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New $^{40}Ar/^{39}Ar$ Dating of Alunite from the Cerro Quema Au-Cu Deposit, Azuero Peninsula, Panama

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Abstract

Cerro Quema is a high-sulfidation epithermal Au-Cu deposit located in the Azuero Peninsula, southwestern Panama. It is hosted by a dacite dome complex of the Río Quema Formation, a volcanosedimentary sequence of the Cretaceous – Paleogene magmatic arc. Cerro Quema has oxide resources of 24.60 Mt at 0.71 g/t Au and 0.04% Cu, and sulfide resources of 11.38 Mt at 0.41 g/t Au and 0.31% Cu. Alunite $^{40}Ar/^{39}Ar$ dating of a sample from Cerro Quema yielded a final age of 48.8 ± 2.2 Ma (weighted average of plateau age), and of 49.2 ± 3.3 Ma (weighted average of total gas age). This age is interpreted to represent the formational age of the Cerro Quema deposit at ~49 Ma, linking it to the Valle Rico Batholith intrusive event. Based on the new alunite $^{40}Ar/^{39}Ar$ data and a re-examination of published geochronological data, magmatic-hydrothermal deposits such as the Río Pito porphyry copper and the Cerro Quema high-sulfidation epithermal deposit formed during the early arc stage (68 – 40 Ma) in the Chagres-Bayano Arc (Eastern Panama) and the Soná-Azuero Arc (Western Panama), respectively. They formed in a similar geodynamic setting at ~49 Ma, when diorites and quartz-diorites intruded Cretaceous volcanosedimentary sequences. Cerro Quema and Río Pito provide evidence for the exploration potential of Cretaceous – Paleogene arc segments.

Exploration should focus on Cretaceous volcanic and volcanosedimentary sequences intruded by Paleogene batholiths of intermediate to felsic composition.

Introduction

Southern Central America is a region characterized by a long-lived intra-oceanic subduction zone with a magmatic arc active since the Late Cretaceous (Lissinna, 2005; Buchs *et al.*, 2010, 2011). It displays many of the metallogenic features commonly associated with convergent plate boundaries including epithermal Au-Cu deposits (e.g., Cana, Cerro Quema, Cerro Molejón, Remance and Santa Rosa) and porphyry Cu-Au deposits (e.g., Cerro Chorcha, Cobre Panamá-Petaquilla, Cerro Colorado, Río Pito; Fig. 1; Kesler et al., 1977; Nelson, 1995; Corral et al., 2011, 2016; Baker et al., 2016).

Understanding the relationships between magmatic arc evolution and mineralization is fundamental for mineral exploration, and metallogenic studies at the Panamanian magmatic arc. Initial attempts to relate Caribbean geological evolution and mineralization by Kesler et al. (1975; 1977) and Kesler (1978) were followed up by a metallic mineral resources compilation of South Central America by Nelson (2007) and studies of the metallogenic evolution of the Greater Antilles by Nelson et al. (2011). There have been no comprehensive studies of the metallogeny of Panama, although individual publications document the geology, geochemistry and geochronology of the magmatic arc (e.g, Lissinna, 2005; Wörner et al., 2009; Buchs et al., 2010; Corral et al., 2013;) and mineral deposits (e.g., Cerro Chorcha, Druecker and Sandefur, 2008; Cerro Quema, Corral et al., 2011, 2016; Cobre Panamá-Petaquilla, Baker et al., 2016).

This study focuses on the age of the Cerro Quema Au-Cu deposit (Fig. 1). Located in the Azuero Peninsula, Cerro Quema consists of several mineralized bodies, La Pava, Cerro Quemita, Mesita, and Cerro Quema. Global measured, indicated, and inferred oxide resources for the four orebodies total 24.60 Mt at 0.71 g/t Au and 0.04% Cu, global sulfide resources total 11.38 Mt at 0.41 g/t Au and 0.31% Cu (Sutcliffe et al., 2014; Table 1).

Although several studies have documented the geology of Cerro Quema (Leach, pers. commun., 1992; Nelson, 1995; Corral et al., 2011), its origin and evolution (Corral et al., 2016, 2017), and its metal content and ore distribution (Sutcliffe et al., 2014; Corral et al., 2018), the only available radiometric age determinations are Re-Os dates by Perelló et al. (2020). The current manuscript presents the first $^{40}Ar/^{39}Ar$ dating results of alunite from Cerro Quema, discussing their significance within the geological framework of Panama. These data contribute to a better understanding of the metallogenic evolution of the Panamanian magmatic arc.

