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# **Cerro Quema (Azüero Peninsula, Panama): Geology, Alteration, Mineralization and Geochronology of a Volcanic Dome-Hosted High Sulfidation Au-Cu Deposit.**

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## **Abstract**

Cerro Quema (Azüero Peninsula, SW Panama) is a high sulfidation epithermal Au-Cu deposit hosted by a dacite dome complex of the Río Quema Formation (Late Campanian to Maastrichtian), a fore-arc basin sequence. Mineral resource estimate (Indicated + Inferred) are 30.86 Mt @ 0.73 g/t Au, containing 728,000 Oz Au (including 76.900 Oz AuEq of Cu ore). Hydrothermal alteration and mineralization are controlled by an E

trending regional fault system. Hydrothermal alteration consists of an inner zone of vuggy quartz with locally developed advanced argillic alteration, enclosed by a well-developed zone of argillic alteration, grading to an external halo of propylitic alteration. Mineralization produced disseminations and microveinlets of pyrite and minor chalcopyrite, enargite and tennantite, with traces of sphalerite, crosscut by late stage base metal veins. New  $^{40}\text{Ar}/^{39}\text{Ar}$  data of igneous rocks combined with biostratigraphic ages of the volcanic sequence indicate a maximum age of Lower Eocene (~55-49 Ma) for the Cerro Quema deposit. It was probably triggered by the emplacement of an underlying porphyry-like intrusion associated with the Valle Rico batholith. The geologic model suggests that in the Azuero Peninsula high sulfidation epithermal mineralization occur in the Cretaceous-Paleogene fore-arc. This consideration should be taken into account when exploring for this deposit type in similar geologic terranes.

## **Introduction**

South Central America is a region characterized by a long lived intra-oceanic subduction zone with a volcanic arc active since the Late Cretaceous (e.g., Lissinna, 2005; Buchs *et al.*, 2010, 2011a). It displays many characteristics of zones where epithermal, porphyry copper and VMS deposits are found around convergent plate boundaries (e.g., Roberts and Irving, 1957; Levy, 1970; Ferencic, 1971; Weyl, 1980; Nelson, 2007).

High sulfidation epithermal deposits (Hedenquist *et al.*, 2000) are commonly hosted by subaerial, calc-alkaline volcanic rocks that formed at convergent margins, generally within island or continental arcs as a direct result of plate subduction (Sillitoe, 1993, 2010; Arribas and Tosdal, 1994; Cooke and Simmons, 2000). Mineralization style related to high sulfidation deposits display a wide variety, including veins, hydrothermal breccia bodies, stockworks, and dissemination or replacements (Arribas, 1995). A distinguishing

feature of this deposit type is the presence of alteration halos (grading from the fluid conduit outwards) characterized by quartz  $\pm$  alunite  $\pm$  pyrophyllite  $\pm$  dickite  $\pm$  kaolinite  $\pm$  illite, and montmorillonite  $\pm$  chlorite (Steven and Ratté, 1960; Stoffregen, 1987; Arribas, 1995; Hedenquist *et al.*, 2000). The most common geologic setting documented for this deposit type is a volcanic dome complex, however, they may also occur in a central-vent volcano setting and in a spatial association with maar-diatremes or calderas (Sillitoe *et al.*, 1984; Arribas, 1995; Sillitoe, 1999; Hedenquist *et al.*, 2000). Furthermore, submarine high sulfidation epithermal Au-Cu deposits have been reported in the Izu-Bonin-Mariana arc, Tonga-Kermadec arc, and in the Bismark archipelago (e.g., Hannington and Herzig, 1993; Binns and Scott, 1993; de Ronde *et al.*, 2003; Embley *et al.*, 2004).

In Panama, gold and copper are the most economically important metals, and they are mainly hosted by epithermal (e.g., Cana, Santa Rosa and Cerro Quema deposits; Woakes, 1923; Wleklinski, 1969; White, 1993; Nelson, 1995, 2007; Corral *et al.*, 2011a), and porphyry copper deposits (e.g., Petaquilla and Cerro Colorado, Kesler *et al.*, 1977; Kesler, 1978; Nelson, 1995; Speidel, 2001). The present study focuses on the Cerro Quema deposit, located in the Azuero Peninsula, SW Panama (Fig. 1A). This region hosts several epithermal deposits and prospects (e.g., Juan Diaz, Pitaloza, Las Minas, Cerro Viejo, Fig. 1B). Cerro Quema, considered one of the most promising Au-Cu prospects in the country, is a structurally and lithologically controlled high sulfidation epithermal deposit, hosted by dacite domes, in a calc-alkaline volcanic arc environment (Corral *et al.*, 2011a). Mineral resource estimate (Indicated + Inferred) are 30.86 Mt @ 0.73 g/t Au, containing 728,000 Oz Au, including 76.900 Oz (AuEq) of Cu ore (Valiant *et al.*, 2011; Puritch, *et al.*, 2012).

Hypogene sulfides at Cerro Quema deposit include pyrite, enargite and tennantite. The associated hydrothermal alteration minerals include alunite, kaolinite-dickite and

pyrophyllite. All of these are diagnostic of a high sulfidation state and acidic hydrothermal conditions (Arribas, 1995). Although Cerro Quema shows characteristics of high sulfidation epithermal deposits, its age and geodynamic setting are not well understood. It has been interpreted to be a volcanic dome-hosted high sulfidation deposit related to fore-arc magmatism (Corral *et al.*, 2011a; Corral, 2013), in contrast to the classical high sulfidation epithermal models (e.g., Hedenquist, 1987; Sillitoe, 1989, 1999; White, 1991; Hedenquist and Lowenstern, 1994; Arribas, 1995). Cerro Quema is hosted by fore-arc basin volcano-sedimentary rocks that have been intruded by different plutonic rocks through time (Corral *et al.*, 2011a).

We document the geological setting, mineralogy, geochemistry and  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology of Cerro Quema. A geologic model is developed from these data that contributes to the understanding and exploration of high sulfidation Au-Cu deposits in ancient and modern terranes, with similar geological features.

