Porphyry-related high-sulfidation mineralization early in Central American Arc development: Cerro Quema deposit, Azuero Peninsula, Panama

Mineralización de alta sulfuración en relación con pórfidos en el desarrollo del Arco Centroamericano: El depósito de Cerro Quema, Península de Azuero, Panamá

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ABSTRACT

The 70.74 to 70.66 Ma age range for three molybdenite samples accompanying pyrite- and enargite-bearing assemblages effectively constrains an earliest Maastrichtian age for the high-sulfidation Au-Cu mineralization at Cerro Quema, Panama. The epithermal system was contemporaneous with emplacement of a composite dacite dome complex in a geotectonic setting transitional from mafic, primitive intraoceanic (Azuero Protoarc) to more evolved island arc magmatism (Azuero Arc), during initial construction of the Central American land bridge at the trailing edge of the Caribbean Large Igneous Province (CLIP). The molybdenite ages confirm the rapid evolution of the earliest stages of the Central American Arc, from subduction initiation at 75–73 Ma to arc maturation at 71 Ma. A porphyry connection is apparent at Cerro Quema and characterized by highly contorted, banded, and planar quartz-veinlet stockworks and sheeted zones in pyrophyllite- and sericite-bearing patchy-textured rock. These are cut by ledges of quartz, alunite, and dickite, which implies overprinting of the advanced argillic lithocap onto the underlying porphyry environment. Hydrothermal telescoping resulted from synmineralization uplift congruent with an actively emerging volcanic arc, which the Re-Os molybdenite dates accurately constrain at 71 Ma, presumably as a far-field effect of collision between the leading edge of the CLIP with parts of North and South America.

Keywords: Azuero, Caribean Large Igneous Province, Central American Arc, High-sulfidation, Molybdenite.

RESUMEN

La edad maastrichtiana temprana, entre los 70,74 y 70,66 millones de años, de la mineralización epitermal de Cu-Au de alta sulfuración en Cerro Quema queda definida mediante dataciones Re-Os en molibdenita contenida en vetillas de pirita y enargita. El sistema epitermal evolucionó durante el emplazamiento de un complejo de domos dacíticos en un ambiente geotectónico transicional entre un arco intraoceánico máfico primitivo (Proto Arco Azuero) y un arco de islas más evolucionado (Arco Azuero), durante la construcción inicial de América Central sobre el borde terminal de la provincia magmática caribeña ("Caribbean Large Igneous Province, CLIP"). Las edades en molibdenita confirman la rápida evolución de los estadios tempranos del Arco Centroamericano, desde el inicio de subducción a los 75 – 73 Ma, hasta uno de madurez a los 71 Ma. Se destaca la relación geológica entre el sistema epitermal de Cerro Quema y un ambiente de tipo pórfido en profundidad, caracterizado este último por un conjunto de vetillas de cuarzo de hábito variable, principalmente irregulares, bandeadas y sinuosas (tipo A), distribuidas en forma de enrejados ("stockworks") y/o como corredores unidireccionales dentro de un pórfido dacítico. Este último desarrolla textura moteada de tipo "patchy", con ensambles de alteración dominados por pirofilita y sericita. Estas zonas de intenso vetilleo están cortadas por cuerpos ("ledges") silíceos con abundante alunita y dickita asociados al desarrollo de una litocapa sobreimpuesta al ambiente de pórfido. Se estima que esta sobreimposición hidrotermal habría resultado como parte del surgimiento del arco volcánico contemporáneo con la mineralización de Cerro Quema, alzamiento que queda constreñido de manera precisa por las edades en molibdenita en los 71 Ma. Este alzamiento del arco habría sido, a su vez, gatillado por procesos tectónicos regionales, entre los que se incluye la colisión entre el borde frontal de la CLIP y ciertas regiones continentales de Norte y Sudamérica.

Palabras clave: Azuero, Provincia Magmática Caribeña, Arco Centroamericano, Alta Sulfuración, Molibdenita.

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1. Introduction

1.1. TECTONIC ASPECTS

The geotectonic setting and evolution of the Caribbean realm have long been subjects of much debate and controversy (Malfait and Dinkelman, 1972; Burke, 1988; Pindell *et al.*, 1988, 2005, 2006, 2011; Frisch *et al.*, 1992; Meschede and Frisch, 1998; Kerr *et al.*, 1999, 2003; Kerr and Tarney, 2005; James, 2006; Iturralde-Vinent and Lidiak, 2006; Pindell and Kennan, 2009; Hastie and Kerr, 2010b; Geldmacher *et al.*, 2008). Plate interactions in Cretaceous time, subduction polarity and reversals during construction of the Great Caribbean Arc, the nature and inception of the Caribbean Large Igneous Province (CLIP; also known as Caribbean Plateau) as well as its role in Caribbean tectonics, and the establishment of the Central American land bridge are among the key aspects of this debate (*e.g.*, Pindell *et al.*, 2006). Competing models of the evolution of the CLIP invoke either an allochthonous, Galapagos-related origin for the thick buoyant crust that was later displaced northeastward between the Americas (Malfait and Dinkelman, 1972; Burke, 1988; Duncan and Hargraves, 1984; Kerr *et al.*, 1999; Hoernle *et al.*, 2004; Hastie and Kerr, 2010; Hastie *et al.*, 2010a, 2010b; Whattam *et al.*, 2012; Nerlich *et al.*, 2014), or an autochthonous alternative in which the Caribbean lithosphere formed in an inter-American position, between the North and South American continental blocks (Frisch *et al.*, 1992; Meschede and Frisch, 1998; James, 2006).

With some notable exceptions, most models, particularly those concerned with the geodynamic evolution of the leading, eastern edge of the CLIP during its northeastward migration, pay little attention to its southwestern trailing border and do not constrain the precise timing of the birth of the inter-American land bridge. Various lines of evidence support the hypothesis that this arc segment, also called Central American Arc or South Central American Arc (Buchs *et al.*, 2010, 2011a,2011b, 2016), formed in the latest Cretaceous on top of the southwestern edge of the CLIP (Lissinna, 2005; Buchs, 2008; Wörner *et al.*, 2009; Wegner *et al.*, 2011; Buchs *et al.*, 2010, 2011a, 2016), with arc initiation timing defined on regional and biochronologic grounds. The reasons for subduction initiation along this trailing part of the CLIP are also poorly established, but traditionally hypothesized to be in response to the diachronous collision between the CLIP and separate North and South American continental blocks (Mitchell, 2003; Kerr and Tarney, 2005; Hastie *et al.*, 2010a, 2010b; Whattam *et al.*, 2012; Boschman *et al.*, 2014; Nerlich *et al.*, 2014; Braz *et al.*, 2018; Cardona *et al.*, 2018) or due to plume-induced spontaneous subduction initiation (Whattam and Stern, 2015; Whattam, 2018).

1.2. MINERAL DEPOSIT ASPECTS

High-sulfidation epithermal deposits are characterized by sulfide-rich mineral assemblages with a high sulfidation state (Einaudi *et al.*, 2003), typically pyrite and enargite, hosted by advanced argillic-altered rocks (Sillitoe, 1983, 1995, 1999; Hedenquist, 1987; White, 1991; Arribas, 1995; Hedenquist *et al.*, 2000). The Cu-Au mineralization is genetically related to andesitic–dacitic arc complexes of calc-alkaline composition (Sillitoe, 1993, 1999; Arribas, 1995; Sillitoe and Hedenquist, 2003), and the zones of advanced argillic alteration form lithocaps, which are integral parts of porphyry copper systems (Sillitoe, 1995, 2010). Domes are typical settings for shallow- (500 m) and intermediate-depth (<1000 m) deposits. Vuggy residual quartz and alunite are common in shallower examples, and massive sulfide lodes increase at depth, together with the proportion of pyrophyllite, dickite, and sericite. Tetrahedrite-tennantite plus chalcopyrite characterize intermediate depths, whereas bornite and chalcocite-group minerals hosted by quartz-pyrophyllite and/or sericite alteration occur at the transition to the deeper porphyry environment (Hedenquist *et al.*, 2000; Sillitoe, 1995, 2010). The vuggy residual quartz, together with massive sulfide bodies, mark the principal fluid upflow channels (Sillitoe, 1995,

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1999; Hedenquist *et al.*, 2017), and both alteration and mineralization can be coeval with porphyry copper emplacement at depth (Hedenquist *et al.*, 1998, 2017; Sillitoe, 1995, 2010).

