground drill holes immediately east and south of Brecha Central (see below; Fig. 3). They are generally 3 to 10 m thick, commonly have 20- to 30-cm-wide

Fig. 3. Geology of long section AN-00, looking northeast. Most of the long section is occupied by the three granite types and the large breccia body (Brecha Central) on the northwest side of the long section, Brecha Central.
chilled margins, and generally strike north and northwest. Although volumetrically minor, these dikes are significant because they cut both the main stage of pyrite-enargite mineralization and the later silver stage and thus provide a minimum age for mineralization.

**Breccias (Tertiary)**

There are several generations of breccias in the deposit. Two breccia types, a milled quartz- and a gray matrix-bearing variety, predate development of the Brecha Central breccia pipe, which contains ~25 percent of the gold mineralization. A subordinate coeval body, Brecha Pedro, has similar features to Brecha Central (Figs. 2, 3). Pebble dikes and breccias containing a matrix of alunite and jarosite postdate mineralization.

The premineralization breccias are minor, fault related, and locally form dikes. The silicified milled quartz-breccia occurs in Granite B within a fault zone along the southern margin of Brecha Central (Fig. 2). The gray-matrix breccia dikes occur throughout the deposit, are commonly less than 1 to 2 m wide, and are controlled by lithological contacts and faults (Fig. 2).

Brecha Central is a large breccia pipe that contains clasts of previously altered and veined rocks and an altered rock-flour matrix. This breccia formed prior to the main stage of mineralization at Pascua and is an important host for the later gold, silver, and copper. The pipe was emplaced along a regional lineament, Quebrada de Pascua (280°–315°), and has dimensions of 275 by 520 m at the erosional surface and 170 by 400 m at a depth of 300 m. At a ~700-m depth, the pipe splits into several smaller structurally controlled pipes. The surface expression of the pipe is a 100-m-deep depression, extending west-northwest, which is filled with subhorizontal sedimentary breccias and fine clastic sediments (Figs. 2, 3).

At the level of the Alex tunnel (4,680 m), Brecha Central can be subdivided into three zones: (1) a heterolithic, matrix-supported central zone (Fig. 4A); (2) a dominantly monomictic, matrix- or clast-supported marginal zone; and (3)}
a surrounding stockwork zone (Fig. 4B). In the central zone, subrounded to rounded fragments range from 0.1 to 1 cm and locally are up to 3 cm in diameter. The clasts comprise ~70 percent of the total volume of Brecha Central, and fragments are variable in composition. Clasts in the central zone are composed of unmineralized granite and granodiorite, with minor quartz porphyry, dike, and fine-grained pyrite (Fig. 4A). The matrix is a strongly altered, fine-grained mix of clasts and rock flour with compositions similar to those of the coarser fragments. The matrix averages ~40 percent by volume in the central zone of the breccia body and is now composed of altered rock flour, alunite, pyrite, enargite, native sulfur, clays and soluble sulfates.

The marginal zone of the breccia is between 10 and 30 m but generally 10 to 20 m thick and contains larger fragments than the central zone, with over 60 percent of fragments being > 5 cm in diameter. Clasts are fragments of Granite B or C or hybrid diorite and/or granite (i.e., the wall rocks to the breccia pipe).

The surrounding stockwork zone contains veins, many of which were reactivated after breccia emplacement and prior to mineralization. Postbrecciation stockwork veins contain, in order of appearance from the margins inward, quartz, alunite, ± pyrite, ± enargite, ± baryte (Fig. 4B). Larger veins are locally laminated, in which case they repeat, completely or partially, the previously mentioned mineral sequence.

On the 4,680-m level, there is a small breccia body adjacent to the eastern edge of Brecha Central with a clast-supported outer part and a 1- to 2-m-wide subvertical matrix-supported core. The clasts in this breccia are mainly angular to subangular and range in size from 0.5 to 5 cm. They are composed of granite and account for 40 to 55 percent of the rock. A feature of particular interest is that the matrix is composed of ore-related minerals, including barite, with lesser alunite, pyrite, and enargite (Fig. 4C). Locally, the breccia is strongly mineralized, containing up to 120 g/t Au, 50 g/t Ag, and 1.8 wt percent Cu over 1 m. This breccia is distinctive because it is the only known body of rock in which barite precipitated before alunite and, based on its matrix composition, may be the only breccia that formed contemporaneously with main-stage mineralization.

Numerous postmineralization breccia dikes occur throughout the deposit area. Late breccias generally consist of het erotlitic, subangular to angular fragments, and an alunite-jarosite matrix. They are up to 25 m in width but are generally less than a meter wide, crosscut mineralization, and contain mineralized fragments (Fig. 4D). A 2-m-wide, subvertical, west-northwest–trending pebble dike cuts the lower, western margin of Brecha Central. It consists of subrounded, 0.5- to 15- to 20-cm-diam, Granite A and B clasts in a beige to cream rock-flour matrix altered to subequant alunite, opal, and ± jarosite.

Structure

Faults and fractures have been mapped in detail at a scale of 1:250 underground and 1:500 on the surface. The more detailed underground data set was collected from thirty-seven 10- to 25-m traverses in the Alex tunnel (4,680 level). The structures have been divided into three groups based on their dip: low-angle faults dipping less than 30° (20% of the data), intermediate-angle faults dipping between 30° and 50° (17%), and high-angle faults dipping over 50° (63%). On the basis of strike, there are six major sets of high- to intermediate-angle structures and one set of low-angle structures in the deposit area. The high- to intermediate-angle faults, all of which contain gold-copper mineralization, have been subdivided in order of decreasing age into trends named Pascua (280°–315°), Pedro (345°–010°), Esperanza (010°–030°), José (315°–345°), Raúl (030°–065°), and Escondite (065°–100°). Commonly, mineralization is concentrated along high- to intermediate-angle faults, and fault intersections have formed loci for breccia pipes and widespread mineralization (Fig. 5). Low-angle fractures also locally contain significant gold-copper mineralization. The importance of each set of faults and/or fractures varies in different parts of the deposit. For example, the Pascua, Pedro, and José trends control most of the mineralization in the Brecha Central part of the deposit (Fig. 5), whereas the Raúl, José, and Esperanza trends control mineralization in the Seis Esquinas and Escondite mineralized centers (Fig. 6). Overall, alteration and mineralization are mostly constrained to the south and north by the presence of faults and fractures oriented along the Pascua trend (280°–315°).