Metallogeny of Panamanian Porphyry and Epithermal Deposits

Geochronological data for Panamanian mineral deposits is scarce but provide reliable data on deposit ages, their host rocks and their related volcanic and volcanosedimentary sequences. Table 2 summarizes all the published dating results of the mineral deposits shown in Figure 1, as well as their proposed ages based on indirect dating and crosscutting relationships.

The Río Pito porphyry copper deposit (NE Panama) was discovered during the regional stream sediment survey financed by the United Nations Development Program (UNDP). Mineralization is hosted in the Río Pito batholith, a 49.23 ± 0.57 Ma to 48.45 ± 0.55 Ma granodiorite-quartz diorite body intruded in basalts and andesites of Upper Cretaceous age (Kesler et al., 1977; Nelson et al., 1995). The age of the causative intrusion (~49 Ma) has been interpreted as the mineralization age. Río Pito is associated with the first stage of arc magmatism from late Cretaceous to middle Eocene (68 – 40 Ma), produced after the subduction initiation of the Farallon plate beneath the Caribbean plate (late Campanian; ~75 – 73 Ma) and the proto-arc magmatism on the westernmost edge of the Caribbean plate (Buchs et al., 2010). This magmatic stage is characterized by the development of the Soná-Azuero Arc (Western Panama), and the Chagres-Bayano Arc (Eastern Panama). These magmatic arcs document a major phase of tholeiitic to calc-alkaline arc magmatism, mostly derived from a hydrated mantle wedge, and emplaced in an oceanic plateau crust (Lissina, 2005; Buchs et al., 2010; Wörner et al., 2009; Corral et al., 2011; Montes et al., 2012; Cardona et al., 2018).

Cobre Panamá-Petaquilla is an Oligocene porphyry copper deposit located in N Panama. It formed when multi-phase diorite-granodiorite porphyries derived from an enriched, volatile-rich magma through fractional crystallization intruded the 32 – 28 Ma Petaquilla batholith at 29 – 28 Ma (Villenueve, pers. commun., 1997; Speidel et al., 2001; Whattam et al., 2012; Baker et al., 2016; Sepp and Dilles, 2018). Cobre Panamá-Petaquilla is associated with sporadic arc-related plutonism of central Panama that occurred during a magmatic gap (~40 – 20 Ma) coincident with a tectonic reorganization driven by: (1) breakup of the Farallon plate, (2) initial interaction of the Panamanian arc with Colombia, (3) arc collision with thickened oceanic crust or a plateau, and (4) accretion of seamounts (Lissinna, 2005; Lonsdale, 2005; Whattam et al., 2012; Barat et al., 2014; Buchs et al., 2019a; Redwood, 2019).

Molejón (N Panama) is a vein-type, low-sulfidation epithermal deposit located within the Cobre Panamá-Petaquilla district. It formed as peripheral epithermal mineralization associated with Cobre Panamá-Petaquilla during the Oligocene (Speidel et al., 2001; Baker et al., 2016). The age of Molejón corresponds to the age of the intrusive rocks (29 – 28 Ma).

The Cana low-sulfidation epithermal deposit (SE Panama) was first exploited by the Spanish between 1665 and 1727, producing an estimation of 1 Moz Au (Nelson et al., 1995). High-grade auriferous quartz veins and breccia pipes are hosted by andesites and fragmental volcanic rocks that were intruded by hornblende-feldspar porphyry dikes and stocks of Oligocene age (Nelson, 2007). Cana formed in a similar geologic setting and timing to Molejón. Due to the scarce geochronological constraints on this deposit, a maximum age of Oligocene is assumed for Cana, corresponding to the age of the host rocks.

The Remance and Santa Rosa low-sulfidation epithermal deposits (Veraguas gold belt; SW Panama) are characterized by auriferous quartz veins and stockworks, and by sulfide disseminations and stockworks, respectively (Nelson, 2001). Mineralization is associated with volcanic domes hosted by the basaltic to rhyolitic volcanic rocks of the Cañazas Formation (18 – 17 Ma; Wleklinski, 1969, Nelson, 2001). These volcanic rocks are discordantly overlain by unaltered and unmineralized ignimbrites from La Yeguada Formation (12.6 ± 0.8 Ma; Wleklinski, 1969). Crosscutting relationships indicate that mineralization occurred prior to the deposition of La Yeguada Formation, and after the emplacement of the Cañazas Formation volcanic domes. Therefore, an age range of 18 – 13 Ma is estimated for Remance and Santa Rosa. Numerous low-sulfidation deposits in the Veraguas Belt formed when calc-alkaline arc magmatism resumed in the Miocene (20 – 5 Ma), displaying a more mature volcanic arc signature than previous magmatic suites in Panama (Lissinna, 2005; Wörner et al., 2009; Buchs et al., 2019a, 2019b).