This contribution reports four Re-Os (molybdenite) ages from the porphyry-related Cerro Quema high-sulfidation epithermal Cu-Au deposit in the Azuero Peninsula, Panama (Corral, 2013; Corral *et al.*, 2016; Figure 1). Because a genetic connection between porphyry and high-sulfidation epithermal deposits and subduction-related arc terranes has long been recognized (*e.g.*, Sillitoe and Hedenquist, 2003), these molybdenite ages constrain formation of the epithermal Cu-Au mineralization and its underlying porphyry source, and assist with better definition of the timing of inception of arc magmatism and mineralization in the Central American Arc. The precise Re-Os molybdenite ages reported herein are also significant because, with a few modern exceptions (Montes *et al.*, 2012; Ramírez *et al.*, 2016), the majority of geodynamic and tectonomagmatic reconstructions for the region are based on less-reliable K-Ar and ^{40}Ar-^{39}Ar age determinations (Del Giudice and Recchi, 1969; Kesler *et al.*, 1977; Bourgois *et al.*, 1982; Hoernle *et al.*, 2004; Lissinna,

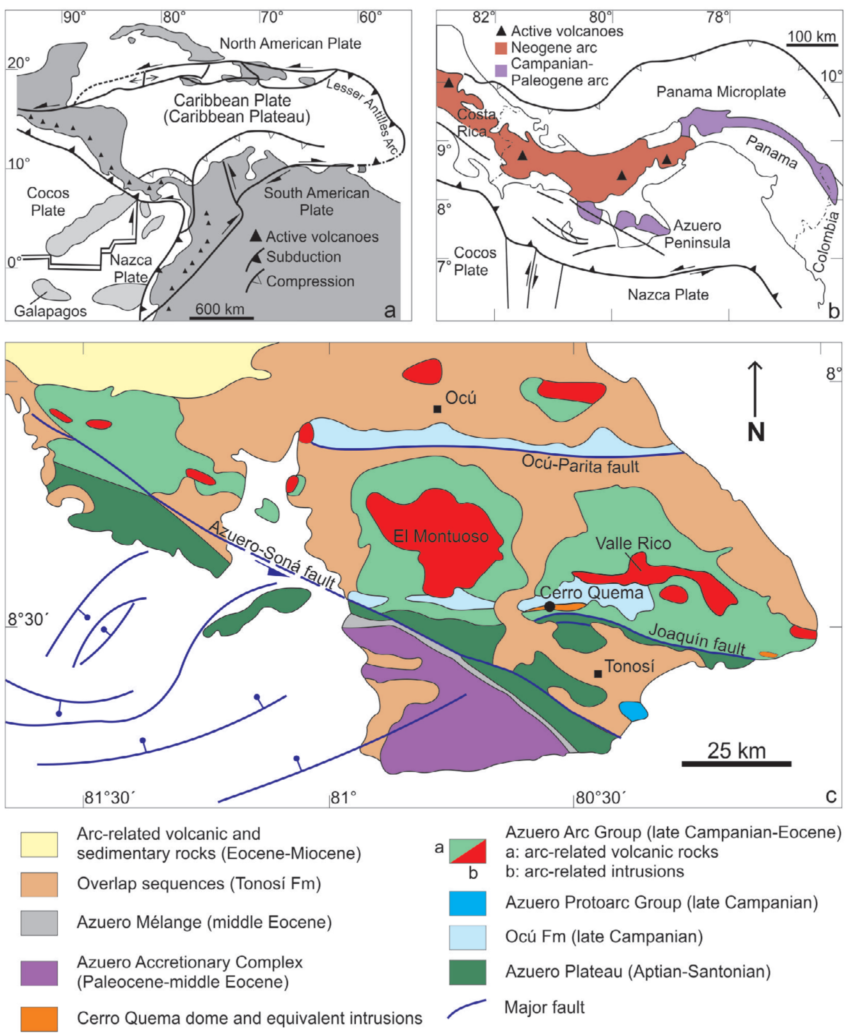

Figure 1 Geologic and geotectonic elements of the Central American region. (a) Sketch map showing the regional geotectonic setting of the Central American land bridge in a Caribbean context (after Wegner *et al.*, 2011). (b) Tectonic setting of the Isthmus of Panama (simplified from Montes *et al.*, 2012). (c) Simplified geological map of the Azuero Peninsula. Mainly after Buchs *et al.* (2010, 2011a), with additions from Corral *et al.* (2016).

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2005; Wegner *et al.*, 2011; Corral *et al.*, 2016). Many of these ages are likely compromised by disturbed isotopic systems, including the presence of excess argon and partial to complete resetting and neocrystallization during younger heating events (*e.g.*, Lissinna, 2005, and references therein; Buchs *et al.*, 2011b; Corral *et al.*, 2016).

2. Central American Arc and Azuero Peninsula

The Central American fore-arc region, including the Azuero Peninsula and nearby areas of southern Panama and Costa Rica (Figure 1), comprise an assemblage of in situ CLIP-derived units, volcanoplutonic arcs, and related volcanosedimentary sequences as well as exotic, accreted oceanic blocks (Lissinna, 2005; Denyer *et al.*, 2006; Buchs *et al.*, 2010, 2011a; Corral *et al.*, 2016). Four main lithostratigraphic units are distinguished (Buchs, 2008; Buchs *et al.*, 2010, 2011a): the Azuero Plateau, the Ocú Formation, the Azuero Protoarc Group, and the Azuero Arc Group (Figures 1 and 2). These are partially covered by younger sedimentary and volcanosedimentary overlap sequences (*e.g.*, Tonosí Formation; Figures 1 and 2). To the south, rocks of the Azuero Plateau are in tectonic contact with Paleocene to Eocene seamounts, pieces of CLIP, and kilometer-wide mélange zones of the Azuero Accretionary Complex (Buchs *et al.*, 2010, 2011a; Figure 1). The Río Quema Formation (Figure 2), a stratigraphic unit introduced by Corral *et al.* (2011) for the area of Cerro Quema in the central Azuero Peninsula, comprises detrital calcareous strata interbedded with Azuero Arc Group components.

The Azuero Plateau contains massive, columnar, and pillowed lava flows of basaltic composition. The interbedded radiolarian chert defines a Coniacian to early Santonian (~89–85 Ma) age for the sequence (Kolarsky *et al.*, 1995; Buchs *et al.*, 2010). The volcanic rocks and associated gabbro intrusions have the geochemical features of low-K oceanic tholeiitic plateau basalts and are interpreted to be uplifted parts of the CLIP (Lissinna, 2005; Buchs, 2008; Wörner *et al.*, 2009; Buchs *et al.*, 2010, 2011a; Corral *et al.*, 2011, 2016; Wegner *et al.*, 2011; Wattham and Stern, 2015). The radiolarian age assignment is broadly consistent with modern ^{40}Ar-^{39}Ar geochronological data that confirm basaltic magmatism between ~93 and 83 Ma (Lissinna, 2005), in general agreement with the timing of principal CLIP plateau formation (Kerr *et al.*, 1999, 2003; Hoernle *et al.*, 2004). The Azuero Plateau basalts have a geochemical signature similar to other oceanic plateau sequences from the Caribbean and so have been considered to represent the southwestern trailing edge of the CLIP and the autochthonous basement over which the Central American Arc was initiated in the late Campanian (Buchs *et al.*, 2010, 2011a).The Ocú