Mineralized Centers

The Pascua deposit consists of a large, well-mineralized, gold-silver zone (Brecha Central), and several smaller gold and silver zones of varying size and grade. There are 14 significant mineralized intersections large enough to be named, four of which are within and around breccia pipes (Central, Pedro, Morro Oeste, and Huerfano). Mineralized centers are defined as potentially mineable zones of mineralization with a gold grade of >2 g/t and/or a silver grade of >60 g/t. Based on gold and silver concentrations, the most significant mineralized centers, in addition to Brecha Central, are Brecha Pedro, Frontera, and Esperanza Norte (Fig. 6). Brecha Central and peripheral mineralized centers are linked by fault and/or fracture sets as described above. Alteration patterns and sequences are similar for all centers.

Hydrothermal Alteration

Hydrothermal alteration at Pascua is widespread but is most intense in and around the mineralized centers. The various types of alteration were mapped at a scale of 1:2,500 based on drill core logging as well as surface and underground mapping. The mineralogy of the ore and alteration assemblages was evaluated in the field with a portable spectrometer (PIMA and Field SpecPro: 350–2,500 nm) and in the laboratory by polished thin section petrography, X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron microprobe analyses.

Two major episodes and one minor episode of hydrothermal alteration have been identified: an early, pre-Brecha Central stage (stage I), with a restricted silicic, argillic and jarositic overprint (stage Ib), and a late-stage alteration, post-Brecha Central, prior to and in part overlapping with the main Au-Ag-Cu mineralization event (stage II). Stage I was dominated by advanced argillic and minor vuggy silica alteration and was accompanied by subordinate argillic and propylitic alteration (Figs. 7, 8). Stage II alteration includes both
advanced argillic and vuggy silica alteration and overprints stage I and Ib altered rocks. Supergene alteration produced jarosite and soluble sulfates such as coquimbite, copiapite, voltaite, and romerite (Chouinard, 2003).

**Early alteration (stage I)**

**Advanced argillic alteration:** Stage I advanced argillic alteration is characterized by quartz, alunite, pyrite, and rutile; minor pyrophyllite, kaolinite, and/or dickite occur locally. The alunite forms tabular crystals or bladed clusters that occur with quartz and pyrite I (Fig. 9A). Generally, alunite crystals are free of solid inclusions and show little evidence of compositional zoning (Deyell et al., 2005). Early pyrophyllite co-precipitated with alunite contains corroded margins and overgrowths of alunite, suggesting that some of the alunite-pyrophyllite assemblage may have formed in a deep zone of the early stage I advanced argillic alteration (Deyell et al., 2005). Quartz crystals are anhedral, generally less than 40 µm in diameter, and commonly form intergrowths with alunite that are interpreted to have replaced feldspar (Fig. 9A). Pyrite I commonly has replaced biotite and hornblende, occurs as euhedral to subhedral crystals, and is texturally homogeneous except for minor solid inclusions, most commonly of rutile and less commonly of sphalerite, zircon, magnetite, or quartz. The euhedral habit of this pyrite and the presence of rutile inclusions are characteristics that distinguish it from later generations of pyrite. Drill core logging indicates that pyrite I accounts for 3.7 percent of the total pyrite in the deposit (Chouinard et al., submitted). Disseminated enargite is present in rocks altered by this stage, but enargite clearly postdated alteration, as it is restricted to fractures and pores (see section on “Mineralization”).

**Vuggy silica alteration:** Stage I vuggy silica has been identified mainly in and around Brecha Central and especially from
the nature of fragments in the marginal and central zones of the breccia pipe. Vuggy silica in the Pascua sector contains coarse-grained primary quartz in a groundmass of fine-grained quartz that increases in grain size toward cavities. Cavities, which account for ~5 percent of the rock, are commonly lined by quartz and locally chalcedony (Fig. 9B). Vuggy silica I lacks sulfide and sulfosalt minerals. An unidentified Ti-K-(Fe) soluble sulfate occurs in some vugs.

Argillic alteration: Stage I argillic alteration is characterized by illite without alunite and grades outward to smectite, interlayered illite-smectite, and minor kaolinite and/or dickite that variably replaced primary feldspars. Argillic alteration is commonly well developed and pervasive but generally does not destroy primary textures of the host granite.

Propylitic alteration: Propylitically altered rocks contain mainly quartz, chlorite, illite, epidote, gypsum, and kaolinite, with minor carbonate and pyrite. Primary plagioclase (An$_{30-35}$) was altered to more sodic compositions and/or locally to epidote, sericite, and ankerite. Biotite was replaced variably by chlorite and calcite and irregular patches of epidote. Fine-grained sericite, calcite, and chlorite are common in the groundmass, and gypsum occurs in veinlets up to 5 mm across, which make up 1 to 5 percent of the rock. Propylitized rocks do not host ore but locally contain up to 5 ppm Au in veins and/or fractures <1 cm wide.

Early alteration (stage Ib)

Transitional argillic (illitic) alteration: Alunite formed during stage I advanced argillic alteration is variably rimmed by illite and crosscut by illite veinlets in the Brecha Central area (Fig. 9C). The illite is fine grained and forms halos around alunite crystals and aggregates in stage I advanced argillic alteration. Illite-altered fragments are common in Brecha Central, but illite is absent from the matrix, constraining the timing of this alteration to between stage I advanced argillic alteration and the main brecciation event. Illite occurs locally in veinlets that cut the matrix and fragments along the margins of Brecha Central, suggesting that argillic alteration may have occurred early in the emplacement history of Brecha Central. In the Brecha Central area, the overprint of illite on alunite helps to distinguish early and late alunite (stages I and II advanced argillic alteration, see below).