## **Geologic setting**

### *Regional geology*

Panama, located in South Central America, is the youngest segment of the land bridge between the North and South American plates. It is a tectonic block that lies at the junction of the Caribbean, South American, Cocos, and Nazca plates (e.g., Duque-Caro, 1990; Kellogg *et al.*, 1995; Harmon, 2005). A volcanic arc developed during the Late Cretaceous as a result of the subduction of the ancient Farallon plate (nowadays Cocos and Nazca plates) beneath the Caribbean plate. Volcanic arc magmatism continued until the Miocene (~23 Ma; Barckhausen *et al.*, 2001; Werner *et al.*, 2003; Lonsdale, 2005; Buchs *et al.*, 2009, 2010; Wörner *et al.*, 2009; Pindell and Kennan, 2009). The accretion

and obduction of seamounts and oceanic plateaus (Middle Eocene; Buchs *et al.*, 2010), and the collision of the Panamanian volcanic arc with Colombia during the Middle to Late Miocene (e.g., Keigwin, 1978; Trenkamp *et al.*, 2002; Coates *et al.*, 2004; Barat *et al.*, 2012, 2014), produced a change in the subduction direction and the migration of the volcanic arc towards the north (Lissinna, *et al.*, 2002; Lissinna, 2005). The Cordillera Central in north Panama is the present-day expression of the active Panamanian volcanic arc.

#### *Geology of the Azuero Peninsula and the Cerro Quema deposit*

The Azuero Peninsula is composed of igneous basement overlain by fore-arc sediments (Buchs *et al.*, 2011). This region contains volcanic, plutonic, sedimentary and volcanoclastic rocks ranging in age from ~98 Ma to ~40 Ma (Del Giudice and Recchi, 1969; Bourgois *et al.*, 1982; Kolarsky *et al.*, 1995; Lissinna, 2005; Wörner *et al.*, 2009; Buchs *et al.*, 2010; Wegner *et al.*, 2011; Corral *et al.*, 2013).

Five distinct rock associations have been recognized in the Azuero Peninsula (Fig. 1B). 1) The Azuero Igneous Basement (AIB) is composed of Late Cretaceous (Aptian to Santonian) basalts and pillow basalts with geochemical affinities similar to the Caribbean Large Igneous Province (CLIP), interpreted as the arc basement (Del Giudice and Recchi, 1969; Kolarsky *et al.*, 1995; Hauff *et al.*, 2000; Hoernle *et al.*, 2002, 2004; Lissinna, 2005; Buchs *et al.*, 2009; Corral *et al.*, 2011a). 2) The Azuero Primitive Volcanic Arc (APVA), a non mappable unit at regional scale, consisting of tholeiitic basalts and volcanoclastic rocks, locally interbedded with Late Campanian-Maastrichtian hemipelagic limestones, which are equivalent to the proto-arc defined by Buchs *et al.*, (2010). It corresponds to the initial stages of arc volcanism. 3) The Azuero Arc Group (AAG), consists of volcano-

sedimentary, volcanic and arc-related intrusive rocks with calc-alkaline character, representing the Cretaceous and Paleogene volcanic arcs (Lissinna, 2005; Wörner *et al.*, 2009; Buchs *et al.*, 2010, 2011a; Wegner *et al.*, 2011; Corral *et al.*, 2011a, 2013). 4) The Tonosí Formation, a Middle Eocene to Early Miocene sedimentary sequence that unconformably overlies the older units (Recchi and Miranda, 1977; Kolarsky *et al.*, 1995; Krawinkel and Seyfried, 1994; Krawinkel *et al.*, 1999). 5) The Azuero Accretionary Complex consists of Paleocene to Middle Eocene seamounts, oceanic plateaus and mélanges accreted along the ancient subduction trench (Hoernle *et al.*, 2002; Lissinna, 2005; Hoernle and Hauff, 2007; Buchs *et al.*, 2011b).

The Azuero Peninsula is transected by several regional-scale subvertical faults (Fig. 1B). These include the NW trending Soná-Azuero Fault zone (SAFZ), the E trending Ocu-Parita fault and the Río Joaquín Fault Zone (RJFZ) (Kolarsky *et al.*, 1995; Buchs, 2008; Corral *et al.*, 2011a, 2013). The Río Joaquín Fault Zone is 30 km in length, shows evidence for reverse dip-slip motion, and juxtaposed the Azuero Igneous Basement against the Azuero Arc Group (e.g., Río Quema Formation). Secondary NW trending regional structures such as the Pedasí Fault Zone and the Punta Mala Fault, both with a sinistral strike-slip motion, have disrupted the eastern Azuero Peninsula (Fig. 2). In the central Azuero Peninsula mesoscale open folds with SW-plunging fold axes and moderate limb dips indicate dextral transpression with dominant reverse dip-slip motion (Corral *et al.*, 2011a, 2013).

The local stratigraphy was initially defined by two units (C.F. Horlacher, pers. commun., 1993): 1) the Ocu Formation, composed of limestones and volcano-sedimentary rocks, and 2) the Quema Formation, composed of dacites and massive andesites. Corral *et al.*, (2011a, 2013) used new field, geochemical, and biostratigraphic data to define a new lithostratigraphic unit, the Río Quema Formation (Fig. 3). This newly

defined unit, which hosts the Cerro Quema deposit, is a volcano-sedimentary sequence enclosed within the Azuero Arc Group. It is interpreted as the volcanoclastic apron of the Panamanian Cretaceous volcanic arc. The volcanic sequence is exposed from the central to southeastern Azuero Peninsula and represents the fore-arc basin, the region between the subduction trench and the magmatic arc (e.g., Stern *et al.*, 2012). On the basis of biostratigraphic data the volcano-sedimentary sequence is Late Campanian to Maastrichtian in age (Corral *et al.*, 2013). The Río Quema Formation is subdivided into three units (Fig. 3). The lower unit contains andesitic lava flows and well bedded crystal-rich sandstone to siltstone turbidites, interbedded with hemipelagic thin limestone beds. The limestone unit is a thick light grey biomicritic hemipelagic limestone, interlayered with well bedded cherts, thin bedded turbidites and fine ash layers. The upper unit consists of volcanoclastic sediments interlayered with massive to laminar andesitic lava flows, dacite domes, dacite hyaloclastites (Fig. 3B), and polymictic conglomerates. Dacites are characterized by quartz and hornblende phenocrysts (up to 5 cm in hornblende) and smaller plagioclase crystals in a microcrystalline quartz-feldspar groundmass. The total thickness of the Río Quema Formation is approximately 1,700 m. It overlies both the Azuero Igneous Basement (Fig. 3A) and the Azuero Primitive Volcanic Arc, and is discordantly overlain by the Tonosí Formation (Fig. 3C).