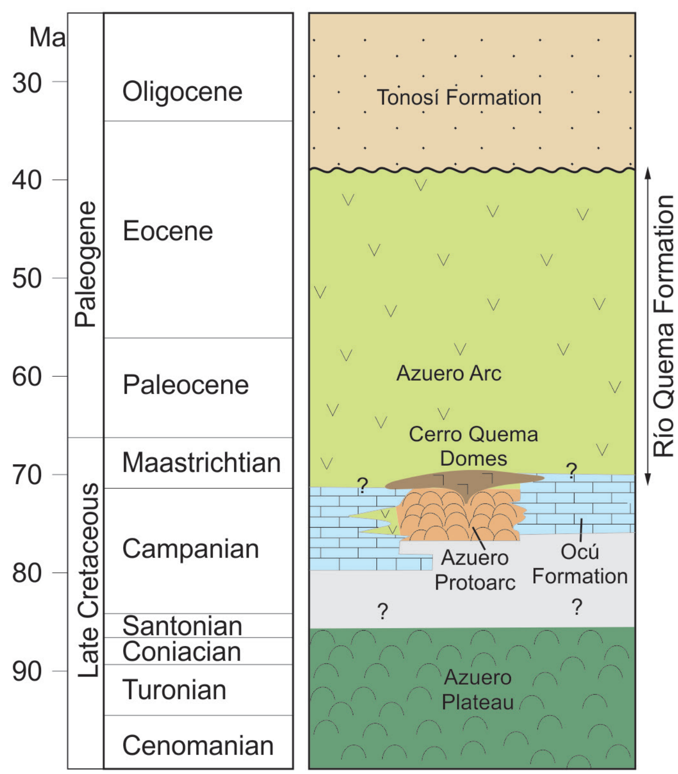

Figure 2 Simplified stratigraphic column for the Azuero Peninsula. Elements from Buchs *et al.* (2010, 2011a) and Corral *et al.* (2016 and references therein). Note the close relationships between the composite Cerro Quema dacite dome at the transition from Azuero Protoarc primitive lava flows and more differentiated Azuero Arc volcanic rocks, with intervening Ocú Formation carbonate rocks. The transition from Protoarc to Arc assemblages at the Campanian–Maastrichtian boundary reflects major regional geodynamic changes.

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Formation (Figures 1 and 2) is a foraminifera-bearing sequence of pelagic and hemipelagic limestone interbedded with volcanosedimentary rocks and basaltic flows of the Azuero Protoarc and basal parts of the Azuero Arc groups (Del Giudice and Recchi, 1969; Buchs *et al*., 2010, 2011a; Corral *et al*., 2013). The calcareous rocks vary from clean micritic through detrital to tuffaceous limestone, the last rich in quartz, feldspar, amphibole, and pumice fragments suggestive of an intermediate-composition volcanic source (Buchs *et al*., 2010, 2011a; Corral *et al*., 2013). Local tuffaceous layers together with conglomeratic strata imply a shallow depositional environment and the presence of nearby subaerial conditions (Buchs *et al*., 2010, 2011a). The formation is interpreted to rest upon the basalts of the Azuero Plateau and its age to be late Campanian (~75–73 Ma; Buchs *et al*., 2010), although formaminiferal assemblages from similar rocks in the vicinity of Cerro Quema (Río Quema Formation) expand this age to include the early Maastrichtian (Corral *et al*., 2013). The Ocú Formation accumulated on top of the Azuero Plateau during the earliest stages of the Central American Arc and correlates with equivalent strata in fore- and back-arc regions of Costa Rica as well as with pelagic carbonate rocks that rest upon the CLIP in the Caribbean Basin (Bowland and Rosencrantz, 1988; Bowland, 1993). The calcareous rocks of the Río Quema Formation (Corral *et al*., 2016), as well as similar sequences elsewhere in the region, are considered to represent facies variations of the Ocú Formation (Buchs *et al*., 2010, 2011a).

Exposures of Azuero Protoarc Group rocks are mainly present in islands offshore the peninsula and by equivalent units in Costa Rica (Buchs *et al*., 2011a). The scattered outcrops assigned to the Group in the Azuero Peninsula consist of pillowed mafic lava flows interbedded with Ocú Formation limestone together with abundant crosscutting mafic dikes (Buchs *et al*., 2010, 2011a). Pyroxene-bearing, porphyritic basaltic lava flows and dikes are common and possess petrochemical features transitional between CLIP oceanic basement and early, primitive arc rocks (Wörner *et al*., 2009; Wegner *et al*., 2011; Buchs *et al*., 2010, 2011a; Whattam and Stern, 2015). In the Azuero Peninsula, the MORB and within-plate tholeiitic chemistry of these rocks suggest that the Protoarc Group represents a late Campanian to early Maastrichtian primitive island arc sequence at the onset of magmatism in the Central American Arc (Buchs *et al*., 2010, 2011a; Corral *et al*., 2013, 2016; Whattam and Stern, 2015).

Rocks of the Azuero Arc Group are well exposed in the Azuero Peninsula (Figure 1), where the Group is dominantly composed of basaltic to intermediate volcanic rocks interbedded with calcareous and tuffaceous sedimentary rocks (Kolarsky *et al*., 1995; Lissinna, 2005; Wörner *et al*., 2009; Wegner *et al*., 2011; Buchs *et al*., 2010, 2011a; Corral *et al*., 2013, 2016). The volcanic rocks are typically porphyritic in texture, range from pyroxene-bearing basalt to quartz- and amphibole-bearing dacite, and occur as massive lava flows and flow-dome complexes. Lower parts of the Group possess petrochemical features characteristic of intraoceanic volcanic arc settings, with MORB, island arc tholeiitic, and within-plate tholeiitic signatures (Buchs *et al*., 2010, 2011a; Corral *et al*., 2013). Large variations in composition exist in the upper parts of the sequence, implying that the Group is the product of several different events during the Late Cretaceous to middle Eocene (Lissinna, 2005; Buchs *et al*., 2011a). Stratigraphic, paleontological, and geochronological data constrain the age of the lower part of the Azuero Arc Group to the late Campanian to Maastrichtian (Buchs *et al*., 2010, 2011a; Corral, 2013; Corral *et al*., 2013, 2016). In the Cerro Quema area, these rocks are intruded by the dome-related, amphibole-bearing dacitic stocks of the Río Quema Formation that yield ^{40}Ar-^{39}Ar (amphibole) ages of ~71–70 Ma (early Maastrichtian; Wegner *et al*., 2011; Corral *et al*., 2016; Figures 1 and 2), thereby confirming the Group's age assignment. Younger ages of ~68 to 65 Ma obtained for the Cerro Quema dacite dome (Corral *et al*., 2016) as well as ages of 65 to 52 Ma for Azuero Arc basaltic rocks (Lissinna, 2005, and references therein) could have been affected by thermal events generated by El Montuoso and Valle Rico batholith emplacement. These arc-related intrusions, of granodioritic to dioritic composition, occur along an east–west corridor to the north and northwest of the Cerro Quema area (Figure 1) and possess U-Pb zircon ages of 68 to 66 Ma (El Montuoso; Montes *et al.*, 2012; Ramírez *et al.*, 2016) and 49 Ma (Valle Rico; Montes *et al.*, 2012).

In summary, broadly coeval rocks of the Azuero Protoarc Group, lower parts of the Azuero Arc Group, and regional equivalents (Azuero-Soná Arc; Wörner *et al.*, 2009; Wegner *et al.*, 2011) are characterized by primitive suprasubduction arc signatures that support earliest evolution of the Central American Arc between the late Campanian and early Maastrichtian (~75–70 Ma; Buchs, 2008; Buchs *et al.*, 2010, 2011a; Corral *et al.*, 2013, 2016), whereas more differentiated, calc-alkaline, emergent arc volcanism is recorded higher in Azuero Arc stratigraphy (Buchs *et al.*, 2011a; Corral *et al.*, 2013).