The world-class Cerro Colorado porphyry copper deposit (W Panama) is hosted in a thick pile of subaerial basaltic to rhyolitic volcanic rocks of the Oligocene Chichica Formation (~32 Ma; Stewart, pers. commun., 1957; Clark et al., 1977). Cerro Colorado is associated with a cluster of high-level intrusive bodies of the Escopeta granodiorite pluton and quartz-feldspar-hornblende porphyry stocks (4 – 3 Ma; Issigonis, 1973; Issigonis et al., 1974; Clark et al., 1977;

Kesler et al., 1977). A Pliocene age (~3 Ma) was proposed by Kesler et al. (1977) as the age of Cerro Colorado based on K-Ar dating of biotite from a weakly chlorite-altered sample of the Escopeta granodiorite. Cerro Colorado formed after the magmatism shift from calc-alkaline to Adakite-like magmatism at ~5 Ma due to the collision of the Cocos Ridge with Central America (Hoernle et al., 2002; Lissinna, 2005; Wörner et al., 2009; Gazel et al., 2009, 2011). This adakite-like magmatism was produced by melting the leading edge of the subducted Cocos Ridge and older Caribbean Large Igneous Province basement, either at the margin of a slab window or after slab breakoff below west-central Panama (Johnston and Thorkelson, 1997; Abratis and Wörner, 2001; Wörner et al., 2009; Whattam et al., 2012).

Cerro Chorcha is a gold-bearing porphyry copper prospect (W Panama). It was discovered by a regional stream sediment sampling program conducted by ASARCO (Nelson, 1995). Porphyry mineralization is associated with the Tabasara Group intrusive complex (Pliocene – Miocene) of diorite to quartz diorite composition. Porphyry stocks intruded the andesite to basaltic flows and volcaniclastic rocks of the Cañazas Formation (18 – 17 Ma; Wleklinski, 1969; Nelson, 1995, 2001; Folk, 2005; Druecker and Sandefur, 2008). The porphyry stocks have not been dated but Folk (2005) and Druecker and Sandefur (2008) proposed a similar geologic setting and timing to Cerro Colorado, assuming a formational age at 3 Ma or younger for Cerro Chorcha.

Cerro Quema Exploration History

In 1965, a regional stream sediment survey financed by the United Nations Development Program (UNDP) was undertaken to evaluate Panama’s mineral resource potential. This survey targeted porphyry copper mineralization and resulted in the discovery of the Río Pito and Cobre Panamá (formerly Petaquilla) deposits. The survey also revealed other areas with significant copper and gold anomalies on the Azuero Peninsula (e.g., Del Giudice and Recchi, 1969; Ferenčić, 1970, 1971; Kesler et al., 1977). In 1986 – 1988, the Compañía de Exploración Mineral S.A. (CEMSA) followed up on UNDP stream sediment anomalies and discovered Cerro Quema. From 1990 to 1994, Cyprus Amax Minerals carried out several exploration programs including soil geochemistry and drilling campaigns. In 1996, Campbell Resources Inc. carried out an infill drilling program to further define the resources and completed a project feasibility study. In 2007, Bellhaven Copper & Gold Inc. acquired the project, and completed a feasibility study and metallurgical tests. Pershimco Resources Inc. acquired the project in 2010 and performed an intensive drilling campaign. Additionally, they conducted lithological and structural mapping of the area, with channel and geochemical sampling. Recently, several geophysical surveys have been carried out, including an Induced Polarization (IP) survey and, airborne radiometric, magnetic, and VTEM surveys (Kwan et al., 2016). In 2016, Pershimco Resources Inc. merged with Orla Mining Ltd. to continue the exploration and development of Cerro Quema under the name Orla Mining Ltd.

Geologic Setting

Geology

The Azuero Arc Group (late Cretaceous to Eocene) overlies the Azuero Igneous Basement (Conacian to Santonian) and is discordantly overlain by the Tonosí Formation (Eocene to Miocene; Buchs et al., 2010, 2011; Corral et al., 2011, 2013). The Azuero Arc Group consists of three arc-related batholiths (El Montuoso, Valle Rico and Parita) and volcanic and volcanosedimentary sequences.

The Cerro Quema high-sulfidation epithermal Au-Cu deposit covers an area of ~20 km^2 in the center of the Azuero Peninsula (Figs. 1 and 2). The mineralization is hosted in a dacite dome complex of the Río Quema Formation (late Campanian to Maastrichtian; Corral et al., 2013, 2016), a volcanosedimentary sequence that records the earliest calc-alkaline volcanism related to the Azuero Arc Group.