Silicification: Rocks that have been altered by stage I advanced argillic alteration were locally silicified. Silicification
FIG. 7. Map showing the distribution of alteration types in and around the Pascua deposit. Stage II alteration is superimposed on early alteration types. Therefore, the advanced argillic alteration zone encompasses both early and late (stages I and II) advanced argillic events.
FIG. 8. A. Distribution of alteration types in long section AN-00, looking northeast. Stage II alteration is superimposed on earlier alteration types. Therefore, the advanced argillic alteration zone encompasses both early and late (stages I and II) advanced argillic events. Faults shown in Figure 3 have been omitted for clarity. B. Distribution of alteration types on cross section CA-00, looking northwest. The distribution and intensity of alteration, although discontinuous, are similar to those presented in long section AN-00. In general, alteration zones are narrower in the southwest-northeast cross sections through the hydrothermal system.
FIG. 9. Photographs and photomicrographs of the principal alteration types. A. Photomicrograph of advanced argillic I alteration, showing feldspars replaced by fine-grained quartz, alunite, and fracture-controlled pyrite. Cross-polarized light. B. Photograph of stage I vuggy silica rock from a fragment within Brecha Central. C. Argillic alteration superimposed on stage I advanced argillic alteration. The photomicrograph shows illite along alunite grain margins and the occurrence of illite pockets in alunite-rich zones. Cross-polarized light. D. Photograph from the Alex tunnel (4,680-m elev), showing jarosite-bearing rocks (yellow) cut by alunite-pyrite-enargite stockwork veins. Hammer for scale: 45 cm. E. Photograph of stage II advanced argillic alteration with stockwork veins, cutting stage I advanced argillic alteration. The gray halos contain abundant quartz and lesser alunite, and the veins consist of alunite and pyrite with minor enargite. F. Sample of Brecha Central in which the matrix and most fragments have been replaced by stage II vuggy silica. Red marks are paint. G. Photomicrograph of vuggy silica II alteration infilling by later pyrite (opaque) and szomolnokite (highly birefringent). Cross-polarized light.
occurs as halos up to 2 m wide along fractures cutting stage I advanced argillic alteration. The quartz is fine grained, forms veinlets, fills voids, or completely replaced the altered rocks. Silification is associated locally with quartz ± hematite veinlets that cut the matrix and fragments along the margins of Brecha Central. However, the extent of this silification is not well constrained.

Jarositic alteration: Jarosite occurs predominantly as a supergene alteration mineral. However, in the Alex tunnel (4,680-m elev.), jarosite veins and patches are cut locally by mineralized stockworks, suggesting that some jarosite precipitated during the hypogene event, but we cannot rule out the possibility that this jarosite too was supergene (i.e., that hydrothermal activity was intermittent and that there were intervening periods of supergene alteration). The jarosite forms rims around pyrite-rich patches in rocks that were affected by stage I advanced argillic alteration and is cut by later mineralization (Fig. 9D).

Late alteration (stage II)

Advanced argillic alteration: Stage II advanced argillic alteration postdated emplacement of Brecha Central and overprinted previously altered rocks (e.g., Fig. 9E). Generally, stage II advanced argillic alteration is restricted to halos containing quartz and alunite around veins that cut stage I advanced argillic alteration. However, in several parts of the deposit, vein densities were sufficiently high to produce pervasive stage II advanced argillic alteration. Below 4,500 m, pyrophyllite occurs locally instead of dickite or kaolinite and is associated with zinnyte and diaspore.

Some of the quartz in stage II was deposited during the earlier alteration but can be distinguished by its occurrence as fine-grained aggregates along vein walls and in vugs. Similarly alunite of stage II locally can be distinguished from alunite of stage I because it forms overgrowths on earlier alunite that was partially altered to illite (as noted above). Stage II alunite is commonly zoned (Deyell et al., 2005) and also occurs in veins, and along with quartz, as disseminations and open-space fillings in the Brecha Central matrix and fragments.

Vuggy silica alteration: Stage II vuggy silica alteration includes variably leached and porous rocks and massive silicified rocks. This vuggy silica replaced rocks affected by stage I advanced argillic alteration and stage Ib argillic alteration, including fragments and matrix in Brecha Central above ~4,750-m elevation (Fig. 9F). Stage II vuggy silica consists of fine-grained secondary quartz, locally preserved primary quartz phenocrysts, and minute relict grains of rutile. Rocks that are replaced by stage II vuggy silica have variable porosity, in part due to local redistribution of silica that filled vugs, producing rocks with an average <5 percent pore space (Fig. 9F), and subsequent infilling by later main-stage and Ag-rich mineralization (Fig. 9G). Stage II vuggy silica was produced by leaching of earlier alunite with remobilization of quartz and variable addition of silica (Chouinard, 2003). Zones of stage II vuggy silica were the locus of extreme leaching, in which even titanium was mobile, and contain significantly less rutile than the zones of stage I vuggy silica (Chouinard, 2003).

Steam-heated argillic alteration

Quartz-kaolinite alteration dominates the top of the preserved hydrothermal system where it is observed at elevations greater than 4,950 m and locally along structures down to an elevation of ~4,750 m. The alteration assemblage is quartz, chalcedony, opal, kaolinite and native sulfur. Although primary igneous textures are commonly preserved, there is a strong overprint of opaline silica on altered and locally fresh rocks. Native sulfur occurs irregularly above the mineralized centers in the Pascua area, in west-northwest– and northeast–trending zones along a subhorizontal layer between 5,000 and 5,100 m. Deyell et al. (2005) found that oxygen and hydrogen isotope analyses of rare alunite are consistent with the steam-heated origin of the alteration.

Distribution of alteration types

Stage I advanced argillic alteration is widespread, dominates the advanced argillic alteration zone, which includes both stages I and II alteration, and formed prior to significant brecciation. It is also the dominant alteration type in fragments within the Brecha Central and Brecha Pedro pipes. Minor amounts of dickite and kaolinite in stage I advanced argillic alteration occur in the periphery of mineralization centers. Dickite typically occurs closer to the core zones and kaolinite farther away, although this varies. The outer limit of stage I advanced argillic alteration is also the limit of potentially economic mineralization. However, the distribution of stage I alteration is difficult to map owing to the overprint by stage II variable degrees of development of the two alteration stages. Therefore, advanced argillic alteration has been mapped as a single facies (Fig. 8). Based on common patches of stage I advanced argillic alteration and its occurrence above vuggy silica II, it is thought to have been more widely distributed than can be observed today and to have been the dominant alteration type prior to the development of stage II vuggy silica alteration.

Argillic alteration is not significant in the main Brecha Central area but defines the northern and southern limits of the hydrothermal system (Figs. 7, 8B). Argillic alteration also occurs eastward toward the Argentinean side of the deposit. Significant mineralization does not occur within the argillic zones. Propylitic alteration is only developed locally, commonly in diorite and andesite stocks and dikes, and occurs mainly on the edges of or between mineralized centers (Figs. 7, 8B). Stage I vuggy silica and silicification have limited distribution and cannot be shown at the map scale of 1:2500.