3. Synopsis of Cerro Quema Geology

Mineralization in the Cerro Quema area occurs as several centers of which La Pava, Cerro Quema, and Cerro Quemita are the most important (Figure 3). A combined total (measured, indicated, and inferred) oxide resource of 24.6 Mt at 0.71 g/t Au and 0.04% Cu plus 11.4 Mt at 0.41 g/t Au and 0.31% Cu of sulfidic material has been estimated (Sutcliffe *et al.*, 2014), with a large proportion of it (26.8 Mt) at La Pava. Each center is funnel shaped and comprises near-surface supergene oxide ore underlain by sulfide protore, all occurring in association with advanced argillic alteration (Yang *et al.*, 1997; Corral, 2013; Corral *et al.*, 2010, 2016, 2017, 2018; Figure 3). All the centers are hosted by a west-trending quartz-, feldspar-, and hornblende-bearing dacite dome complex with a strike extent of ~25 km that, together with other dacite bodies farther east, forms a ~70 km long corridor along the Azuero Peninsula (Corral *et al.*, 2016). The dacite dome complex was emplaced in a volcaniclastic sedimentary sequence of the Azuero Arc Group (Figure 2), which in the Cerro Quema area also contains limestone and andesitic lava flows of the Río Quema Formation (Corral *et al.*, 2011, 2016; Figure 2). The dome complex comprises intrusive porphyritic and flow-banded phases of coarse-grained dacite, together with fine-grained crystal- and lithic-bearing tuffaceous rocks and blocky and brecciated hyaloclastite apron deposits. The regional Joaquín fault system marks the structural contact with Azuero Plateau units just south of Cerro Quema (Buchs, 2008; Buchs *et al.*, 2011a; Corral *et al.*, 2013, 2016; Figure 1). The alteration and mineralization at Cerro Quema were previously interpreted to have taken place under subaerial conditions in genetic association with a blind, subvolcanic porphyry intrusion emplaced during the Eocene Valle Rico magmatic episode (~55–49 Ma), some 15 to 20 My after dacite dome emplacement (Corral *et al.*, 2016, 2017).

A typical concentric alteration zoning pattern is apparent in all the centers, with central vuggy residual quartz and alunite followed outward by zones of kaolinite and dickite and, more externally, illite and chlorite. At La Pava, alteration and mineralization are associated with a large, multiphase, polylithic, clast- or matrix-supported hydrothermal breccia body (*e.g.*, Corral *et al.*, 2016, 2017; Figure 4), which cuts the dacite dome complex. The central silicic parts of the breccia contain both vuggy residual quartz and introduced quartz in the form of fine-grained silicification (Figures 3 and 4), with voids partly filled and lined by one or more of alunite, barite, rutile, pyrite, and enargite, plus localized chalcopyrite. Alunite and natroalunite are present as hydrothermal breccia cement, together with barite, dickite, and aluminum phosphate-sulfate minerals (Corral *et al.*, 2016). Pyrite, enargite, and tennantite are typical phases in the breccia cement, in which chalcopyrite is also a conspicuous component.

The central silicic core at La Pava is surrounded by a zone of quartz, dickite, and kaolinite alteration that gradually changes with depth to a

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mixed assemblage in which pyrophyllite dominates along with sericite and illite in various proportions (Figure 3). Ledges with quartz, alunite, and dickite overprint a zone of patchy-textured rock characterized by irregular, interspersed patches of pyrophyllite, plus lesser sericite and illite, and fine-grained quartz similar to assemblages described from upper parts of porphyry systems elsewhere (Gustafson *et al*., 2004; Sillitoe *et al*., 2013). Moderate to intense stockworks of irregular, sinuous, and contorted vein-like forms of fine-grained quartz, but also containing semicontinuous banded quartz veinlets and granular quartz veinlets of A-type (*cf*. Gustafson and Hunt, 1975), are present (Figure 4). These textures suggest proximity to underlying potential porphyry copper mineralization (*cf*. Gustafson *et al*., 2004; Sillitoe, 2010). The quartz stockworks contain principally pyrite, but chalcopyrite also occurs locally.

Deep drilling (~900 m) at other centers in the Cerro Quema area has revealed similar features to those at La Pava, with pyrophyllite-bearing assemblages rich in pyrite and enargite plus lesser covellite and hypogene chalcocite as well as

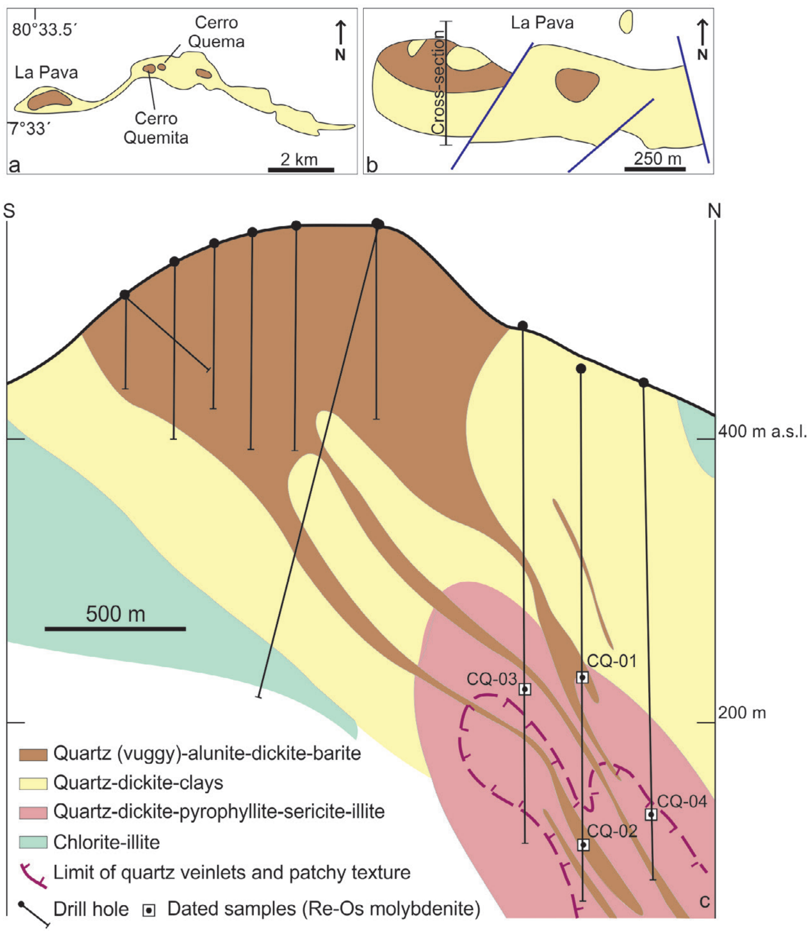

Figure 3 Elements of Cerro Quema geology. (a) Extent of the advanced argillic lithocap with location of three principal centers at La Pava, Cerro Quema, and Cerro Quemita (Yang *et al*., 1997). (b) Close-up of La Pava alteration zone (Corral *et al*., 2016) with location of cross-section shown in (c) (Yang *et al*., 1997; Sutcliffe *et al*., 2014). (c) Schematic cross-section through La Pava showing the funnel-like geometry of the advanced argillic alteration, with quartz-alunite preserved in the upper part (after Yang *et al*., 1997) and pyrophyllite-sericite-illite becoming widespread at depth. Note the contour of the patchy-textured rock and associated quartz-veinlet stockworks and sheeted zones defining the apical part of the porphyry copper environment (see Figure 4 for details of textures and assemblages) and the transgressive advanced argillic alteration ledges. The overall geometry suggests tilting to the south. The locations of dated samples CQ-01 to CQ-04 are also shown.