The Río Quema Formation is bounded to the north by the Valle Rico batholith, a series of Eocene (55 – 49 Ma) diorite and quartz diorite intrusions with calc-alkaline affinity (Del Giudice and Recchi, 1969; Lissinna, 2005; Corral et al., 2016). The Late Cretaceous Azuero Igneous Basement (Aptian to Santonian; Kolarsky et al., 1995; Kerr et al., 1997; Hoernle et al., 2002; Lissinna, 2005; Buchs et al., 2010) comprises tholeiitic basalts and pillow basalts of oceanic plateau affinity that bounds the Río Quema Formation to the south (Fig. 2). Geochemical characterization of the igneous rocks of the Azuero Peninsula is provided by Hoernle et al. (2002, 2004), Lissinna, (2005), Wörner et al. (2009), Buchs et al. (2010, 2011), Corral et al. (2010, 2011), and Wegner et al. (2011).

The main tectonic structures in the Cerro Quema area include the east-trending Agua Clara and Río Joaquín Fault zones, associated with an extensive network of minor northwest- to northeast-trending subvertical faults with normal dip-slip and minor strike-slip components. Mesoscale southwest-plunging open folds with moderately dipping limbs are also present in the area. Overall, the structures suggest dextral transpression with dominant reverse dip-slip motion during late Campanian to middle Eocene time (Corral et al., 2013).

Alteration and mineralization

Hydrothermal alteration at Cerro Quema occurred along an eastward trend that is parallel to secondary faults related to the Río Joaquín Fault Zone. Multiple concentric alteration halos are mainly restricted to dacite domes of the Río Quema Formation. According to Corral et al.

(2011, 2016), four distinct alteration zones can be identified at Cerro Quema (Fig. 3): several vuggy quartz centers (quartz – barite – rutile; up to ~600 m in length) and local advanced argillic alteration zones (quartz – alunite – kaolinite/dickite ± pyrophyllite – barite – illite – diaspore – rutile; up to ~250 m in length) form the central core of the deposit, enclosed by an argillic alteration zone (quartz – kaolinite – illite – illite-smectite ± chlorite; up to ~1900 m in length). Propylitic alteration (chlorite – epidote – calcite ± rutile) forms an outermost halo surrounding the argillic alteration zone.

Mineralization at Cerro Quema is subdivided into two different zones. Hypogene mineralization was produced by magmatic-hydrothermal fluids, whereas supergene mineralization was produced by oxidation of the hypogene ores, resulting in the precipitation of secondary sulfides (Corral et al., 2016, 2018). Hypogene mineralization is generally developed below the oxidized zone. Pyrite is the most abundant sulfide, with diverse accompanying sulfides (enargite, tennantite, chalcopyrite, sphalerite, and bornite) also associated with Au-Cu mineralization. Main ore stages consist of veinlets of pyrite, chalcopyrite, enargite, and tennantite, with traces of bornite, and ~5 cm thick breccia bands, composed of pyrite, chalcopyrite, and minor enargite. Gold occurs as submicroscopic grains and as invisible gold within pyrite. Copper occurs as Cu-bearing sulfides and sulfosalts such as chalcopyrite, enargite, bornite, and tennantite. Supergene weathering affected the Cerro Quema area to depths of 150 m, developing a thick quartz- and iron oxide-rich zone that overprinted the primary sulfide-bearing zone. Supergene mineralization is characterized by abundant hematite and goethite occurring within the vuggy quartz groundmass. Gold has been found as submicroscopic grains (< 1 μm). Below the oxidation zone, supergene enrichment caused deposition of secondary Cu-sulfides (e.g., chalcocite, covellite) that replaced chalcopyrite, tennantite, and enargite as well as filled thin fractures.

Age of host rocks

The first geochronological studies of igneous rocks in the Azuero Peninsula were conducted by Del Giudice and Recchi (1969) and Kesler et al. (1977) who performed K/Ar dating on hornblende and feldspar to constrain the age of the El Montuoso and Valle Rico batholiths. Later studies (e.g., Lissinna, 2005; Wegner et al., 2011; Montes et al., 2012; Corral et al., 2016, Ramírez et al., 2016) applied U-Pb and Ar/Ar radiometric dating techniques to constrain both the age of the main batholiths and the volcanic rocks of the Azuero Peninsula.

Published geochronological data are summarized in Table 3. Arc-related magmatism began in the Late Cretaceous with intrusions of the El Montuoso batholith and the deposition of the Río Quema Formation (68 – 66 Ma). Paleocene magmatism (61 – 59 Ma) resulted in basalts on NE Azuero and a diorite intrusion on Coiba Island (W Azuero). Eocene rocks (55 – 49 Ma) crop out as part of the Valle Rico (E Azuero) and Punta Mala (SE Azuero) batholiths, and as plutons on Coiba Island (W Azuero) and the Soná Peninsula (W Azuearo). The youngest magmatic rocks cropping out in the Azuero Peninsula are Eocene (48 – 36 Ma) plutons of the Parita batholith (NE Azuero), and basaltic andesites from Coiba Island (W Azuero).