The Cerro Quema deposit is located in the center of the Azuero Peninsula. It covers an area of ~20 km<sup>2</sup> (Fig 1B and Fig 2) and is associated with an E-trending regional fault system, parallel to the Río Joaquín Fault Zone (Corral *et al.*, 2011a). The deposit is hosted by the dacite dome complex of the Río Quema Formation, and contains several ore bodies. From east to west, these are Cerro Quema, Cerro Quemita and La Pava (Fig. 4). Although mineralization and hydrothermal alteration persist to the east (e.g., Cerro Idaida, Pelona and Peloncita), the economic potential of this zone is poorly known. Data



from Cerro Idaida are presented below in order to complement the geological characterization of Cerro Quema.

### **Hydrothermal alteration**

Wall-rock alteration at Cerro Quema was initially described by T.M. Leach (pers. commun., 1992), and subsequently by Corral *et al.* (2011a). We provide new data on hydrothermal alteration mineralogy and zoning based on field mapping and core logging, and on analysis of surface and drill core samples by petrographic microscope, XRD, SEM-EDX and EMPA. Hydrothermal alteration at Cerro Quema appears mainly restricted to the dacite domes of the Río Quema Formation (Fig. 5) due to the difference in permeability and porosity with respect to other rock types of the volcano-sedimentary sequence (Corral, 2013).

Hydrothermal alteration follows an easterly trend that is parallel to secondary faults of the Río Joaquín Fault Zone. Volcaniclastic sedimentary rocks and andesite lava flows affected by the E-trending faults to the east and west of Cerro Quema have also been weakly affected by hydrothermal alteration. Dacites are easily distinguished, due to their characteristic porphyritic texture, even when hydrothermally altered (Fig. 5, 6A and 7A). Although hydrothermal alteration had a strong structural control, a lithological control is also evident in the mushroom-shaped alteration domains at shallow levels (e.g., La Pava).

The Cerro Quema alteration pattern consists of an inner zone of vuggy quartz (30 to 230 m wide), with local quartz-alunite and pyrophyllite (advanced argillic alteration, 30 to 200 m wide), enclosed by a kaolinite, illite and illite/smectite-bearing widespread alteration zone (argillic alteration, 100 to 400 m wide) (Fig. 5). Propylitic alteration has

only been observed in some drill-core samples, and forms a halo surrounding the argillic alteration zone.

#### *Vuggy quartz*

This innermost alteration zone (Fig. 5) occurs as irregular, generally vertical funnel and tabular-shaped bodies, and is commonly found on top of mineralized zones. Patches of massive quartz and silicified breccias are also present in this zone.

Vuggy quartz is made up of a groundmass of microcrystalline anhedral quartz grains, disseminated pyrite, barite and minor rutile, with traces of sphalerite. At depth, vuggy quartz contains disseminated pyrite, chalcopyrite, enargite and tennantite. Vuggy quartz texture is characterized by voids preserving the crystal morphology of hornblende and plagioclase (Fig. 6B and 7B). Drusy quartz, pyrite, and rutile have partially filled some void spaces. Quartz phenocrysts preserved within dacite contain secondary two-phase (liquid rich) fluid inclusions, possibly recording the fluids responsible for hydrothermal alteration and mineralization.

#### *Advanced argillic*

The advanced argillic alteration zone is an irregular halo developed around the vuggy quartz alteration zone (Fig. 5). The advanced argillic alteration zone has different mineralogical expressions depending on its occurrence (surface / subsurface).

Quartz-alunite alteration associated with a massive quartz-cemented breccia zone is exposed at surface at La Pava (Fig 6C). Alunite is a very fine grained minor component

that is only identifiable by XRD and is associated with the breccia cement. A more representative association of the advanced argillic alteration at surface is characterized by quartz, dickite, pyrophyllite, barite, illite, and minor diasporite (at La Pava, Chontal Edge and Cerro Quema). These minerals altered the massive and brecciated dacites (Fig. 6D) to quartz. Clay minerals (dickite, pyrophyllite and illite) replaced hornblende and plagioclase, and also occur in the breccia as cement (Fig. 7C). Barite occurs along fractures and as part of breccia cement. Disseminated pyrite is characteristic of the advanced argillic alteration zone.

At depth, the advanced argillic alteration assemblage consists of quartz, alunite-natroalunite, aluminum-phosphate-sulfate minerals (APS), dickite, pyrophyllite, barite and rutile. This assemblage has only been observed in drill-core samples, associated with hydraulic breccias (Fig. 7D).

### *Argillic*

The argillic alteration zone defines a halo surrounding the vuggy quartz and advanced argillic alteration zones (Fig. 5). The argillic envelope generally bounds the vuggy quartz zone with a sharp contact, whereas the contact with the advanced argillic zone is gradational. The whitish-grey hydrothermally altered rock typically preserves the original volcanic textures (Fig. 6E). Argillic alteration produced quartz, kaolinite, illite and illite-smectite with minor chlorite, which replaced hornblende and plagioclase crystals (Fig. 7E). Disseminated pyrite is found locally.

Minerals within the argillic alteration zone are zoned outwards from the mineralized centers. Kaolinite is dominant proximal to ore, and the assemblage grades to kaolinite  $\pm$  illite, and then to  $\pm$  illite-smectite. Kaolinite  $\pm$  smectite  $\pm$  chlorite-smectite, and chlorite

have been recognized in distal locations. At La Pava, there are subvertical pipe-like structures where dacites with hornblende and plagioclase phenocrysts have been replaced by quartz, dickite, barite and pyrite alteration (advanced argillic alteration; Fig. 6F). These pipes have crosscut the argillic altered rocks (Fig. 6F).

### *Propylitic*

A propylitic assemblage constitutes the most distal alteration halo, affecting dacites, andesites and volcanoclastic sedimentary rocks (e.g., turbidites and debris flows; Fig. 6G). It is characterized by chlorite, epidote, carbonate, rutile, pyrite and chalcopyrite, with minor hematite and magnetite. Hornblende has been partially to completely replaced by chlorite and epidote, and plagioclase by carbonate (Fig. 7F). Carbonates also occur as patches and veinlets. Minor amounts of pyrite, chalcopyrite, rutile, magnetite and hematite have replaced hornblende, and also occur as disseminated grains. The propylitic zone has a transitional contact with the argillic alteration zone, where clay minerals have partially overprinted propylitic alteration minerals.