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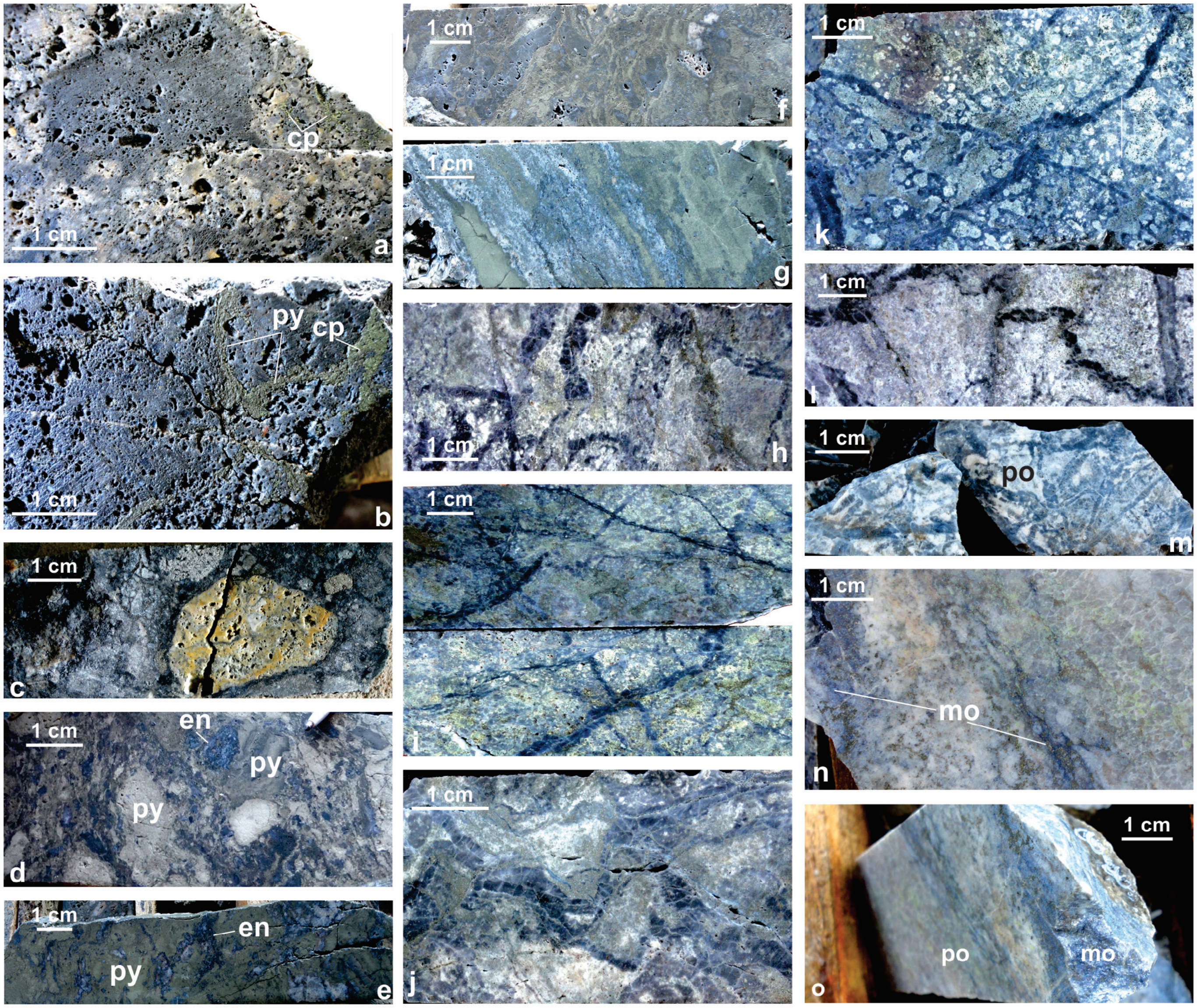

Figure 4 Selected photographs of La Pava. (a,b) Vuggy residual quartz rock with pyrite and chalcopyrite mineralization. (c–f) Various examples of the hydrothermal breccia body that hosts the bulk of the mineralization, including clast of vuggy residual quartz, sulfide-cemented zones, and massive sulfide zones following bedding planes. (h–m) Aspects of the quartz-veinlet stockwork zones highlighting the contorted and banded nature of early veinlet events crosscut by younger, more planar veinlets. The pyrophyllite-dominated patchy texture (m) involves intense quartz veining. (n,o) Samples of molybdenite in pyrophyllite-sericite-illite-altered rock, with molybdenite occurring as irregular seams and fractures in ledges with quartz-alunite, pyrite, and enargite. Abbreviations: cp: chalcopyrite; en: enargite; mo: molybdenite; py: pyrite; po: pyrophyllite.

anastomosing stockworks of quartz and anhydrite veinlets, some carrying chalcopyrite and molybdenite (Sutcliffe *et al*., 2014). B-type quartz veinlets are described together with inter- to late-mineral quartz-feldspar porphyry dikes and associated phreatomagmatic breccia bodies, all of which are interpreted as porphyry indicators (Sutcliffe *et al*., 2014). Overprinting of deeper, pyrophyllite-stable, chalcopyrite-molybdenite mineralization by shallower advanced argillic assemblages and associated high-sulfidation pyrite-enargite mineralization has been observed in most holes (Sutcliffe *et al*., 2014). Shallow, funnel-shaped upflow zones at Cerro Quema contain central quartz-pyrophyllite alteration surrounded by assemblages in which quartz and pyrophyllite are accompanied by kaolinite and interlayered clays (Yang *et al*., 1997). The prograde downward

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advance of the pyrophyllite front, the transgressive nature of the vuggy residual quartz and quartz-alunite ledges over pyrophyllite-bearing, patchy-textured rock and porphyry-type quartz-veinlet stockworks, and the presence of important chalcopyrite and tennantite as breccia cement and vuggy quartz infill are together taken to indicate that the Cerro Quema system is preserved at the transition between the basal parts of a lithocap and the top of the porphyry environment. Molybdenite is common in the deeper parts of the downward transgressive ledges at La Pava (Figure 3), confirming that the zone represents the upflow from a causative porphyry intrusion at depth (*cf*. Sillitoe, 1995, 1999, 2010). Contouring of alteration zones and quartz-veinlet stockworks suggest an apparent 60° southerly tilt of the coupled porphyry-epithermal system at La Pava (Figure 3), although this observation requires further confirmation.

4. Re-Os Molybdenite Geochronology

Dated samples CQ-01, CQ-02, CQ-03, and CQ-04 were collected from various hydrothermal breccia dikes and ledges, ranging from meter to decimeter widths and cutting fine-grained tuffaceous and porphyritic dacite at La Pava (Figure 3). In accord with the descriptions above, the breccia bodies display intense silicification and advanced argillic alteration, the latter comprising vuggy residual quartz, alunite, dickite, kaolinite, and barite. Petrographic work shows that the millimetric vugs are filled by barite, pyrite, and enargite whereas remnants of tabular plagioclase phenocrysts are replaced by well-crystallized kaolinite, rosettes of dickite, and peripheral alunite. In the transgressive ledges, the rock was transformed to fine-grained, sugary aggregates of quartz, rutile, dickite, and alunite, with hairline cracks filled by well-crystallized dickite, alunite, prismatic barite, pyrite, and enargite. Sulfide minerals occur as disseminations that nucleate in former plagioclase and ferromagnesian sites as well as along irregular hairline fractures. The pyrite is fine grained and microgranular, and forms aggregates with enargite and microneedles of molybdenite in a paragenetic sequence from pyrite through molybdenite to enargite. Where pyrite and chalcopyrite occur together, contact relationships indicate that the pyrite formed first, with local chalcopyrite containing inclusions or preserving cores of pyrite. A similar sulfide paragenetic sequence has been established at the Cerro Quema center (Corral *et al*., 2016).