Stage II vuggy silica and local silicification (post-Brecha Central) are dominant above the zones of advanced argillic alteration and below the quartz-kaolinite ± alunite (steam-heated) zone (Fig. 8). Stage II vuggy silica forms a cap generally above the Alex tunnel level (4,680 m), comprising a subhorizontal undulating tabular zone ranging in thickness from 100 to >300 m. It extends from an elevation of 4,625 to 5,000 m through most of the deposit area and is best developed between 4,720 and 4,900 m. Small zones or pockets of advanced argillic alteration occur locally within the area dominated by stage II vuggy silica. Rocks replaced by stage II vuggy silica are an important host for the main Au-Ag-Cu mineralization. Their present distribution is irregular but is interpreted to have been widespread at the time of mineralization and replaced by the latter.

Early alteration (stage I) had strong structural control and displays significant lateral zonation. Similarly there was strong
structural control of stage II advanced argillic and vuggy silica alteration, but these were also influenced by the distribution and intensity of the previous alteration. Stage II alteration is best developed in the upper parts of the deposit where it is vertically zoned, with vuggy silica overlying the advanced argillic alteration. Overall, stages I, Ib, and II are interpreted to represent a continuum of hydrothermal activity, although separate episodes of alteration represented by each stage are distinguished by clear crosscutting relationships.

Au-Ag-Cu Mineralization

The main ore minerals and hosts of gold are pyrite and enargite; gold also occurs in native form. Based on petrographic and field studies, the main-stage Au-Ag-Cu mineralization can be divided into four main zones (1) alunite-pyrite-enargite (APE), (2) pyrite, (3) pyrite-szomolnokite (Py-Sz; FeSO₄·H₂O), and (4) native gold. These zones formed after emplacement of Brecha Central and slightly overlapped in time the stage II alteration. Figure 10 shows the distribution of mineralized zones in sections AN-00 and CA-00, and Figure 11 shows the gold distribution. Distribution of the mineralized zones appears to be relatively consistent in sulfide-rich mineralized areas of the deposit. Relationships among these zones and the various alteration facies are summarized in Table 1.

Distribution of mineralized zones

Stockwork mineralization is concentrated in the deeper and outer parts of the deposit, particularly in the APE zone. Most of the other parts of the deposit contain disseminated mineralization. The pyrite zone generally has greater vertical than horizontal extent and occurs locally both above and below the native gold zone. The pyrite-szomolnokite zone surrounds the APE mineralization and also extends downward along fault zones to an elevation of ~4540 m. The native gold zone is dominant in the upper levels of the deposit in stage II vuggy silica rocks that are generally located above the pyrite and pyrite-szomolnokite zones.

Northwest-oriented longitudinal sections, approximately parallel to the Quebrada de Pascua fault system, best illustrate lateral variations in the hydrothermal system. Brecha Central and Seis Esquinas in section AN-00 show a complete sequence of main-stage mineralized zones (Fig. 10A).

In the Brecha Central area, the pyrite-szomolnokite zone forms an intermittent, 50- to 100-m-thick, tabular blanket at elevations from 4,700 to 4,840 m. It occurs above the APE zone and above and to the west of the pyrite zone (Fig. 10A). Mineralogical zonation from bottom to top includes native gold and silicification at depth, followed by APE, pyrite, pyrite-szomolnokite, and native gold in the uppermost zones. The eastern side of Brecha Central appears partially in section AN-00, and the vertical extent of the zone of mineralization is partly fault and/or fracture controlled.

The Seis Esquinas mineralized center is also fault and/or fracture controlled (Fig. 3). The sequence of mineralized zones is similar to that observed in the Brecha Central area, but the zonation at Seis Esquinas is more horizontal than vertical. The Seis Esquinas center is near the margin of the deposit as defined by gold grades. Early alteration is mainly fault and/or fracture controlled, breccias are minor, and mineralized zones in the Seis Esquinas area lack significant lateral distribution.

<table>
<thead>
<tr>
<th>Alteration type</th>
<th>Characteristics</th>
<th>Spatially associated mineralized zones</th>
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<tbody>
<tr>
<td>Pre- to postmineralization</td>
<td>Steam-heated</td>
<td>Quartz and opal, kaolinite, native sulfur</td>
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<tr>
<td>Late alteration prior to mineralization</td>
<td>Vuggy silica II</td>
<td>Native gold</td>
</tr>
<tr>
<td>(post-Brecha Central)</td>
<td>Variation from vuggy silica to massive</td>
<td>Pyrite</td>
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<td></td>
<td>silicification, variable throughout upper</td>
<td>Pyrite-szomolnokite</td>
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<td>elevations</td>
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<td></td>
<td>Advanced argillic II</td>
<td>Quartz-alumite sulfides</td>
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<td></td>
<td>Quartz and alumite superimposed on</td>
<td>Alumite-pyrite-enargite (APE)</td>
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<td>previously altered rocks</td>
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<tr>
<td>Stage Ib alteration (superimposed on stage</td>
<td>Argillic, silicic, and jarositic</td>
<td>Illite-bearing argillic superimposed on alunite</td>
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<td>I, syn-Brecha Central)</td>
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<tr>
<td>Stage I alteration (pre-Brecha Central)</td>
<td>Vuggy silica I</td>
<td>Minor alteration</td>
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<td></td>
<td>Advanced argillic I</td>
<td>Quartz-alumite-pyrite</td>
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<td></td>
<td>Argillic and propylitic</td>
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<td>smectite; propylitic alteration dominated by</td>
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<td></td>
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<td>chlorite, illite, and epidote</td>
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Fig. 10. A. Distribution of mineralized zones in long section AN-00, looking northeast. The location of the section is indicated in Figure 2. Blank areas are generally unmineralized. B. Distribution of mineralized zones in cross section CA-00, looking northwest. The location of the section is indicated in Figure 2. The section cuts the Brecha Central mineralized center.
Fig. 11. A. Gold contours in long section AN-00, looking northeast. The location of the section is indicated in Figure 2. The high-grade zone corresponds mainly to the fine-grained breccia core of Brecha Central. Note the well-developed vertically oriented zones of mineralization, which reflects strong fault control. The subhorizontal distribution of the gold values reflects the distribution of vuggy silica II alteration (Fig. 8). High grades coincide with the location of Brecha Central.