## **Mineralization**

Gold occurs as disseminated submicroscopic grains and as invisible gold within pyrite (Corral *et al.*, 2011a). Copper is associated with hypogene chalcopyrite, enargite, bornite and tennantite, and supergene covellite and chalcocite. Mineralization (gold and copper) is mainly associated with the vuggy quartz and advanced argillic alteration zones. However, minor gold and copper occurrences have been found in the argillic and propylitic alteration zones.

### *Hypogene mineralization*

Hypogene mineralization is generally developed below the oxidized zone, even though small (meter scale) outcrops are found at surface. Pyrite is the most abundant sulfide at the Cerro Quema deposit, however, there is a group of accompanying sulfides also associated with the Au-Cu mineralization.

Hypogene mineralization is divided into five stages (Fig. 8), where Stages 3 and 4 are the main ore-forming stages. Stage 1 consists of disseminated, fine grained, idiomorphic and subidiomorphic pyrite, accompanied by rutile and barite in voids and groundmass (Fig. 9A), with minor enargite, tennantite and chalcopyrite at depth. Sphalerite is a trace mineral that occurs disseminated in the groundmass. Stage 2 is constituted by disseminated pyrite in the cement of a hydraulic breccia, associated with alunite-natroalunite, dickite and traces of chalcopyrite. Stage 3 consists of pyrite, chalcopyrite, enargite and tennantite veinlets crosscutting stages 1 and 2 (Fig. 9B). Replacement textures of pyrite by enargite, enargite by tennantite and tennantite by chalcopyrite are observed in the veinlets. Bornite occurs as a trace mineral. Stage 4 occurs as breccia bands ~5 cm thick, composed of pyrite, chalcopyrite and minor enargite. Breccia bands crosscut all the previous stages (Fig. 9C). Stage 5 reflects intermediate sulfidation mineralization. These 5 to 10 cm thick base metal sulfide-rich veins are composed of pyrite, quartz and barite together with minor chalcopyrite, sphalerite and galena (Fig. 9D).

### *Supergene mineralization and alteration*

Intense weathering typical of tropical latitudes has affected fresh and hydrothermally altered rocks in the Cerro Quema area to depths of 150 m. Sulfide oxidation in high sulfidation systems is largely controlled by rock permeability (Sillitoe, 1999). At Cerro Quema, high permeability was provided by the vuggy quartz, hydrothermal breccias, fracture zones and hyaloclastites (Fig. 6H).

Weathering of the high sulfidation ores has produced a thick quartz- and iron oxide-rich zone that overprinted the primary sulfide-bearing zone. This zone developed in the upper part of mineral bodies, and is characterized by vuggy quartz containing abundant hematite and goethite within the groundmass, replacing the cement of hydrothermal breccias, and filling voids in the vuggy quartz zone (Fig. 9E). Supergene jarosite, kaolinite, halloysite and gypsum are also found in fractures, vugs and breccia matrix. Hypogene pyrite, barite and rutile remain as trace minerals in the oxidation zone.

Below the oxidation zone, supergene enrichment has caused deposition of secondary Cu-bearing minerals such as chalcocite and minor covellite. The secondary Cu-sulfides are found replacing chalcopyrite, tennantite and enargite as well as filling small fractures (Fig. 9F).

The enrichment factor of the oxide zone with respect to the sulfide zone in terms of gold and copper is 2.41 and 0.61, respectively (Corral, 2013). At Cerro Quema, the oxidation zone has higher gold grades (up to 2,400 ppb Au), and the enrichment zone has higher copper grades (up to 1 % Cu).

### **Trace Element Geochemistry**

Trace element data from high sulfidation epithermal deposits are not abundant (e.g., Nansatsu, Japan - Hedenquist *et al.*, 1994; Rodalquilar, Spain - Hernandez *et al.*, 1989; Pueblo Viejo, Dominican Republic - Kesler *et al.*, 2003). Co/Ni and S/Se ratios in pyrite have been used as empirical indicators of the depositional environment (e.g., Goldschmidt, 1954; Edwards and Carlos, 1954; Loftus-Hills and Solomon, 1967; Bralía *et al.*, 1979). Pyrite compositions combined with major- and trace-element contents of alunite- and APS-group minerals may provide significant information for understanding their origin. Chemical composition of enargite, alunite and APS minerals can be used as ore guide in mineral exploration as they can be related in time and space to epithermal and porphyry mineralization (e.g., Bove, 1990; Dill, 2003; Chang *et al.*, 2009, 2011; Deyell and Hedenquist, 2011).

Analyses of S, Fe, Co, Ni, Cu, As, Se, Ag, Cd, Sb, Au and Hg have been performed by EMPA for 55 pyrites from six drill-hole samples of the vuggy quartz and advanced argillic alteration. The content of Al, Fe, Ca, Na, K, P, F, S, Cu, As, Sr, Ba, Ce and Pb of 20 alunites and 21 APS minerals were analyzed by EMPA from two drill core samples of the advanced argillic alteration. All the analyses were performed at the Serveis Científics i Tecnològics of the University of Barcelona.

### *Pyrite*

Several pyrite types have been analyzed (e.g., idiomorphic, sub-idiomorphic, zoned, massive, framboidal and brecciated; Fig. 10 A, B). The aim was to determine the chemical composition of the different pyrite types. However, they have similar Ag, Cd, Sb and Se concentrations but some differences exist in Co and Ni concentrations (Table 1; Appendix 1). Co/Ni ratios (N= 11) range from 0.58 to 5.50 (Fig. 11 A), and S/Se ratios (N=21) are

between 1050 and 2694. Pyrites are generally Cu-rich, varying from 0.03 to 3.67 wt % Cu. The Au, Hg and As concentrations of pyrite are below detection limits.