4.1. ANALYTICAL METHODS AND RESULTS

Molybdenite separates from samples CQ-01, CQ-02, CQ-03, and CQ-04 were obtained by means of standard metal-free crushing, followed by gravity and magnetic concentration (Selby and Creaser, 2004; Kellog and Vega, 1995). The ^{187}Re and ^{187}Os concentrations in molybdenite were determined by isotope dilution mass spectrometry using Carius-tube, solvent extraction, anion chromatography and negative thermal ionization mass spectrometry techniques. A mixed double spike containing known amounts of isotopically enriched ^{185}Re, ^{190}Os, and ^{188}Os was used (Markey *et al*., 2007). The isotopic analyses were made using a ThermoScientific Triton mass spectrometer by Faraday collector. Total procedural blanks for Re and Os are <3 picograms and 2 picograms, respectively. These procedural blanks are insignificant in comparison to the Re and Os concentrations in molybdenite. A Chinese molybdenite powder (HLP-5; Markey *et al*., 1998) is used routinely as control sample. The uncertainty for all ages is quoted at 2σ level and includes all known analytical uncertainties, including a ~0.31% uncertainty in the decay constant of ^{187}Re.

Samples CQ-01, CQ-02, and CQ-03 yielded model ages between 70.74 ± 0.29 and 70.66 ± 0.29 Ma, whereas sample CQ-04 reported a younger age of 68.72 ± 0.29 Ma (Figure 3; Table 1). However, this last sample contains significant common Os (1226 pg; Table 1), unusually high for molybdenite and possibly implying the presence of some sulfide impurity, rendering the age less reliable.

Table 1. Re-Os isotopic and age data. Cerro Quema, Panama

Sample	Re ppm	± 2σ	187Re ppm	± 2σ	187Os ppb	± 2σ	Common Os pg	Model Age (Ma)	± 2σ (Ma)
CQ-01	1027	3	645	2	760.2	0.5	<5	70.66	0.29
CQ-02	3649	9	2294	6	2703	2	<5	70.70	0.29
CQ-03	660.6	1.7	415.2	1.1	489.7	0.3	37	70.74	0.29
CQ-04	6016	16	3782	10	4332	5	1226	68.72	0.29

5. Discussion

5.1. TECTONOMAGMATIC SETTING

The 70.74 to 70.66 Ma age range for the three reliable molybdenite samples from La Pava clearly constrain the earliest Maastrichtian age for the high-sulfidation alteration and mineralization at La Pava and for the entire Cerro Quema deposit. This age range is in agreement with the ^{40}Ar-^{39}Ar dates of ~71 Ma for amphibole-bearing dacitic rocks from the Cerro Quema area (Wegner *et al.*, 2011; Corral *et al.*, 2016) and confirms the volcanic dome-related setting for the epithermal Cu-Au mineralization: a classic environment for high-sulfidation epithermal deposits in magmatic arcs (Sillitoe, 1993, 1999; Arribas, 1995; Sillitoe and Hedenquist, 2003).

Although originally considered to be exclusively constructed of CLIP material (*e.g.*, Hoernle *et al.*, 2004), many oceanic terranes in Panama and Costa Rica have, more recently, been shown to contain mature suprasubduction igneous associations that represent various stages of arc construction atop the CLIP (Denyer *et al.*, 2006; Buchs, 2008; Wörner *et al.*, 2009; Buchs *et al.*, 2010, 2019; Wegner *et al.*, 2011; Whattam *et al.*, 2012). The 93 to 83 Ma oceanic rocks, upon which this early stage of the arc evolved, represent the southernmost trailing edge of the CLIP, which is interpreted to form the bulk of the Caribbean Plate (*e.g.*, Kerr *et al.*, 2003; Figures 1 and 5). Early arc construction, involving protoarc mafic lavas that mark the transition from intraplate oceanic to arc magmatism, was followed by generation of typical arc-like lavas and related intrusions (Lissinna, 2005; Wörner *et al.*, 2009; Buchs *et al.*, 2010; Wegner *et al.*, 2011). In this context, Azuero Protoarc Group rocks represent the earliest stages of intraoceanic arc construction in the late Campanian, with subduction initiation estimated at between ~75 and 73 Ma, to be followed by the more formal calc-alkaline Azuero Arc (Buchs, 2008; Buchs *et al.*, 2010, 2011a; Corral *et al.*, 2010; Figure 5).

The exact timing of establishment of the Azuero Arc is not well constrained in the literature, with the onset of island arc construction being broadly estimated as somewhere between the Maastrichtian and earliest Paleocene (~71–66 Ma) in parts of Panama and Costa Rica (Buchs, 2008; Buchs *et al.*, 2010, 2011a) or, more generally in the region, during the Campanian (84–71 Ma; Pindell and Kennan, 2009). The molybdenite ages reported herein are the first to more accurately constrain the timing of the transition from primitive intraoceanic arc magmatism (Azuero Protoarc) to the more formal calc-alkaline Azuero Arc, which must have been active in the earliest Maastrichtian, at ~71 Ma, to generate the dacite dome complex and associated mineralization at La Pava and elsewhere at Cerro Quema (Figures 5 and 6). In this sense, the molybdenite ages help to confirm establishment of the Central American Arc (or South Central American island arc) by the earliest Maastrichtian, with initiation of subduction of the Farallon plate beneath the CLIP-dominated Caribbean plate at ~75–73 Ma (*cf*. Buchs *et al.*, 2010, 2011a; Figure 5b). This 2 to 4 My period is shorter than the average 5 to 8 My estimate modeled for transitional processes between subduction initiation and arc maturation (Stern and Gerya, 2017, and references therein), but compares favorably with present-day examples as short as 2 My (*e.g.*, Patriat *et al.*, 2019)

The reasons for subduction initiation along the Central American Arc are still controversial. However, most tectonic models favor east-dipping

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subduction at the trailing southwestern edge of the CLIP being triggered by arrival of the leading, eastern edge of the CLIP at the subduction zone beneath the Great Antillean Arc, with consequent jamming of the subduction system (Kerr *et al.*, 1999; Pindell *et al.*, 2005; Pindell and Kennan, 2009; Hastie *et al.*, 2010a, 2010b; Whattam *et al.*, 2012). Collisions with parts of the Americas (Mitchell, 2003; Hastie *et al.*, 2010a, 2010b; Hastie and Kerr, 2010; Whattam *et al.*, 2012; Boschman *et al.*, 2014; Nerlich *et al.*, 2014; Braz *et al.*, 2018; Cardona *et al.*, 2018) are also possibilities (Figure 5c) that could have imposed major tectonic changes in the Central American Arc that, in turn, caused arc maturation. A far-field effect of such collisions, whereby a significant component of inter- and intraplate compression, uplift, and exhumation resulted from a marked increase in coupling of the Caribbean and North and South American plates at ~71–70 Ma (Kerr and Tarney, 2005; Kennan and Pindell, 2009; Buchs *et al.*, 2010), is also plausible (Figure 5c).