B. Contours showing the distribution of gold in cross section CA-00, looking northwest. The location of the section is indicated in Figure 2. As in section AN-00, the Au distribution shows an important vertical component related to faulting, and the high-grade area corresponds to the core of the Brecha Central.
Alunite-pyrite-enargite zone (APE)

Alunite-pyrite-enargite mineralization fills open spaces in the Brecha Central area, occurs in veins with halos of stage II advanced argillic alteration and as minor disseminations in host rocks in stockwork zones (Figs. 12A, 13). Gold, silver, and copper minerals are hosted mainly by stage II pyrite and enargite. The alunite in the APE zone belongs to stage II advanced argillic alteration and locally contains rare inclusions of native gold. Pyrite IIa is characterized by a dull luster and locally coprecipitated with alunite but was deposited mainly after alunite. It contains most of the gold in this zone and in the other zones (see below). Pyrite IIb formed mainly after pyrite IIa and is distinctively brassy and gold free (Fig. 12B). Native gold, calaverite (AuTe2) and minor electrum occur locally as inclusions in pyrite IIa and along fractures in pyrite IIa and IIb and in alunite. Enargite occurs as isolated grains and massive aggregates and contains a variety of solid inclusions (Fig. 12C) of pyrite IIa, native gold, calaverite, stibnite, cassiterite, muthmannite [(Au,Ag)Te], goldfieldite [Cu11(As,Te,Sb)3S3], yuanjiangite (AuSn), and unidentified (<1 µm) Cu-Sn-Zn-S phases. Cassiterite inclusions are particularly common. Yuanjiangite inclusions are less than 10 µm in diameter and represent the first reported occurrence of this mineral outside China and the first occurrence with a known genetic context (cf. Chen et al., 1994). Native gold and calaverite are the most abundant gold-bearing minerals in enargite. Minute crystals (<1 µm) of electrum also are present in some enargite grains.

Chalcopyrite is observed in veins in a few deep drill holes at depths below 4600 m elevation but is not common. It is associated with pyrite and enargite and occurs as inclusions and intergrowths with pyrite. Early quartz formed prior to precipitation of chalcopyrite in the veins and contains liquid-vapor fluid inclusions with halite cubes; these inclusions are not observed in quartz from areas of the deposit without chalcopyrite. Greigite (Fe2S3), alunite, possible luzonite, tetrahedrite-tennantite, marlshite (CuI) and miersite (CuAgI) precipitated toward the end of or after main-stage Au-Cu mineralization and are restricted to rocks of the APE zone. They commonly occur in reopened APE-mineralized veins (Fig. 12D).

Pyrite zone

In the pyrite zone, Pyrite IIa is the principal gold-bearing mineral and is disseminated in the stage II vuggy silica cap. It is very fine grained and generally has a powdery texture due to apparent leaching. Brassy pyrite IIb is present locally in this zone but is not abundant. Alunite is rare in this zone, and enargite occurs in variable but commonly minor proportions. These features distinguish the pyrite zone from the APE zone. Rocks of the pyrite zone are characterized by lower porosity than the APE or pyrite-szomolnokite zones and relatively low metal grades, averaging 0.93 g/t Au and 0.08 percent Cu.

Pyrite-szomolnokite zone

The pyrite-szomolnokite assemblage is mainly disseminated in the stage II vuggy silica. This zone contains submicroscopic gold, silver and copper in pyrite IIa, enargite and locally szomolnokite (Figs. 12E, 14). Minor native gold inclusions occur in both pyrite IIa and enargite.

Both pyrite IIa and IIb are disseminated in the pyrite-szomolnokite zone. Pyrite IIa occurs as anhedral to rare euhedral grains, is locally colloform (Fig. 12F), has a dull greenish luster, and contains galena inclusions, whereas pyrite IIb is generally subhedral and inclusion free. Szomolnokite is typically massive or present in veinlets (0.1–5 mm diam), is dark orange-brown to reddish orange, and decomposes on exposure to heat or sunlight to a pale orange powder (Fig. 12G). Commonly, it contains liquid-vapor fluid inclusions (Fig. 12H) that start leaking at T>80°C. Most of the szomolnokite in the pyrite-szomolnokite zone formed after main-stage Au-Ag-Cu mineralization and appears to correspond to the late barren stage that overprinted the APE zone (see below).

Pyrite IIa and IIb appear to have been replaced locally by szomolnokite (Figs. 12F, 15), and enargite has been replaced locally by arsenolite (As2S3) and szomolnokite. Rare covellite fills fractures in pyrite. Gravity of pyrite IIa locally contain small, tabular holes that are inferred to represent former alunite crystals from early advanced argillic alteration, which occurs above and below the stage II vuggy silica zone. This is interpreted to indicate that alunite was at least locally stable at the time of pyrite IIa and, by inference, gold mineralization in the pyrite-szomolnokite zone.

Native gold zone

The native gold zone consists of gold-bearing stage II vuggy silica, in which alunite, pyrite, and enargite are absent or rare. This mineralization is hosted mostly by pale gray quartz veins and silicified rocks, in which the gold is attached to or included in quartz and later Ag halides. Precipitation of native gold occurred after the stage II vuggy silica alteration and is interpreted to have been coeval with deposition of gold in pyrite and enargite in other mineralized zones.

In the deeper levels of the deposit, below the APE mineralization, quartz-bearing stockwork zones also contain native gold without sulfides.

Postore minerals

Barite, which formed after enargite and gold, occurs as anhedral to subhedral grains in massive aggregates and commonly fills vugs that host ore minerals. Angleite occurs as anhedral grains, commonly associated with barite, and in fractures in pyrite and enargite. In the pyrite-szomolnokite zone, anglesite and barite occur as anhedral grains filling cavities and fractures, and some rhombic anglesite prisms occur in szomolnokite. These sulfate minerals mark the end of the gold mineralization stage.

Silver Enrichment

Economically significant, late-stage Ag-rich mineralization occurs in the upper parts of the deposit (∼4,700 m) and overprints the main-stage Au-Ag-Cu mineralization. The silver zone is subhorizontal, between 100 to 200 m thick, and has an Ag/Au ratio >100, whereas the Au-Ag-Cu mineralization typically has an Ag/Au ratio of less than 25. This silver zone overlies the high-grade Brecha Central mineralized center and other smaller centers and may permit mining of the entire volume rather than a group of separate relatively gold-rich
zones (Figs. 16, 17). Most high-grade silver in the deposit occurs in this blanket, which dips gently east and lies above an elevation of ~4,500 m. However, silver minerals locally occupy fractures in enargite down to an elevation of at least 4,630 m.

The principal silver minerals are iodargyrite (AgI) and chlorargyrite (AgCl), which are accompanied by minor proportions of calomel (HgCl), native silver, native selenium, and silver selenides that have filled void spaces and fractures, mainly in stage II vuggy silica and APE rocks (Fig. 15). The silver minerals are generally less than 10 µm in size and too fine grained to establish mineralogical zoning in the silver-rich ores.