Age of Mineralization

Prior to this study, the age of the Cerro Quema deposit has been constrained by field observations, crosscutting relationships and known radiometric and biostratigraphic ages. Corral et al. (2016) proposed a lower Eocene age (55 – 49 Ma) for Cerro Quema based on a combination of detailed mapping and petrographic analysis of the different rock units in the Cerro Quema area, and a geochronological (Ar/Ar) study of the different intrusive bodies and host rock from the Cerro Quema area. A lower Eocene age is supported by the absence of hydrothermally altered clasts/pebbles or grains in the Río Quema Formation (Campanian-Maastrichtian), including in conglomerates derived from the erosion of the dacite dome complex (68 – 66 Ma) that hosts Cerro Quema. Therefore, hydrothermal alteration and mineralization should be younger than the age of the dacite dome complex. A second argument supporting a lower Eocene age for mineralization is related to the origin of high-sulfidation epithermal deposits. These deposits can be considered as the top of larger intrusion-driven hydrothermal mineralizing system such as porphyry intrusions that may be enriched in Cu and/or Au (Hedenquist and Lowenstern, 1994; Arribas et al., 1995; Hedenquist et al., 1998; Sillitoe, 2010). In Cerro Quema area surroundings, the first recorded post-Cretaceous magmatic event occurred in the lower Eocene (55 – 49 Ma), represented by the Valle Rico batholith. After this magmatic event the arc migrated to the north ~50 km, represented by the Parita batholith (48-41 Ma). Thus, Cerro Quema can only be related to the lower Eocene (55-49 Ma) magmatic event.

A recent study by Perelló et al. (2020) reported the first results of Re-Os dating on molybdenite from La Pava. Four samples were dated yielding ages of 70.74 ± 0.29, 70.70 ± 0.29, 70.66 ± 0.29 and 68.72 ± 0.29 Ma. Results of this study indicate that the age of Cerro Quema mineralization is Late Cretaceous, contrasting with previous studies.

Sampling and Analytical Methods

Alunite is present in the advanced argillic alteration zone of Cerro Quema. The coarse grain size, platy crystal habit, local Na-enrichment and presence of inner cores of APS minerals observed for alunite at Cerro Quema (Fig. 4; Corral et al., 2016), together with its stable isotope composition ($\delta^{34}S$= ~15 ‰, $\delta^{18}O_{SO4}$= 10 ‰ to 0 ‰; Corral et al., 2017) are consistent with a magmatic-hydrothermal origin (Rye et al., 1992; Rye; 2005). Alunite is a key mineral for the study of high-sulfidation epithermal deposits, in part because it can be dated using K/Ar and Ar/Ar (Rye et al., 1992; Itaya et al., 1996; Arribas et al., 2011; Sahlström et al., 2018). Therefore, dating this mineral provides a time constraint on magmatic-hydrothermal activity at Cerro Quema.

The selected sample for dating was collected from drill hole PDH0308 (at 61 m; Fig. 4). This sample (0308-61) consists of a pyrite-alunite cemented breccia formed during the magmatic-hydrothermal activity that lead the Au-Cu mineralization at Cerro Quema (Fig. 4). Alunite separates from this breccia were dated using step heating $^{40}Ar/^{39}Ar$ geochronology.

Mineral separates were prepared by crushing, sieving, washing and handpicking to obtain ~100 mg of alunite. Sample purity was checked both optically and via scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS). Two alunite mineral separates (sample and duplicate; 100-200 μm grain size) were irradiated with fast neutrons at the McMaster Nuclear Reactor at McMaster University, Canada. The irradiated samples were subsequently analysed for $^{40}Ar/^{39}Ar$ at the Argon Geochronology Laboratory at the University of Michigan, USA. The samples were step-heated using a continuous 5-W Ar-ion laser and Ar isotopes were measured in a VG-1200S mass spectrometer, following the procedure described in Frey et al. (2007) and Rooney et al. (2009).

Results

Step heating $^{40}Ar/^{39}Ar$ results are shown in Table 4, Figure 5 and Appendix 1. Calculated final age for alunite using the weighted average of plateau age is 48.8 ± 2.2 Ma, and its calculated final age using the weighted average of total gas age is 49.2 ± 3.3 Ma. Calculation of the final age from the alunite $^{40}Ar/^{39}Ar$ spectra was done using 2σ for error including a 1%

of external error accounting for uncertainties in decay constants, the age of the standards $^{40}K/^{39}K$. Obtained ages (plateau and total gas age) are consistent, conferring a ~49 Ma age to the alunite from Cerro Quema.