#### *Alunite and APS minerals*

At Cerro Quema, alunite and APS minerals occur as cement in the hydraulic breccias associated with pyrite and dickite, filling voids in the vuggy quartz zone, and replacing plagioclase crystals (Fig. 10 C, D). In general, alunite is zoned (~ 1 to 7  $\mu\text{m}$  wide), which is mainly due to the variation in Na, K and Ca contents. Alunite have typical flaky shapes, indicating a hypogene origin (e.g., Arribas et al., 1995a, Itaya et al., 1996), and commonly have a core of APS minerals (e.g., svanbergite; Fig. 10 C). Representative chemical data for alunite and APS minerals from Cerro Quema are shown in Table 2 and Appendix 2. Alunite is Na-rich, exhibiting a compositional range within the alunite-natroalunite solid solution (Fig. 11 B). P is generally present as a trace, excepting few alunite crystals that show P enrichment, which is also correlated with an enrichment in Sr and Ba. In contrast, APS minerals show irregular element content (e.g., Na, Ca, Sr, Ba and Fe), with typically enrichment in Sr, and locally in Ca and Ba (Fig. 11 C), which is characteristic of the svanbergite-woodhouseite solid solution.

#### **$^{40}\text{Ar}/^{39}\text{Ar}$ Geochronology**

The first geochronological studies of arc rocks in the Azuero Peninsula were conducted by Del Giudice and Recchi (1969) and Kesler *et al.* (1977). Recent studies have focused on dating igneous rocks such as El Montuoso, Valle Rico and Parita batholiths as well as quartz-diorites from the Punta Mala area, NE Azuero basalts and Central Azuero arc rocks



(Fig.1; Lissinna, 2005; Wegner *et al.*, 2011; Montes *et al.*, 2012). Results of the previous geochronological studies are summarized in Table 3.

Ar/Ar step-heating dating has been conducted in this study in order to complete the existing radiometric and biostratigraphic ages of the volcanic, volcanoclastic, sedimentary and plutonic rocks of the Azuero Peninsula, and to constrain the age of the Cerro Quema deposit. Mineral separates of eight hornblende phenocrysts were prepared by crushing 1 kg of rock, sieving, washing and handpicking to obtain 100 mg of optically pure mineral. The  $^{40}\text{Ar}/^{39}\text{Ar}$  step-heating analyses were performed at the U.S. Geological Survey on samples irradiated at the U.S. Geological Survey TRIGA reactor in Denver, Colorado (Dalrymple *et al.*, 1981). Dated samples are from El Montuoso, Valle Rico and Parita batholiths, the Cerro Quema host rock (dacite dome complex) and volcanoclastic andesite (Fig. 1). Results and sample locations are shown in Table 4 and in Figure 12.

#### *El Montuoso*

Two hornblendes from the El Montuoso batholith yielded  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau ages of  $65.7 \pm 1.0$  Ma and  $67.5 \pm 1.1$  Ma (Fig. 12; Table 4), consistent with previous hornblende K/Ar ages ( $69 \pm 10$  Ma and  $64.87 \pm 1.34$  Ma; Del Giudice and Recchi, 1969; Kesler, 1977), and also with the zircon U/Pb ages ( $67.7 \pm 1.4$  Ma,  $66.0 \pm 1.0$  Ma and,  $67.6 \pm 1.0$  Ma) of Montes *et al.* (2012). Kesler (1977) also obtained a younger plagioclase K/Ar age ( $52.58 \pm 0.63$  Ma) and interpreted to reflect partial post-crystallization argon loss from the plagioclase.

#### *Valle Rico*

$^{40}\text{Ar}/^{39}\text{Ar}$  dating of a sample of the Valle Rico quartz-diorite (Fig. 12; Table 4) provided an integrated age of  $54.8 \pm 1.2$  Ma, which is consistent with the hornblende K/Ar age of  $53 \pm 3$  Ma (Del Giudice and Recchi, 1969). However our age is considerably older than plagioclase  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of  $49.5 \pm 0.2$  Ma and  $50.6 \pm 0.3$  Ma for the same batholith reported by Lissinna (2005). A recent zircon U/Pb age of  $49.2 \pm 0.9$  Ma (Montes *et al.*, 2012) suggests that this is the true age of this quartz diorite. The Valle Rico hornblende  $^{40}\text{Ar}/^{39}\text{Ar}$  date is therefore interpreted to have been compromised by the presence of excess argon.

### *Parita*

A hornblende from the Parita batholith yielded a small plateau-like segment at  $40.9 \pm 1.3$  Ma, in agreement with previous zircon U/Pb ages of  $48.1 \pm 1.2$  Ma and  $41.1 \pm 0.7$  Ma (Montes *et al.*, 2012) of the Parita batholith. However, the  $^{40}\text{Ar}/^{39}\text{Ar}$  spectra show evidence for excess argon (Fig. 12; Table 4).

### *Río Quema Formation*

Four hornblende separated from the dacite dome complex of the Río Quema Formation yielded  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau ages of  $67.9 \pm 1.1$  Ma,  $66.0 \pm 1.0$  Ma,  $65.6 \pm 1.3$  Ma and an integrated age of  $69.7 \pm 1.2$  Ma (Fig. 12; Table 4). Wegner *et al.* (2011) reported hornblende  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of  $71.0 \pm 2.0$  and  $67.5 \pm 1.9$  Ma for two dacite samples found in the Tonosí River (central Azuero Peninsula), probably corresponding to boulders coming from the erosion of the dacite dome complex of the Río Quema Formation.

An attempt to date the volcanoclastic rocks of the Río Quema Formation was made. Unfortunately, the integrated age of  $143 \pm 11$  Ma and the plateau age of  $105 \pm 3$  Ma; Fig. 12; Table 4) have no geologic sense within the geologic framework of the Azuero Peninsula (the  $143 \pm 11$  Ma age indicates that the rock is older than the Azuero Igneous Basement).

#### *Hydrothermal alteration and mineralization*

Geochronologic dating of the Cerro Quema hydrothermal alteration-mineralization was attempted by the performance of  $^{40}\text{Ar}/^{39}\text{Ar}$  step-heating analysis on alunite (advanced argillic alteration). Unfortunately we had no success due to the fine grained size of the alunite crystals and their intergrowths with kaolinite, which prevented the preparation of a pure alunite sample.

### **Discussion**

#### *Deposit type*

Classification of Cerro Quema has been a matter of debate since the first studies carried out in the area. T.M. Leach (pers. commun., 1992) and Nelson (1995) considered the deposit to be a high sulfidation epithermal deposit potentially related to an underlying porphyry-style intrusion. In contrast, Nelson and Nietzen (2000) and Nelson (2007) proposed that Cerro Quema could be an oxidized Au-Cu deposit transitional between epithermal deposits and volcanogenic massive sulfide deposits, similar to the Pueblo Viejo deposit, Dominican Republic.