Chronology of Hydrothermal Events

The deposit is interpreted to have evolved in several stages, as summarized in Figure 18. Hydrothermal activity started with widespread, stage I advanced argillic alteration, which is interpreted to have occurred at 9.0 ± 0.2 Ma, based on 40Ar/39Ar dating of alunite (Bissig et al., 2001). This was followed locally by weak argillic alteration prior to or contemporaneous with the emplacement of Brecha Central. A second stage of advanced argillic and widespread vuggy silica alteration followed at between 8.6 ± 0.4 and 8.76 ± 0.63 Ma, based on 40Ar/39Ar ages of stage II alunite (Bissig et al., 2001; Deyell et al., 2005). Although the errors on the age determinations do not allow clear separation of the stage I and stage II advanced argillic alteration events, the presence of stage I-altered fragments in Brecha Central cut by veins with stage II alteration envelopes indicates that stages I and II alteration predated and postdated emplacement of Brecha Central, respectively. Main-stage Au-Ag-Cu mineralization commenced during the waning stages of stage II alteration and was followed by later Ag mineralization. 40Ar/39Ar age determinations of biotite-bearing rhodacitic dikes that cut the main mineralization and later Ag-rich zones indicate that hydrothermal activity terminated between 7.83 and 7.86 ± 0.3 Ma (K.A. Foland, unpub. report for Barrick Gold Corp., 1999; Bissig et al., 2001). The Pascua hydrothermal system is thus interpreted to have been active for a maximum period of 1.2 Ma.

Discussion

Although similar in many respects to typical high-sulfidation deposits (cf. Heald et al., 1987; White, 1991; Arribas, 1995; Sillitoe, 1999; Cooke and Simons, 2000; Hedenquist et al., 2000), the Pascua deposit differs from other deposits of this type in several important aspects. Most notable among these differences are the lack of a genetic relationship between the host rocks and the hydrothermal system, the precipitation of gold with pyrite and enargite, the multistage evolution of the system, and the considerable silver enrichment that followed the main-stage gold mineralization.

Host rocks and source of fluids

High-sulfidation epithermal ore deposits typically form contemporaneously with volcanism, and related intrusions and volcanic rocks are the most common host to mineralization (Hedenquist et al., 2000). At Pascua, epithermal alteration and mineralization occurred in granitic intrusions of the Pascua-Lama intrusive complex, which are approximately 184 m.y. older than the alteration and mineralization. There is thus little direct evidence of an association between igneous activity and mineralization. The only demonstrably young igneous rocks are the biotite-bearing rhodacitic porphyry dikes that cut mineralization on the eastern side of the deposit. A strong electrical self-potential anomaly to the east of the Pascua deposit could indicate the presence of an unexposed intrusion on the Argentine side of the property (Fig. 19).

A magmatic fluid source is indicated by oxygen and hydrogen isotope data for alunite from both early and late alteration (Deyell et al., 2005). The occurrence of fluid inclusions with halite daughter crystals in chalcopyrite-bearing quartz veins in the deepest parts of the deposit (below 4,500 m) is also consistent with a magmatic fluid; fluid inclusions above 4500 m have low salinities (from 1.1–4.6 wt % NaCl equiv; Chouinard, 2003). A similar relationship between high- and low-salinity fluid inclusions has been documented in other high-sulfidation epithermal systems, for example, by Arribas et al. (1995) at Rodalquilar (Spain) and by Hedenquist et al. (1998) at Far Southeast and Lepanto (Philippines). In both cases there is a transition from porphyry-style alteration and mineralization and associated high-salinity brines to higher level high-sulfidation mineralization associated with low-salinity fluid at higher levels.

Multistage fluid evolution

The only fluid inclusions considered primary and large enough to analyze were in two samples of enargite. One of these samples, from the eastern margin of Brecha Central,
yielded an average homogenization temperature of ~169°C, and the second sample from within Brecha Central gave an average homogenization temperature of ~278°C. The only other information on temperature is from Deyell et al. (2005), who used sulfur isotope fractionation between alunite and pyrite in the core of Brecha Central to establish a temperature range of 245° to 305°C for stage II advanced argillic alteration and associated mineralization. We have assumed that the temperature was ~250°C over much of the life of the hydrothermal system.

An important feature of the Pascua deposit is the apparent superposition of two events of high-sulfidation alteration. The first stage involved widespread quartz-alunite-pyrite and minor vuggy silica in the core of the main mineralized centers. Pyrite associated with this alteration contains approximately 0.5 percent of the total gold and no Au- or Ag-bearing solid inclusions (Chouinard et al., submitted). In addition, the stage I vuggy silica rocks contain no sulfides or sulfosalt infillings. The early alteration stage is inferred to have contributed only minor Au or Ag to the total metal budget. From the $f_{O_2}$-pH

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<th>POSTORE</th>
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<tr>
<td>PYRITE (IIa) (Au- and Ag-bearing)</td>
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<td>PYRITE IIb (brassy)</td>
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Fig. 13. Paragenetic sequence for vein halos and disseminated alunite-pyrite-enargite mineralization. The paragenetic diagram includes the associated late-stage premineralization wall-rock alteration and postore minerals. Note that alunite is mainly part of the advanced argillic II assemblage but is included in the alunite-pyrite-enargite zone because it overlaps the gold stage and locally contains native gold inclusions. Muthmannite has the structural formula (Ag,Au)Te and yuanjiangite is AuSn.

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Fig. 14. Paragenetic sequence for pyrite-szomolnokite mineralization.
conditions of alunite stability (Fig. 20), the presence of minor vuggy silica and evidence for magmatic-hydrothermal alunite (Deyell et al., 2005), we conclude that early hydrothermal alteration was the product of pervasive acid leaching by magmatic-hydrothermal fluids at pH <2 (cf. Stoffregen, 1987). Away from the main fluid conduits (fault intersections) and cores of the later mineralized centers, where fluid/rock ratios were low, reaction with the host rocks produced the peripheral zones of argillic and propylitic alteration. The argillic alteration (illite) is represented by muscovite in Figure 20.

The separation of early and late advanced argillic alteration by a stage of argillic alteration and silicification, characterized by the replacement of alunite by illite and the absence of kaolinite, indicates that pH temporarily evolved to higher values (e.g., illite is stable at pH values between 4.1 and 6.6, assuming log $a_K = -2$; Fig. 20). This change, which occurred penecontemporaneously with the emplacement of Brecha Central, was likely the result of a decrease in the flux of magmatic hydrothermal fluids and/or an influx of meteoric water. The latter would have been expected from the drop in pressure that accompanied brecciation. Silicification also would have been promoted by the drop in temperature associated with adiabatic expansion.