Discussion

Age of Cerro Quema

Although alunite is a common mineral used for age determinations of high-sulfidation epithermal deposits, problems may arise due to thermal resetting during deformation and/or magmatism (e.g., Pueblo Viejo, Arribas et al., 2011; Mt. Carlton, Sahlström et al., 2018). Closure temperature for alunite was estimated at 320 – 240ºC by Itaya et al. (1996), Love et al. (1998) and Arribas et al. (2011). Closure is strongly influenced by the cooling rate, and the alunite crystal size, with the closure temperature decreasing proportionally with decreasing crystal size and cooling rate. The grain size of the Cerro Quema alunite sample was 100 to 200 µm, therefore, a blocking temperature similar to the one estimated for the Pueblo Viejo alunite is proposed (~300ºC; Arribas et al., 2011). Based on this inference, two possible scenarios can explain the ~49 Ma age for alunite obtained from Cerro Quema.

The new geochronological data, shows that alunite was above the closure temperature at ~49 Ma, implying that alunite associated with high-sulfidation epithermal Au-Cu mineralization post-dated the host dacite dome complex (66.5 ± 1.6 Ma weighted average of plateau age; Corral et al., 2016). This interpretation supports the previously proposed age range of 55 – 49 Ma (lower Eocene, Corral et al., 2016) for mineralization at Cerro Quema.

Alternatively, this alunite formed at broadly the same time as the dacite dome complex (66.5 ± 1.6 Ma weighted average of plateau age; Corral et al., 2016), which is a common feature of this type of deposits (e.g., Arribas, 1995, Bissig et al., 2001; Holley et al., 2016; Sahlström et al., 2018), and it was subsequently reset during the magmatic event at 55 – 49 Ma. This interpretation contradicts the proposed age range of Corral et al. (2016).

Although this study cannot disprove the hypothesis of resetting, the interpretation of a reset alunite is considered unlikely because: 1) both ^{40}Ar/^{39}Ar spectra show good plateaus with no evidence of argon loss, disruption or thermal resetting; 2) there is no record, within the Cerro Quema area, of any post-alunite heating event capable of producing a large enough temperature increase to reset the alunite as the nearest small-scale intrusion is at 2 – 3 km from La Pava; and 3) it is inconsistent with field and petrographic observations. If reset could be proven, the obtained alunite ^{40}Ar/^{39}Ar age would be interpreted as a minimum age for Cerro Quema. In this case, the maximum age of Cerro Quema is that of the host rocks, 66.5 ± 1.6 Ma (dated at La Pava ore body; Corral et al., 2016).

A recent study by Perelló et al. (2020) reported Re-Os dating on molybdenite from La Pava orebody. Four samples were dated yielding ages of 70.74 ± 0.29, 70.70 ± 0.29, 70.66 ± 0.29 and 68.72 ± 0.29 Ma being the youngest age discarded by the presence of significant common Os. The ~71 Ma age for the mineralization at Cerro Quema proposed by Perelló et al. (2020) conflicts with both, the age range proposed in Corral et al., (2016), and the alunite ^{40}Ar/^{39}Ar results presented in this study.

Some geological issues may arise from Perelló et al. (2020) Re-Os ages on molybdenite and their significance within the Azuero Peninsula geological framework. Perelló et al. (2020) considered that their Re-Os dates (~71 Ma) agree with the ^{40}Ar/^{39}Ar dates of ~71 Ma for amphibole-bearing dacitic rocks from Cerro Quema (Wegner et al., 2011; Corral et al., 2016). They relied on a 71.0 ± 2.5 Ma (weighted average) hornblende ^{40}Ar/^{39}Ar age as the age of the Cerro Quema host rock. However, this sample is a dacite located 10 km from mineralization

(Wegner et al., 2011). At the same time Perelló et al. (2020) discarded the 67.5 ± 1.9 Ma hornblende ^{40}Ar/^{39}Ar plateau age for a dacite located 5 km from Cerro Quema (Wegner et al., 2011), and the 66.5 ± 1.6 Ma hornblende ^{40}Ar/^{39}Ar plateau age (weighted average) of the Cerro Quema host rock collected at La Pava (Corral et al., 2016). Although Wegner et al. (2011) sample PAN-05-017A (Fig. 6A) has a bumpy spectra between 20 – 40% of cumulative ^{39}Ar fraction that compromises the age, a plateau age of 72.3 ± 2.5 Ma was calculated. A duplicate sample (PAN-05-017B; Fig. 6B) has a disturbed spectra between 10 – 30% of cumulative ^{39}Ar fraction with no apparent plateau that compromises the reported plateau age at 68.9 ± 3.3 Ma. The final reported age of this sample (71.0 ± 2.5 Ma) is an average of the two plateau ages, which is questionable given nature of their spectra. Dacite samples reported by Wegner et al. (2011) and Corral et al. (2016; Fig. 6C-F) dated by ^{40}Ar/^{39}Ar on hornblende showing well-defined plateaus with no disturbed spectra, are considered here to be more reliable ages of the Cerro Quema host rocks, constraining their age to 66.6 ± 1.8 Ma (weighted average of plateaus). Dacite domes of the Río Quema Formation are contemporaneous with the El Montuoso Batholith emplacement (Fig. 7). Thus, Perelló et al. (2020) Re-Os age of ~71 Ma is considerable older than the host rock age 66.6 ± 1.8 Ma (weighted average of plateaus; Table 3; Fig. 7).