The spatial distribution of hydrothermal alteration assemblage at Cerro Quema (e.g., vuggy quartz grading outwards to advanced argillic, argillic and propylitic assemblages), and the alteration mineralogy (e.g., alunite, APS minerals, barite, kaolinite, dickite, pyrophyllite), together with the mineralization style (e.g., dissemination and veinlets of pyrite, enargite, tennantite, chalcopyrite), show that Cerro Quema fits well within the classical high sulfidation epithermal model (e.g., Hedenquist, 1987; Berger and Henley, 1989; White, 1991; Hedenquist and Lowenstern, 1994; Arribas *et al.*, 1995a). Therefore, it can be also considered as a mineralized lithocap, possibly overlying a porphyry copper system, in the sense of Sillitoe (1995) and Corbett and Leach (1998). Consequently, in agreement with T.M. Leach (pers. commun., 1992), hydrothermal alteration and high sulfidation epithermal mineralization at Cerro Quema is inferred to be related to the circulation of acidic fluids derived from an underlying porphyry-like intrusion.

### *Pyrite origin*

No relationships between trace element content and pyrite textures (idiomorphic, zoned or framboidal; Fig. 10) were observed. Pyrites do not show significant differences in terms of major and trace elements, except for their Cu, Co and Ni content (Table. 1). Co/Ni ratios in pyrites have been used to distinguish between magmatic-hydrothermal and sedimentary origin. Ratios from ~1 to 5 have been usually assigned to hydrothermal pyrites, whereas Co/Ni ratio values of <1 are typical of pyrites of sedimentary or diagenetic origin (e.g., Loftus-Hills and Solomon, 1967; Price, 1972; Bralier *et al.*, 1979; Bajwah *et al.*, 1987; Brill, 1989; Raymond, 1996; Fintor *et al.*, 2011). Cerro Quema pyrites have Co/Ni ratios ranging from 0.58 to 5.50 (Fig. 11A), with an average of 1.96, suggesting a hydrothermal origin, irrespective of their textures.

S/Se ratios have also been used to discriminate between sedimentary and magmatic-hydrothermal origins of pyrites (e.g., Edwards and Carlos, 1954; Hawley and Nichol, 1959; Huston et al., 1995; Fitzpatrick, 2008). S/Se values of  $< 15,000$  correspond to magmatic-hydrothermal origin whereas those of sedimentary origin have values larger than 30,000. S/Se ratio values of pyrites from Cerro Quema range from 1050 to 2694, pointing to a magmatic-hydrothermal origin.

All these results are in agreement with pyrite sulfur isotopes (-4.8 to -12.7‰), and bulk sulfur isotopic composition (-0.5‰), suggesting a sulfide dominant hydrothermal fluid of magmatic origin (Corral *et al.*, 2011b; Corral, 2013).

#### *Alunite and APS origin*

Analyzed alunite crystals have flaky shape, and are Na-rich, covering a wide range of the alunite-natroalunite solid solution (Fig. 11B; Table 2; Appendix 2). APS minerals in the core of alunite and occurring as single crystals are mainly Sr-rich, locally showing Ca enrichment (Fig. 11C; Table 2; Appendix 2), characteristic to the svanbergite-woodhouseite solid solution.

Studies focused on the alunite geochemistry (e.g., Stoffregen and Alpers, 1987; Arribas *et al.*, 1995b; Deyell *et al.*, 2005a, 2005b; Chang et al., 2011), showed that supergene alunite and low temperature alunite is generally K-rich in comparison with that of higher temperature occurrences which are Na-rich. Aoki *et al.* (1993) suggested that the core of hypogene alunite is commonly enriched in  $\text{PO}_4$  and multi-valent cations such as Ca (crandalite, woodhouseite), Sr (svanbergite) and Ba (groceixite). These inclusions are typically rimmed by minamiite and rhythmic bands of alunite and natroalunite (Stoffregen and Alpers 1987, Aoki *et al.*, 1993). According to the aforementioned studies,

texture and chemical composition of alunite (Na-rich, flaky shapes and with inner core of APS), and svanbergite-woodhouseite (Sr- and Ca-rich APS mineral, occurring as an alunite core as well as single crystals) from Cerro Quema (see Fig. 10, 11 and Table 2) present all of the characteristics indicating a magmatic-hydrothermal origin, related to an intrusion-driven hydrothermal system, such as a porphyry copper intrusion.

### **Geologic evolution and epithermal mineralization**

This section summarize the events that from Late Cretaceous to present times that constrained the geologic evolution of the Azuero Peninsula and the formation of Cerro Quema (Fig. 13).

#### *Arc development*

The Late Campanian (~75-73 Ma) marked the initiation of Farallon plate subduction beneath the Caribbean plate (Buchs *et al.*, 2010). The initial stages of an intra-oceanic subduction are characterized by extension of the overriding plate (Stern and Bloomer, 1992; Stern, 2010). In the Azuero Peninsula, this extension controlled the morphology and evolution of the volcanic arc and fore-arc. From Late Campanian to Maastrichtian (~71-66 Ma) the first stage of magmatism occurred within the Caribbean Plate. This stage is characterized by the intrusion of El Montuoso batholith and the development of the arc and fore-arc basin. The Río Quema Formation, of Late Campanian to Maastrichtian age, represents the fore-arc basin. Contemporaneous intrusions of dacite domes (~71-66 Ma) into the Río Quema formation, resulted in the interstratified volcanic and sedimentary sequences of the fore-arc basin (Fig. 13A).

### *Arc maturation and emplacement of the Cerro Quema deposit*

During the Lower Eocene (~55-49 Ma), a second stage of magmatism occurred (Fig. 13B), where the Paleogene volcanic arc developed on top of the Cretaceous volcanic arc. Valle Rico-like batholiths intruded along E-trending regional faults to the north of the Cretaceous fore-arc basin. However, some Valle Rico-like intrusions (quartz-diorites, diorites and trachyandesites) also occurred in the central and southern limit of the fore-arc basin. Emplacement of Valle Rico intrusions in the fore-arc led to the formation of Cerro Quema.