A second stage of advanced argillic (quartz-alunite) and extensive vuggy silica alteration indicates a return to acidic conditions. Following the approach of Stoffregen (1987), we have calculated the likely pH of the fluids using the observation that alunite was destroyed during the formation of stage II vuggy silica. At K activities of 0.01 and 0.001 and $\Sigma S = 0.01$ (cf. Stoffregen, 1987), alunite would have started to dissolve at a pH near zero (Fig. 20). The extremely low pH estimated for the formation of stage II vuggy silica is consistent with leaching of both titanium and zirconium in stage II vuggy silica rocks (Chouinard, 2003). The only plausible source for a fluid capable of such extreme leaching is the condensate of an SO$_2$-HCl-bearing magmatic vapor. We therefore propose that stage II vuggy silica alteration, which forms a blanketlike body, was caused by downward percolation of an acidic fluid from a temperature-controlled condensation horizon. The
resulting fluid-rock interaction gradually increased the pH of the downward-moving fluid and produced the underlying advanced argillic alteration.

The extensive development of stage II vuggy silica alteration and the inability of these rocks to buffer pH are thought to have resulted in the precipitation of primary szomolnokite. Szomolnokite has been interpreted in other localities to be a secondary mineral produced by oxidation of iron sulfides (cf. Jambor et al., 2000). This is also true at Pascua; however, we consider that much of the szomolnokite is hydrothermal because it is associated with colloform pyrite IIa and postore anglesite and contains liquid-vapor fluid inclusions, indicating that it formed at elevated temperature. Liquid-vapor fluid inclusions (4/1 liquid/vapor vol ratio) in szomolnokite could not be homogenized as they leaked at temperatures ranging from 80° to 150°C. Szomolnokite also
started decomposing (evident from a dark brown discol-oration of the mineral) at a temperature of ~220°C, implying that it probably formed below this temperature. Although there are no thermodynamic data with which to estimate the $f_{O2}$-pH conditions of szomolnokite formation, it is reasonable to predict that pH was very low based on the absence of alunite in szomolnokite-bearing rocks (cf. Fig. 20). This interpretation is consistent with the observation that mine waters currently precipitating szomolnokite elsewhere typically have a pH <–1 (C.A. Alpers, pers. commun., 2001). Considering that szomolnokite appears to have replaced pyrite and anglesite is common in szomolnokite-bearing rocks, $f_{O2}$ conditions were above those of pyrite stability and in the field of stability of anglesite (i.e., at log $f_{O2}$ > −42.1 at 150°C or log $f_{O2}$ > −37.2 at 200°C). The main sulfur species involved in szomolnokite formation is likely to have been HSO$^-+4$, possibly provided by the reaction,

$$\text{FeS}_2 + 2\text{H}_2\text{O} + \frac{7}{2}\text{O}_2 = \text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{HSO}_4^- + \text{H}^+.$$  (1)

**Gold deposition**

In many high-sulfidation deposits, gold enrichment is commonly associated with late-stage veining, open-space filling, and/or hydrothermal breccias, in which enargite is commonly early and predates the gold mineralization (e.g., Lepanto, Hedenquist et al., 1998; Summitville, Gray and Coolbaugh, 1994; Goldfield, Ransome, 1909; part of the El Indio deposit, Jannas et al., 1990; and Rodalquilar, Arribas et al., 1995). Moreover, the gold stage is generally characterized by the occurrence of minerals indicative of lower sulfidation state, such as tennantite-tetrahedrite, chalcopyrite, and tellurides that overprint enargite (Sillitoe, 1999; Hedenquist et al., 2000). At Pascua, main-stage gold-silver mineralization is genetically associated with pyrite and enargite, and gold and silver are structurally bound in both minerals (Chouinard, 2003; Chouinard et al., in press); they also occur as telluride and native gold inclusions, mainly in enargite, and to a lesser extent, in pyrite. Metallurgical studies indicate that sulfide ore accounts for ~62
percent, and the native gold and oxidized ore ~38 percent, of the total gold contained in the deposit (Barrick Gold Corp., unpub. data, 2002). In the sulfide ore, ~81 percent of the gold is interpreted to occur as a solid solution in pyrite; 8 percent in enargite (Chouinard, 2003), accounting for 50 and 5 percent of the total gold in the deposit, respectively. The remaining 11 percent resides in native gold and other gold-bearing minerals that occur mainly as inclusions in enargite.

Deposition of gold in epithermal systems is generally regarded to be the result of precipitation from fluids that were saturated with respect to native gold. Consequently, physicochemical factors influencing mineralization such as temperature, pressure, ligand concentration, and pH, which are controlled by mechanisms such as boiling or fluid mixing, are normally evaluated by examining their effects on the stability of the dominant gold species. However, as documented in Chouinard et al. (submitted), ~9.2 Moz of gold at Pascua was incorporated in the structure of pyrite and enargite, indicating that a significant amount of gold was likely deposited from a fluid that was undersaturated with respect to native gold. Consequently, an important part of the gold mineralization was driven not by saturation due to decreases in the stability of aqueous gold complexes but rather by processes operating at the surfaces of pyrite or enargite crystals (e.g., surface complexation) that favored the adsorption of gold and silver (see also Chouinard, 2003; Chouinard et al., in press).

Overall, the distribution of gold was controlled strongly by secondary porosity caused by extensive development of stage II vuggy silica and hydrothermal brecciation (e.g., Brecha Central and Brecha Pedro). Because stage II vuggy silica and advanced argillic alteration were produced by liquids condensed from magmatic vapor, it is possible that these vapors (highly oxidizing) also transported gold and other metals, including copper, arsenic, and silver (see review in Williams-Jones et al., 2002). This hypothesis is supported by recent fluid inclusion data from Grasberg showing that, at least at high temperature (>550°C), both gold and copper partition preferentially into the vapor rather than the coexisting magmatic brine (Heinrich et al., 1999). Further support at temperatures typical of epithermal mineralization is provided by the experimental studies of Archibald et al. (2001, 2002), which show that HCl-H2O vapors can dissolve relatively high concentrations of gold and copper at temperatures as low as 300°C. We envisage that deposition of the gold and associated metals at Pascua occurred after condensation of similar vapors. This interpretation contrasts with previous interpretations of the mineralizing processes in high-sulfidation

Fig. 19. Contours of electrical self-potential intensity values, in which the strongly anomalous values are inferred to indicate the presence of a porphyry intrusion at depth on the Argentinian side of the property.
epithermal systems, which typically invoke intermediate pH ore fluids unrelated to the condensed vapor responsible for advanced argillic alteration (e.g., White, 1991; Arribas, 1995). However, we believe that it better reflects the mineral paragenesis at Pascua, namely the association of Au-Ag-Cu mineralization with minerals like alunite and szomolnokite that are only stable at low pH and high $f_{O_2}$.