Additionally, Perelló et al. (2020) invoke a previously unrecorded magmatic event to explain the mineralization at Cerro Quema based on their Re-Os ages. As reported in Table. 3 and Figure 7, the Azuero Peninsula geochronological data show strong consistency between the different dating methods (e.g., U-Pb in zircon, ^{40}Ar/^{39}Ar in hornblende and plagioclase), indicating that these ages are representative of the different magmatic events that occurred in the Azuero Peninsula. The proposed magmatic event by Perelló et al. (2020) has not been confirmed by any previous geochronological studies (U-Pb zircon, Montes et al., 2012; Ramirez et al., 2016; ^{40}Ar/^{39}Ar hornblende and plagioclase, Lissinna, 2005; Corral et al., 2016;

K-Ar hornblende and plagioclase, Del Giudice and Recchi, 1969; Kesler et al., 1977). If the newly proposed magmatic event occurred (Table 3; Fig. 7), it would be between the proto-arc (~75 – 73 Ma) and the Azuero Volcanic Arc group (~68 – 40 Ma; Table. 3), which is stratigraphically >500 m below the Cerro Quema host rock (Buchs et al., 2010; Corral et al., 2011, 2016).

Based on weights of evidence, the alunite ^{40}Ar/^{39}Ar date of this study is interpreted as representative of the age of hypogene mineral precipitation (at ~240ºC; Corral et al., 2017), and is therefore concluded to constrain the age of the Cerro Quema Au-Cu deposit. This hypothesis is consistent with geological observations, crosscutting relationships and, previous ^{40}Ar/^{39}Ar and U-Pb dating studies.

Contextualization of Cerro Quema within the Metallogeny of Panama

Figure 8 integrates the tectono-magmatic events, volcanic and intrusive rock ages, and mineral occurrences of Panama (Table 2). Magmatic-hydrothermal deposits such as the Río Pito porphyry copper and the Cerro Quema high-sulfidation epithermal deposit formed during the early arc stage (68 – 40 Ma) in the Chagres-Bayano Arc (Eastern Panama) and the Soná-Azuero Arc (Western Panama). They formed in a similar geodynamic setting at ~49 Ma, when diorites and quartz-diorites intruded Cretaceous volcanosedimentary sequences (Kesler et al., 1977; Nelson et al., 1995; Corral et al., 2011, 2016).

Implications for Regional Scale Exploration

Porphyry systems are usually associated with continental or intraoceanic magmatic arc setting above active subduction zones at convergent plate margins (Sillitoe, 1972, 2010; Richards, 2003). They commonly occur in linear orogen-parallel belts (Sillitoe and Perelló, 2005) associated with precursor plutons of batholithic dimensions and diorite to granite compositions (Sillitoe, 2010). Porphyry systems are also associated with comagmatic calc-alkaline volcanic rocks typically of intermediate to felsic composition (Sillitoe, 1973).

Panama is a region characterized by a long-lived intra-oceanic subduction zone with a magmatic arc active since the Late Cretaceous (e.g., Lissinna, 2005; Buchs *et al.*, 2010, 2011; Corral et al., 2011, 2016). It is mainly constituted by two east-trending parallel magmatic arcs (Fig. 1) of Cretaceous to Paleogene and Neogene to Quaternary ages. These arcs record changes in magmatism (tholeiitic → calc-alkaline → adakite-like) and are intruded by comagmatic batholith scale intrusions of intermediate to felsic composition (Lissina, 2005; Buchs et al., 2010; Wörner et al., 2009; Wegner et al., 2011; Corral et al., 2011; Montes et al., 2012). These conditions favoured the formation of numerous porphyry and epithermal deposits (Fig. 1).

The mature Neogene to Quaternary magmatic arc hosts most of the known porphyry and epithermal deposits in Panama (e.g., Cerro Colorado, Cerro Chorcha, Santa Rosa and Remance; Fig. 8). In contrast, porphyry and epithermal deposits hosted in the early magmatic arc are scarce (Cerro Quema, Río Pito; Fig. 8). The presence of these two deposits indicates that the early magmatic arc was mature enough to produce Au-Cu mineralization of economic interest.