### *Age of the Cerro Quema deposit*

The age of Cerro Quema has been constrained from field evidence coupled with biostratigraphic data of sedimentary rocks of the Río Quema Formation and geochronological data of the igneous rocks of the Azuero Peninsula. The age of the deposit is estimated to be ~55-49 Ma (Lower Eocene), based on the following observations:

- 1) Crystal-rich sandstones and turbidites of the Río Quema Formation, a volcano-sedimentary sequence of Campanian-Maastrichtian age do not contain altered clasts derived from hydrothermally altered rocks. Dacite clasts in conglomerates derived from the erosion of the dacite dome complex that hosts Cerro Quema (~71-66 Ma; Wegner *et al.*, 2011), show no signs of hydrothermal alteration. Therefore, hydrothermal alteration and mineralization should be younger than the age of the dacite dome complex (~71-66 Ma).

2) As a high sulfidation deposit, Cerro Quema will have been related to a magmatic event. In the Azuero Peninsula, the first recorded post-Cretaceous magmatic event occurred during the Lower Eocene (~55-49 Ma; Del Giudice and Recchi, 1969; Kesler *et al.*, 1977; Lissinna, 2005; Montes *et al.*, 2012), corresponding to Valle Rico-like batholith intrusions. Based on correlations with this second magmatic event, the maximum age of Cerro Quema is Lower Eocene (55-49 Ma).

#### *Arc migration*

During the Middle Eocene (~45 Ma), the Azuero Peninsula was an area of accreted intra-oceanic island arcs such as la Hoya and Punta Blanca islands (Buchs *et al.*, 2011b). Subduction erosion and possible slab flattening induced the migration of the arc front towards the Caribbean. The emplacement of the Parita batholith (~48 to 41 Ma) to the north of the Ocu-Parita Fault (Fig. 1) supports arc migration towards the north during Middle Eocene times. This migration is in agreement with geodynamic reconstructions of Buchs *et al.* (2010) and geochronological data of Lissinna *et al.* (2002).

In the Azuero Peninsula, volcanism was less intense in the Cerro Quema and Tonosí area due to arc migration (Fig. 1). It allowed development of an overlapping sedimentary sequence (e.g., Tonosí Formation). This unit overlap all older units, and is composed of reefal limestones, calcarenites, sandstones, conglomerates and coal seams (Recchi and Miranda, 1977; Krawinkel and Seyfried, 1994; Kolarsky *et al.*, 1995; Krawinkel *et al.*, 1999).

#### *Erosion and supergene enrichment*



Some time before the emplacement of the Cerro Quema deposit (~55-49 Ma) and present day, erosion and supergene enrichment affected the Cerro Quema deposit (Fig. 13C). Consequently, oxidation and intense weathering generated a thick Au-bearing, silica- and iron-rich zone of up to 150 m depth, below which a Cu-rich zone was developed.

### **Conclusions**

Cerro Quema is a high sulfidation epithermal deposit hosted by the dacite dome complex of the Río Quema Formation, and was emplaced into a Cretaceous fore-arc sequence. Weathering and supergene oxidation processes at Cerro Quema produced two mineralized zones, an upper quartz and iron oxide zone enriched in Au and a lower supergene enrichment zone where Cu is concentrated.

Field observations, geochronologic and biostratigraphic data, support a maximum Lower Eocene (~55-49 Ma) age for Cerro Quema. The deposit is interpreted to be related to the emplacement of a porphyry-like intrusion associated with the Valle Rico batholith.

The formation of Cerro Quema in the Lower Eocene fore-arc has important implications for exploration in the Panamanian volcanic arc and elsewhere. Our results suggest that high sulfidation deposits can form in a fore-arc environment if acidic intrusions are emplaced between the volcanic arc front and the trench. Exploration for high sulfidation epithermal deposits in the Azuero Peninsula should therefore be focused in the Cretaceous fore-arc sequence, especially in the Río Quema Formation dacite domes, targeting E-trending regional faults (parallel to the Río Joaquín Fault Zone) and Lower Eocene acidic intrusions (Valle Rico-like intrusions). This implies a potential zone about ~70 x 10 km for hosting porphyry-related high sulfidation epithermal deposits (Fig.

14). These findings should also be considered when exploring for high sulfidation deposits in geologically similar terranes globally.

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### **Figure Captions**

Figure 1: A) Plate tectonic setting of South Central America. B) Simplified geological map of the Azuero Peninsula with the main epithermal occurrences. AAG: Azuero Arc Group, ACF: Auga Clara Fault, PMF: Punta Mala Fault, RJFZ: Río Joaquín Fault Zone (after Dirección General de Recursos Minerales, 1976; Buchs *et al.*, 2011a; Corral *et al.*, 2011a, 2013; Corral, 2013). 1) Cerro Quema, 2) Pitaloza, 3) Juan Díaz, 4) Las Minas, 5) Quebrada Barro, 6) Quebrada Iguana, 7) Cerro Viejo.

Figure 2: Simplified geologic map of Central Azuero Peninsula, and location of the Cerro Quema Au-Cu deposit (after Corral *et al.*, 2011a, 2013; Corral, 2013).

Figure 3: Stratigraphic section of the Río Quema Formation indicating emplacement of the Cerro Quema Au-Cu deposit, biostratigraphic and geochronological data (after Corral *et al.*, 2011a, 2013; Corral, 2013). A: Pillow basalts of the Azuero Igneous Basement at los Ciruelos beach, B: Hyaloclastites of the dacite dome complex at Quema River, C: Calcarenites of the Tonosí Formation at Guerita River.

Figure 4: Overview of Cerro Quema including La Pava, Cerro Quemita, Cerro Quema and Cerro Idaida ore zones.

Figure 5: Cerro Quema hydrothermal alteration maps; A) La Pava orebody and Chontal Edge. B) Cerro Quemita and Cerro Quema orebodies (modified from Corral *et al.*, 2011). Topographic map has been extracted from a 90 m SRTM (Shuttle Radar Topography Mission) digital elevation model (DEM).