**Silver enrichment**

Silver enrichment of the type observed at Pascua is commonly attributed to supergene processes. However, both the main Au-Ag-Cu mineralization and later Ag enrichment stages occurred in a very narrow time interval (i.e., between 8.76 and 7.85 Ma: Bissig et al., 2001; Deyell et al., 2005). Secondly, there has been no significant erosion since the termination of hydrothermal activity, and the present erosional surface coincides with a zone of steam-heated rocks containing native sulfur (Bissig et al., 2002). Finally, some of the highest grade Ag mineralization (>100 g/t Ag) is in rocks in which enargite was not affected by supergene fluids. We therefore suggest that the Ag enrichment was likely hypogene in origin and occurred during the waning stages of the hydrothermal activity. In view of our model for main-stage mineralization, and the association of Ag with Hg, the most volatile of all metals, we tentatively propose that highly oxidizing magmatic vapors were also responsible for metal transport during the silver enrichment stage. Moreover, as Ag chloride complexes are generally the dominant silver species in hydrothermal liquids (e.g., Seward, 1976; Zotov et al., 1987; Levin, 1991; Gammons and Williams-Jones, 1995a; Gammons and Yu, 1997), and Migdisov et al. (1999) have shown that silver can be dissolved in significant concentrations by HCl-H$_2$O vapor (as AgCl·3H$_2$O), we further propose that the silver was transported as a halogen-bearing gas species and deposition of silver occurred during condensation of the magmatic vapors. This interpretation is consistent with the fact that halogen-bearing silver minerals are stable only under conditions of unusually low pH and high $f_{O_2}$ (Gammons and Williams-Jones, 1995b).

**Conclusions**

The Pascua Au-Ag-Cu deposit was the product of a magmatic vapor-dominated hydrothermal system, which developed in several stages. The early magmatic vapors condensed to highly acidic liquids, which produced a sequence of advanced argillic, minor vuggy silica, argillic, and propylitic alteration. This was followed by emplacement of Brecha Central and other breccias, which led to an influx of meteoric water and higher pH conditions, causing argillic (illite-bearing) alteration, local silification, and the formation of primary jarosite. A resumption of magmatic vapor-dominated hydrothermal activity produced a second stage of intense
alteration represented by widespread vuggy silica and advanced argillic mineral assemblages. This was succeeded by main-stage Au-Ag-Cu mineralization involving incorporation of Au in pyrite and enargite and deposition of native gold. Gold and associated metals are interpreted to have been transported by magmatic vapors that produced condensates from which pyrite and enargite were precipitated. Deposition of barite and anglesite at lower elevations and barite and anglesite plus hydrothermal szomolnokite at higher elevations marked the end of the gold mineralization stage. These sul- fates formed as a result of the interaction of cooler magmatic fluids with host rocks that had lost their pH and fO₂ buffering capacities due to earlier alteration. The last mineralizing event was a silver-enrichment characterized by halogen-bearing minerals in the uppermost parts of the deposit. The silver chloride minerals are thought to have formed from the condensates of lower temperature magmatic vapors during the waning stages of the hydrothermal system.

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REFERENCES


### APPENDIX

#### fO₂-pH Diagram

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log K (250°C and vapor saturated pressure)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S° + 2O₂(g) = HSO₄⁻ + H⁺</td>
<td>61.97</td>
<td>1, 2, 3</td>
</tr>
<tr>
<td>H₂S° + 2O₂(g) = SO₂⁻ + 2H⁺</td>
<td>40.80</td>
<td>1, 3</td>
</tr>
<tr>
<td>HS⁻ + 2O₂(g) = SO₂⁻ + H⁺</td>
<td>63.75</td>
<td>1, 3</td>
</tr>
<tr>
<td>FeS + 0.5O₂(g) + H₂S° = FeS₂ + H₂O</td>
<td>22.56</td>
<td>1, 3</td>
</tr>
<tr>
<td>FeS + 0.5O₂(g) + HS⁻ + H⁺ = FeS₂ + H₂O</td>
<td>27.98</td>
<td>1, 3</td>
</tr>
<tr>
<td>3FeS + 3H₂O</td>
<td>11 O₂(g) = Fe₂O₃ + 6SO₄²⁻ + 12H⁺</td>
<td>251.25</td>
</tr>
<tr>
<td>2Fe₂O₃</td>
<td>16.19</td>
<td>1, 3</td>
</tr>
<tr>
<td>2KAl₃(SO₄)₂(OH)₆ + 6SiO₂ + 3H₂O = 3Al₂Si₂O₅(OH)₄ + 2K⁺ + 4HSO₄⁻ + 2H⁺</td>
<td>216.63</td>
<td>1, 3, 6</td>
</tr>
<tr>
<td>8Cu₃AsS₄ + 9O₂(g) + 6H₂O = 2Cu₁₂As₄S₁₃ + 12H⁺ + 6SO₄²⁻</td>
<td>249.09</td>
<td>1, 2, 3, 6</td>
</tr>
<tr>
<td>8Cu₃AsS₄ + 9O₂(g) + 6H₂O = 2Cu₁₂As₄S₁₃ + 6H⁺ + 6HSO₄⁻</td>
<td>−121.53</td>
<td>1, 3, 6</td>
</tr>
<tr>
<td>8Cu₃AsS₄ + 6H₂O = 2Cu₁₂As₄S₁₃ + 3O₂(g) + 6H⁺ + 6HS⁻</td>
<td>−165.63</td>
<td>1, 3, 6</td>
</tr>
<tr>
<td>8Cu₃AsS₄ + 6H₂O = 2Cu₁₂As₄S₁₃ + 3O₂(g) + 6H⁺ + 6HS⁻</td>
<td>63.35</td>
<td>3, 7</td>
</tr>
</tbody>
</table>


### APPENDIX REFERENCES