Considering that the Panamanian magmatic arc was ore-productive by ~49 Ma broadens the areas where additional mineral deposits can be found in the overlooked Cretaceous – Paleogene magmatic arc. These would include Cretaceous volcanic and volcanosedimentary sequences intruded by Paleogene batholiths of intermediate to felsic composition, as in the Cerro Quema and the Río Pito deposits. Evidences of this potential are shown by the numerous gold occurrences present in the Azuero Peninusula (e.g., Pitaloza, Juan Díaz, Quebrada Iguana, Cerro Negro; Corral et al., 2011, 2016; Medina-Molero et al., 2014; Fig 2.).

This study reinforces the importance of properly exploring early arc segments in the Panamanian magmatic arc. Additionally, it also highlights the potential of these arc segments for hosting Au-Cu mineralization of economic interest in the Caribbean realm.

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Fig. Captions

Fig. 1: Simplified geologic map of Panama with the location of known porphyry copper and epithermal deposits, including Cerro Quema (Modified from Buchs et al., 2010). Bathymetry based on Smith and Sandwell (1997). Quaternary faults from Cowan et al., (1998), Montero et al., (1998), and Paris et al., (2000). NPDB = North Panama Deformed Belt.

Fig. 2: Simplified geologic map of the Azuero Peninsula with the main epithermal occurrences. AAG = Azuero Arc Group, ACF = Agua Clara fault, PMF = Punta Mala fault, RJFZ = Río Joaquín Fault Zone (after Direccion General de Recursos Minerales, 1976; Buchs et al., 2011; Corral et al., 2011, 2013, 2016). 1) Cerro Quema, 2) Pitaloza, 3) Juan Díaz, 4) Las Minas, 5) Quebrada Barro, 6) Quebrada Iguana, 7) Cerro Viejo.

Fig. 3: Cerro Quema hydrothermal alteration maps A) La Pava orebody and Chontal Edge zone. B) Cerro Quemita and Cerro Quema orebodies (after Corral et al., 2011, 2016, 2017).

Fig. 4: Characteristics of alunite from Cerro Quema. A) Drill core sample of the alunite ± pyrite-cemented hydraulic breccia developed in a quartz – alunite ± dickite altered dacite. B) Microphotography of the alunite ± pyrite-cemented breccia and the host rock (cross-polarized transmitted light). C) BSE image of the quartz - alunite ± dickite - pyrite assemblage. APS

minerals typically occur in the core of alunite crystals. Alunite crystals show compositional banding: Dark grey Na-rich zone; Light grey K-rich zone. D) BSE image of a well crystallized woodhouseite within the advanced argillic alteration. Mineral abbreviations according to Whitney and Evans (2010): alu = alunite, aps = aluminum phosphate-sulfate minerals, dck = dickite, K-alu = K-rich alunite, Na-alu = Na-rich alunite, py = pyrite, qz = quartz, qz-e = quartz eye and wo = woodhouseite.

Fig. 5: ^{40}Ar/^{39}Ar spectra of the dated alunite samples from Cerro Quema.

Fig. 6: Summary of the hornblende ^{40}Ar/^{39}Ar dating of the Río Quema Formation dacite domes and equivalent rocks from the Azuero Peninsula. A – C: Samples form Wegner et al. (2011) collected at 10 and 5 km away from Cerro Quema, respectively. D – F: Samples from Corral et al. (2016) collected at La Pava orebody. Plateau ages of A and B have been discarded in this study, and C to F are the representative ages of the Río Quema Formation (as discussed in the text).

Fig. 7: Comparative diagram showing the geochronological data of the El Montuoso Batholith, Dacites of the Río Quema Formation and the Re-Os molybdenite ages of Perelló et al. (2020). Avg. = average, CQ = Cerro Quema, hbl = hornblende, mo = molybdenite, RQF = Río Quema Formation.

Fig. 8: Summary of age determinations on volcanic and plutonic rocks associated with the described Panamanian ore deposits.

Table 1: Summary of the Cerro Quema mineral resources (after Sutcliffe et al., 2014).

Table 2: Main characteristics summary of the known Panamanian porphyry and epithermal deposits.

Table 3: Summary of the available geochronological data of the Azuero Peninsula (SW Panama). * = Assigned to the Río Quema Formation due to textural, geochemical and geochronological similarities. ** = Not considered in this study as described in the text. *** = Not considered in this study as it is not a plateau age.

Table 4: Age calculations for the dated alunite sample.

Appendix 1: $^{40}Ar/^{39}Ar$ raw data for alunite from Cerro Quema.