Figure 6: Field examples of host rocks and hydrothermal alteration assemblages at Cerro Quema. A) Unaltered porphyritic texture of dacites (Río Quema Formation). B) Dacite altered to vuggy quartz at Cerro Quemita, preserving the original volcanic rock texture. Voids correspond to hornblende and plagioclase crystals are now filled by Fe-oxides. C) quartz-alunite altered breccia zone at La Pava. D) Quartz, dickite, pyrophyllite, barite and illite altered breccia, composed by dacite clasts with argillic alteration in a matrix of advanced argillic alteration (Cerro Quema). E) Kaolinite, illite and illite/smectite altered dacite preserving the original volcanic rock texture (Cerro Quemita). F) Pipe-like structures (dashed-line circles) composed of quartz, dickite, barite and pyrite crosscutting the argillic alteration zone at La Pava. Image width ~20 m. G) Drill core sample showing

a chlorite, epidote, pyrite and carbonate alteration in a sedimentary breccia or microconglomerate, crosscut by carbonate veins. H) Oxidation boundary developed on the advanced argillic alteration zone at Chontal edge.

Figure 7: Microscope images of alteration assemblages at Cerro Quema. A) Relatively fresh dacite showing hornblende phenocrysts and partially calcite-altered plagioclase crystals in a slightly altered groundmass (crossed polarized light). B) Vuggy quartz; dacite groundmass has been totally replaced by microcrystalline quartz preserving the hornblende and plagioclase crystal morphologies (crossed polarized light). C) Dacite altered to quartz + dickite + pyrophyllite + pyrite assemblage, typical of the advanced argillic alteration assemblage (crossed polarized light). D) Hydraulic breccia with fragments of vuggy quartz cemented by alunite-natroalunite, pyrite and dickite (crossed polarized light). E) Dacite affected by argillic alteration (crossed polarized light). Groundmass has been replaced by microcrystalline quartz and plagioclase voids have been filled by kaolinite. F) Crossed polarized light image of a sedimentary breccia affected by propylitic alteration. The matrix has been altered to quartz + chlorite + calcite + pyrite. Volcanic clasts have undergone selective replacement of plagioclase to calcite and hornblende to chlorite. ap: apatite; alu: alunite; cb: carbonate; chl: chlorite; dck: dickite; hbl: hornblende; kao: kaolinite; qz-fs: quartz-feldspar groundmass; plag: plagioclase; prl: pyrophyllite; py: pyrite; qz: quartz.

Figure 8: Paragenetic sequence of ore minerals at Cerro Quema.

Figure 9: Hypogene and supergene mineralization at Cerro Quema. A-A') Vuggy quartz with disseminated pyrite and replacement of hornblende by pyrite and rutile (reflected polarized light). B) Veinlets of pyrite + enargite + chalcopyrite crosscutting a vuggy quartz altered dacite (reflected polarized light), corresponding stage 3. C) Breccia band composed of pyrite + chalcopyrite + enargite (stage 4) crosscutting veinlets of pyrite + enargite + tennantite (stage 3). D) Late stage base metal veins composed of pyrite, quartz and barite with traces of sphalerite and galena. E) Hematite-goethite botryoids in dacite altered by vuggy quartz. The original rock texture (porphyritic dacite) is still preserved (polarized light). F) Supergene enrichment zone of hypogene pyrite, chalcopyrite  $\pm$  enargite to chalcocite (reflected polarized light). bar: barite, cc: chalcocite, cp: chalcopyrite, en: enargite, gn: galena, goe: goethite, hm: hematite, py: pyrite, qz: quartz, rt: rutile, sl: sphalerite, tn: tennantite.

Figure 10: Images of analyzed pyrite and alunite. A) Framboidal pyrite (reflected polarized light). B) Idiomorphic and zoned pyrite (reflected polarized light). C) Alunite crystal showing a core of svanbergite with an intermediate zone of intergrown alunite-svanbergite in a matrix of dickite (BSE image). D) Svanbertite-Woodhouseite crystal in a quartz-pyrite-altered matrix (BSE image). alu: alunite, dck: dickite, py: pyrite, qz: quartz, sv: svanbergite, sv-wh: svanbergite-woodhouseite.

Figure 11: Chemical composition of pyrite, alunite and APS minerals from Cerro Quema. A) Co-Ni content of pyrites and their average composition. B) Normalized K-Na-Ba compositions of alunite. Data points are recalculated EMPA compositions (20 analyses).

C) Normalized K+Na – Sr+Ba+Pb – Ca compositions of APS minerals. Data points are recalculated EMPA compositions (21 analyses).

Figure 12: Hornblende argon age spectra of rocks from Cerro Quema. Arrows indicate the steps used for plateau age calculation. A-B) El Montuoso batholith, C-F) Dacite dome complex (Río Quema Formation), G) Valle Rico batholith, H) Parita batholith, I-J) Volcaniclastic sediments of the Río Quema Formation.

Figure 13: Geologic model of Cerro Quema and the Azuero Peninsula from Late Cretaceous to present. AIB: Azuero Igneous Basement, APVA: Azuero Primitive Volcanic Arc, RQF: Río Quema Formation.

Figure 14: Prospective area for porphyry-related high sulfidation epithermal deposits in the Azuero Peninsula. See Figure 1 for reference. RJFZ: Río Joaquín Fault Zone. 1) Cerro Quema deposit, 2) Pitaloza prospect, 3) Juan Díaz prospect.

Table 1: Quantitative analyses, Co/Ni and S/Se ratios of pyrites from Cerro Quema.

Table 2: Representative analyses of alunites and APS minerals from Cerro Quema.

Oxide content is expressed in wt %. \* Calculated by difference. \*\* Assume 100% sum.

1: Na-rich alunite (natroalunite). 2: Sr-rich natroalunite. 3: Sr-, P- and Ba-rich

natrolaunite (natroalunite-svanbergite). 4: Sr-rich APS (svanbergite). 5: Sr- and Ca-rich APS (svanbergite-woodhouseite).

Table 3: Summary of geochronological studies carried out in the Azuero Peninsula. B: basalt, Dac: dacite, Gd: Granodiorite, Gr: Granite, Qd: quartz diorite, Ton: tonalite.

Table 4: Summary of  $^{39}\text{Ar}/^{40}\text{Ar}$  incremental-heating experiments. a: integrated age, V. Andesite: volcaniclastic andesite.

Appendix 1: Location and quantitative analyses of pyrites from Cerro Queam. Element content is expressed in wt %. B: brecciated, F: framboidal, I: idiomorphic, M: massive, SI: subidiomorphic, Z: zoned.

Appendix 2: Location and quantitative analyses of pyrites and APS minerals from Cerro Quema. Oxide content is expressed in wt %. \*Calculated by difference.