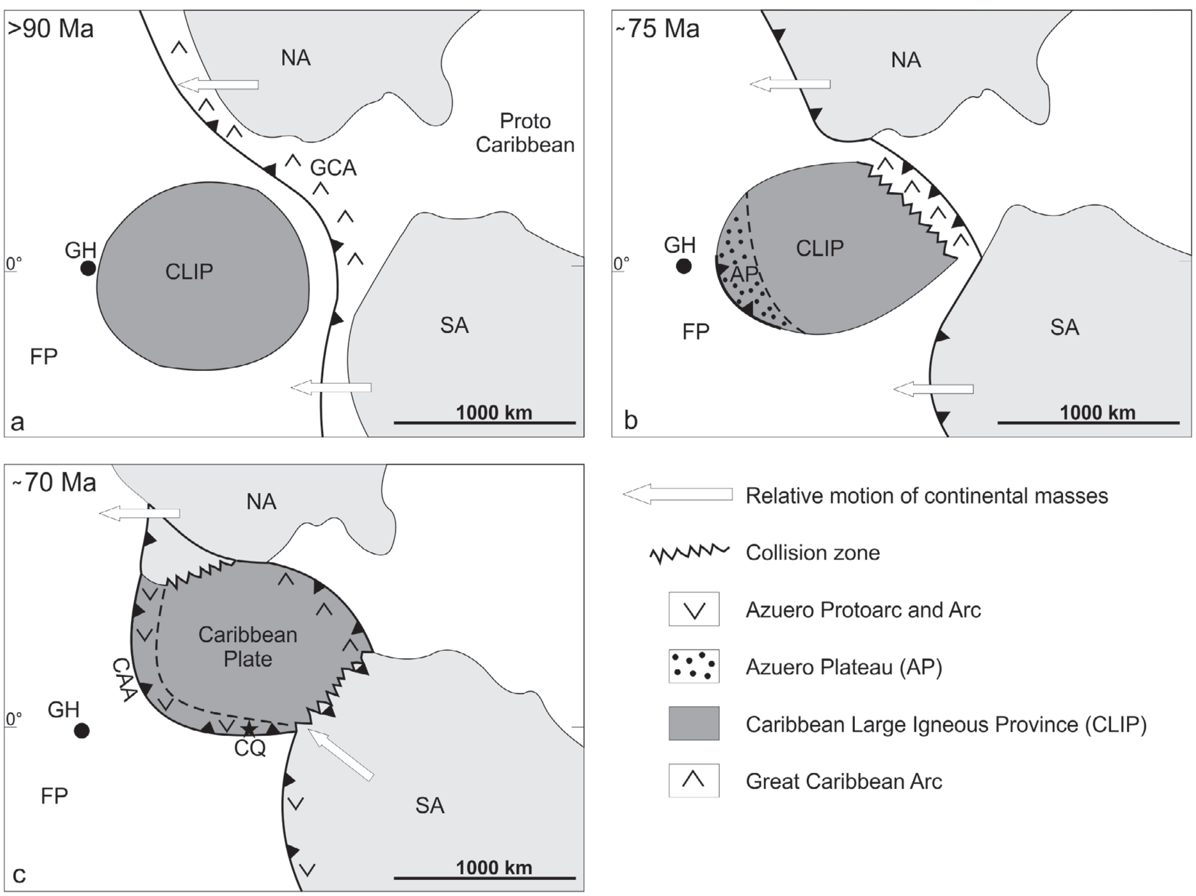

Figure 5 Illustrations showing the interaction between the Caribbean Large Igneous Province (CLIP), proto-Caribbean oceanic crust, and the large continental blocks of North and South America. (a) Displays the setting of the Great Caribbean Arc before arrival of the Galapagos-sourced CLIP. (b) Shows the Caribbean plate during collision of the leading edge of the CLIP with the Great Caribbean Arc and subduction polarity reversal. Note inception of a new subduction zone at the Azuero Plateau on the trailing edge of the CLIP, which forms the primitive Central American intraoceanic arc and associated tholeiitic volcanism. (c) Displays the collision of the CLIP with parts of North and South America and the more evolved development of the Central American Arc. The porphyry-related epithermal mineralization at Cerro Quema (shown by a star) was emplaced in this tectonomagmatic environment. Geologic and tectonomagmatic elements borrowed from multiple sources including Kerr *et al.* (1999), Mitchell (2003), Kerr and Tarney (2005), Kennan and Pindell (2009), Buchs *et al.* (2010, 2011, 2018), Hastie *et al.* (2010a, 2010b), Hastie and Kerr (2010), Wright and Wyld (2011), and Whattam *et al.* (2012). Abbreviations: AP: Azuero Plateau; CAA: Central American Arc; CQ: Cerro Quema; FP: Farallon Plate; GCA: Great Caribbean Arc; GH: Galapagos Hotspot; NA: North American Plate; SA: South American Plate.

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5.2. IMPLICATIONS FOR MINERALIZATION

The 70.74 to 70.66 Ma (early Maastrichtian) molybdenite age range contradicts the ~55 to 49 Ma (early Eocene) age assignment by Corral *et al*. (2016) for the high-sulfidation Cu-Au mineralization at Cerro Quema as well as its genetic association with a blind porphyry stock of the Eocene Valle Rico suite. The porphyry copper environment is indeed present in depth at La Pava as evidenced by the highly contorted and banded granular quartz-veinlet stockworks and sheeted zones together with classic porphyry-type A quartz veinlets in pyrophyllite-bearing alteration (Figures 3 and 4), which together imply the presence of a deeper causative porphyry stock (Figures 6a, b). Similar porphyry copper indicators have also been described for the other mineralized centers at Cerro Quema (Sutcliffe *et al*., 2014). Given the distance of ~3 km between La Pava and the other centers, it may be speculated that La Pava and Cerro Quema–Cerro Quemita were sourced by separate, although simultaneously evolving, porphyry copper stocks.

The relative abundance of chalcopyrite together with enargite in the principal metal-bearing stages at Cerro Quema (Corral *et al*., 2016, 2017) make this deposit an unusual example of the high-sulfidation epithermal class (*cf*., Einaudi *et al*., 2003; Figure 6c). In general, in high-sulfidation systems, chalcopyrite and tennantite-tetrahedrite tend to increase with depth as the porphyry environment is approached (Arribas, 1995; Hedenquist *et al*., 2000; Sillitoe, 2010). The occurrence of multiple stages of mineralization involving various proportions of pyrite, chalcopyrite, enargite, and tennantite, plus local bornite, in which chalcopyrite is paragenetically both early and late with respect to enargite (Corral *et al*., 2016, 2017), may reflect the peculiar, confined pathway followed by the mineralizing fluid during its evolution from intermediate- to high-sulfidation conditions (*cf*. Einaudi *et al*., 2003; Figure 6c). The rapid transition is herein ascribed to synmineralization telescoping of the system as a result of tectonic uplift and arc emergence (Figure 6b). Tectonic surface uplift and erosion during the lifespan of the epithermal-porphyry couple is speculated to have been in part controlled by structural adjustments in the Joaquín structural corridor (Figure 1). The apparent southerly tilting of the system could also have taken place at this time. Although a broad Paleocene timing for the transpressive activity along this fault corridor has been inferred previously (Corral *et al*., 2013, 2016), the mutually crosscutting relationships between the Joaquín structures and the 71-Ma Cerro Quema dacite dome complex would rather suggest a simultaneous evolution. Inversion along the Joaquín fault system could have been the product of far-field strain accommodation associated with collision or accretion of bathymetric objects along southern Central America (Denyer *et al*., 2006; Wegner *et al*., 2011; Montes *et al*., 2012; Rodriguez-Parra *et al*., 2016), some broadly contemporaneous with arc evolution in the Azuero Peninsula, which resulted in demonstrable rapid (~1 km/My), kilometer-scale surface uplift (Andjić *et al.*, 2018). Arc emergence induced by kilometric uplift would have, in turn, favored deposition of shallow-water calcareous sediments and the volcaniclastic turbidites that characterize the volcanosedimentary sequence of the central Azuero region (Buchs *et al*., 2011a; Corral *et al*., 2016; Figure 2). Volcanic-dome emergence and its alteration and mineralization under subaerial conditions at Cerro Quema are also evidenced by the fluid inclusion and isotopic signatures of the hydrothermal fluids, in which dilution of magmatic fluid by meteoric water was a prerequisite, without participation of seawater (*e.g.*, Corral *et al*., 2017).

Regionally, the high-sulfidation epithermal cluster at Cerro Quema, as well as other epithermal prospects associated with dacitic domes and Azuero Arc Group rocks elsewhere in the Azuero Peninsula (Medina Molero *et al*., 2014; Corral *et al*., 2016), are likely to be part of the same metallogenic event. In contrast, epithermal mineralization hosted by younger intrusions (*e.g.*, El Montuoso batholith; Corral *et al*., 2016) must belong to separate metallogenic events linked to arc maturation.

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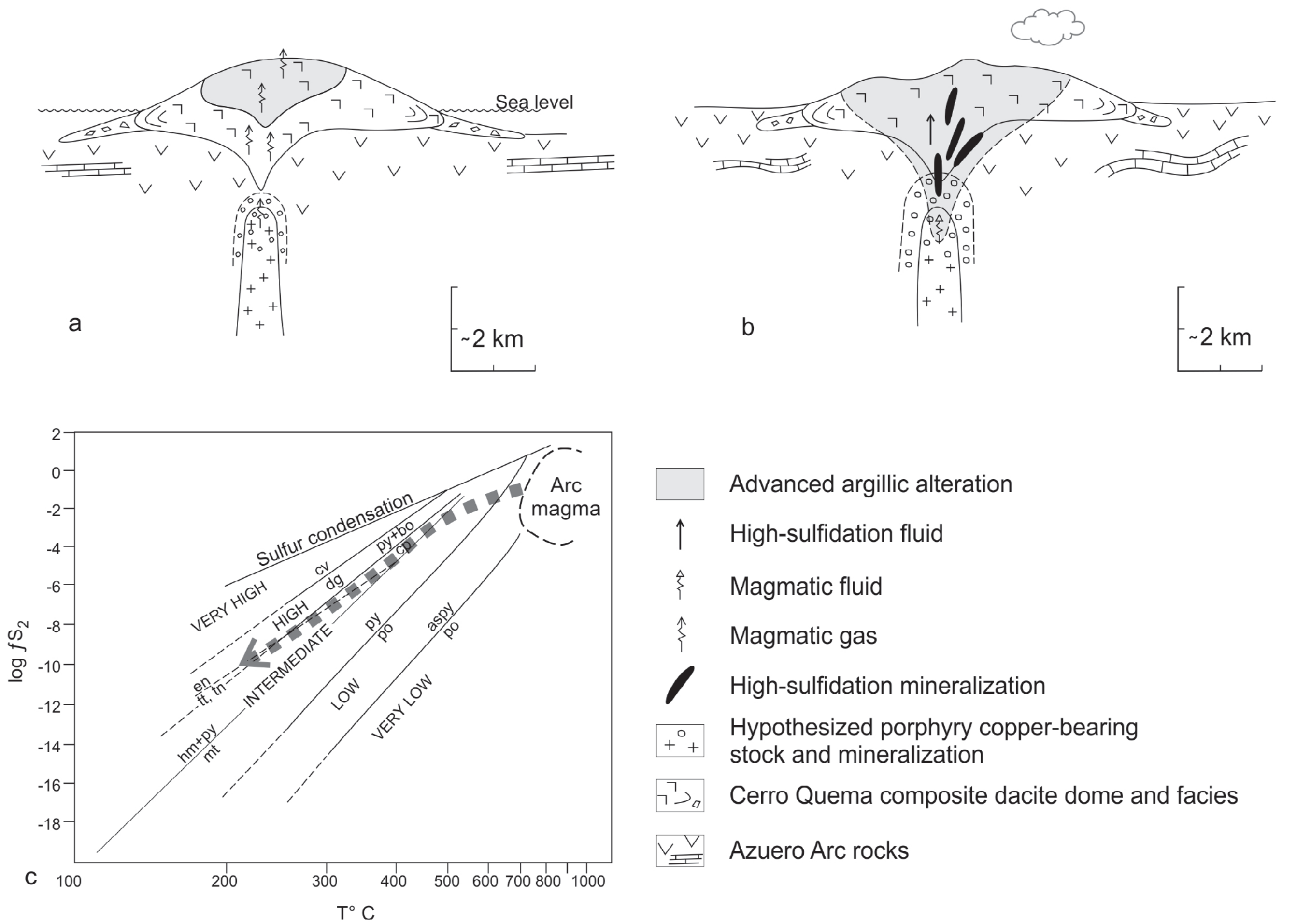

Figure 6 Schematic model for the emplacement of the Cerro Quema dacite dome complex and associated porphyry-epithermal mineralization. (a) Emplacement of Cerro Quema dacite dome in part under subaquatic conditions to form the associated hyaloclastite apron deposits (Corral *et al.*, 2013, 2016). A degassing porphyry stock at depth, decoupled from the shallow epithermal environment, contributed to the formation of initial lithocap assemblages. (b) Progressive development of the porphyry-epithermal couple broadly coincident with regional arc emergence and consequent uplift of the system. The apical part of the porphyry source reaches the epithermal environment, with the bulk of the epithermal mineralization taking place under subaerial conditions (Corral *et al.*, 2017). Tectonic deformation is inferred, and the postulated tilting of the porphyry-epithermal system could have taken place at this time. (c) Inferred pathway of the epithermal fluid from the porphyry environment, showing its confinement to the boundary between chalcopyrite and enargite stability and its evolution from intermediate- toward high-sulfidation conditions. Diagram simplified from Einaudi *et al.* (2003). Mineral abbreviations: aspy: arsenopyrite; bo: bornite; cv: covellite; cp: chalcopyrite; dg: digenite; en: enargite; hm: hematite; mt: magnetite; po: pyrrhotite; py: pyrite; tn: tennantite; tt: tetrahedrite.

5.3. METALLOGENIC IMPLICATIONS

The precise new age data for La Pava clarify the genetic relationship between the Cerro Quema mineralization and the primitive magmatism that represents the transition from intraoceanic to island arc settings during early stages of the Central American Arc (or South Central American Arc) as well as confirming that porphyry-related high-sulfidation epithermal deposits can form in such environments. A similar conclusion was reached for the Pueblo Viejo district in the Dominican Republic, where contemporaneous porphyry and high-sulfidation alteration-mineralization and tholeiitic volcanism characterized the change from subduction initiation to formal subduction during inception of Great Arc of the Caribbean island arc (Torró *et al.*, 2017a, 2017b). However, although

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the arc-related mafic lavas of the Azuero Protoarc Group were in part erupted simultaneously with the more-differentiated, calc-alkaline products of the Azuero Arc Group (Buchs, 2008; Buchs *et al*., 2010, 2011a), the volcanic dome-related alteration and mineralization at Cerro Quema evolved under subaerial conditions in association with the younger, more differentiated suite and not in a submarine mafic environment as envisioned, for example, at Pueblo Viejo (Kesler *et al*., 2005; Kirk *et al*., 2014; Nelson *et al*., 2015).

6. Conclusions

The 70.74 to 70.66 Ma age range for molybdenite accompanying high-sulfidation epithermal mineralization at Cerro Quema confirms rapid evolution of the inter-American land bridge from subduction initiation at ~75–73 Ma through early, primitive intraoceanic mafic to more evolved island arc magmatism at ~71 Ma to form the Central American Arc. The dynamism of the geotectonic setting is inferred to have been primarily a response to far-field effects of regional collision of leading parts of the CLIP with continental North and South America, although accretion of buoyant bathymetric objects on the down-going Farallon plate could also have been important for arc maturation.

Under these active tectonomagmatic conditions, and early during magmatic arc inception, a coupled porphyry-epithermal system was established at Cerro Quema in genetic association with a composite, dacitic dome complex while primitive, mafic volcanism was still regionally active. Subaerial conditions were rapidly attained due to regional volcanic arc emergence, and resulted in variable degrees of hydrothermal telescoping at the various mineralized centers at Cerro Quema. The new radiometric dates reported herein are the first to directly and precisely document the age of the high-sulfidation mineralization and lithocap formation. The stockworks and sheeted zones of highly contorted, banded, and planar quartz veinlets in pyrophyllite-stable alteration at La Pava and elsewhere at Cerro Quema are expressions of the apical parts of the porphyry environment and suggest at least two causative porphyry copper stocks are present at depth. These should be drill tested, particularly in proximity to the more reactive limestone horizons of the Ocú Formation and related calcareous sequences that are common in the area and likely to occur subsurface.

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