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Comment to “Porphyry-related high-sulfidation mineralization early in Central American Arc Development: Cerro Quema deposit, Azuero Peninsula, Panama” by Perelló et al., (2020)

Comentario a “Mineralización de alta sulfuración en relación con pórfidos en el desarrollo del Arco Centroamericano: El depósito de Cerro Quema, Península de Azuero, Panamá” por Perelló et al., (2020)

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ABSTRACT

The Cerro Quema Au-Cu deposit is hosted by a dacite dome complex of the Río Quema Formation, a Late Campanian-Maastrichtian volcano-sedimentary sequence of the Panamanian magmatic arc. Its formational age is constrained at ~49 Ma by field evidences, crosscutting relationships and ⁴⁰Ar/³⁹Ar geochronology (Corral et al., 2016, Corral, 2021). The recent molybdenite Re-Os dates by Perelló et al. (2020) claim that ore is spatially and temporally related to the host volcanic domes at ~71 Ma. After a thorough review of the geologic, geochemical and geochronological data from the Cerro Quema area, it is concluded that the Re-Os dates of Perelló et al. (2020) are not representative of the Cerro Quema formational age. Their proposed formational age at ~71 Ma is significantly older than the age of the host rock (~67 Ma). Furthermore, they invoke a previously unrecognized regional-scale magmatic event solely based on their molybdenite Re-Os dates. Instead, the Cerro Quema genetic model discussed here, in which magmatic-hydrothermal fluids derived from porphyry copper-like intrusions associated with the Valle Rico batholith produced the Au-Cu mineralization at ~49 Ma, is consistent with the geology, geochemistry and geochronology of the Azuero Peninsula.

Keywords: Alunite ⁴⁰Ar/³⁹Ar dating, Cerro Quema, Gold-copper, Porphyry-related high-sulfidation, Panama.

RESUMEN

El yacimiento de Au-Cu de Cerro Quema está encajado en el complejo de domos dacíticos de la Formación Río Quema, una secuencia volcanosedimentaria de edad Campaniense-Maastrichtiense del arco magmático de Panamá. Su edad de formación de ~49 Ma ha sido determinada mediante evidencias de campo, relaciones de corte y geocronología ⁴⁰Ar/³⁹Ar (Corral et al., 2016, Corral, 2021). Las recientes edades de Re-Os en molibdenita presentadas por Perelló et al. (2020) afirman que la mineralización está relacionada espacial y temporalmente con los domos volcánicos, que actúan como roca caja, hace ~71 Ma. Después de una revisión exhaustiva de los datos geológicos, geoquímicos y geocronológicos del área de Cerro Quema, se concluye que las edades Re-Os de Perelló et al. (2020) no son representativas de la edad de formación de Cerro Quema. La edad de formación propuesta de ~71 Ma es significativamente más antigua que la edad de la roca caja (~67 Ma). Además, se propone un evento magmático a escala regional previamente no reconocido basándose únicamente en edades Re-Os en molibdenita. En cambio, el modelo genético de Cerro Quema discutido aquí, donde los fluidos magmáticos-hidrotermales derivados de intrusiones tipo pórfido cuprífero asociadas al batolito de Valle Rico produjeron la mineralización de oro-cobre hace ~49 Ma, es consistente con la geología, geoquímica y geocronología de la Península de Azuero.

Palabras clave: Datación ⁴⁰Ar/³⁹Ar de alunite, Cerro Quema, Oro-cobre, Alta sulfuración relacionado con pórfidos, Panamá.

1. Introduction

The recent molybdenite Re-Os dating study by Perelló *et al.*, (2020) of the Cerro Quema deposit (Azuerro Peninsula, Panama) claims that ore is spatially and temporally related to the volcanic domes of the Río Quema Formation at ~71 Ma. This interpretation contrasts with early observations indicating that mineralization is the product of a hydrothermal system (e.g., porphyry system) driven by concealed intrusions associated with the Valle Rico batholith at 55 – 49 Ma (Corral *et al.*, 2016) as well as with the recently obtained alunite $^{40}\text{Ar}/^{39}\text{Ar}$ date of ~49 Ma (Corral, 2021). Although the ~71 Ma age would indicate that Cerro Quema is similar to other high-sulfidation epithermal deposits in which mineralization is coeval with volcanic dome emplacement (Arribas, 1995; Bissig *et al.*, 2001; Nelson *et al.*, 2015; Holley *et al.*, 2016; Torró *et al.*, 2017; Sahlström *et al.*, 2018), it conflicts with geologic evidences as well as with previous geochronologic studies of the Azuerro Peninsula (Lissinna, 2005; Buchs *et al.*, 2010, 2011; Wegner *et al.*, 2011; Montes *et al.*, 2012; Corral *et al.*, 2013, 2016). Since Cerro Quema stands as the first discovery of a high-sulfidation epithermal Au-Cu deposit in Panama, its correct geologic contextualization, including the formational age and the genetic model, will aid exploration for similar deposits in Panama.

My concern with the manuscript presented by Perelló *et al.*, (2020) centers on their interpretation of the previous field-based, geochemical and geochronological studies of the Azuerro Peninsula, the significance and reliability of the new Re-Os molybdenite ages, and the role of the dacite domes in the gold and copper mineralization. Here, an alternative interpretation to explain the formation of Cerro Quema, consistent with key field evidences and geochronological studies of the Azuerro Peninsula, is presented.

2. Geology and geochemistry of the Cerro Quema area

Perelló *et al.*, (2020) present a complete and updated literature review of the geological and geochronological studies carried out in the Azuerro Peninsula. However, less attention has been paid to the geology of the Cerro Quema area in particular. Contrary to the geologic relationships reported by Perelló *et al.*, (2020), the dacite dome complex is interfingering with volcanic, volcanoclastic rocks and pelagic to hemipelagic limestones (Río Quema Formation upper unit) that sits atop of a ~100 m thick hemipelagic limestone (Río Quema Formation Limestone unit) that in turn sits atop of a ~300 m thick pile of turbidites, siltstones and mudstones (Figure 1; Corral *et al.*, 2011, 2013, 2016). The Río Quema Formation discordantly overlaps the Azuerro Protoarc. Therefore, there is no contact and close relationship between the dacite dome complex and the Azuerro Protoarc as they have >500 m of igneous and sedimentary rocks in between.

The Río Quema Formation volcanic and volcanoclastic rocks have been geochemically characterized by Corral *et al.*, (2010, 2011) and Corral (2013). Their results indicate that rocks of the Río Quema Formation have calc-alkaline signatures consistent with their emplacement in an intra-oceanic magmatic arc (Lissinna, 2005; Wörner *et al.*, 2009; Buchs *et al.*, 2010, 2011; Wegner *et al.*, 2011). This contrasts with the interpretation of Perelló *et al.*, (2020) that the dacite dome complex of the Río Quema Formation was emplaced in a geotectonic setting transitional from mafic, primitive intra-oceanic to more evolved arc magmatism. By the time the dacite dome complex emplaced, the intra-oceanic magmatic arc was well developed and mature enough to be geochemically distinguishable from the Azuerro Protoarc and the Azuerro Igneous basement.

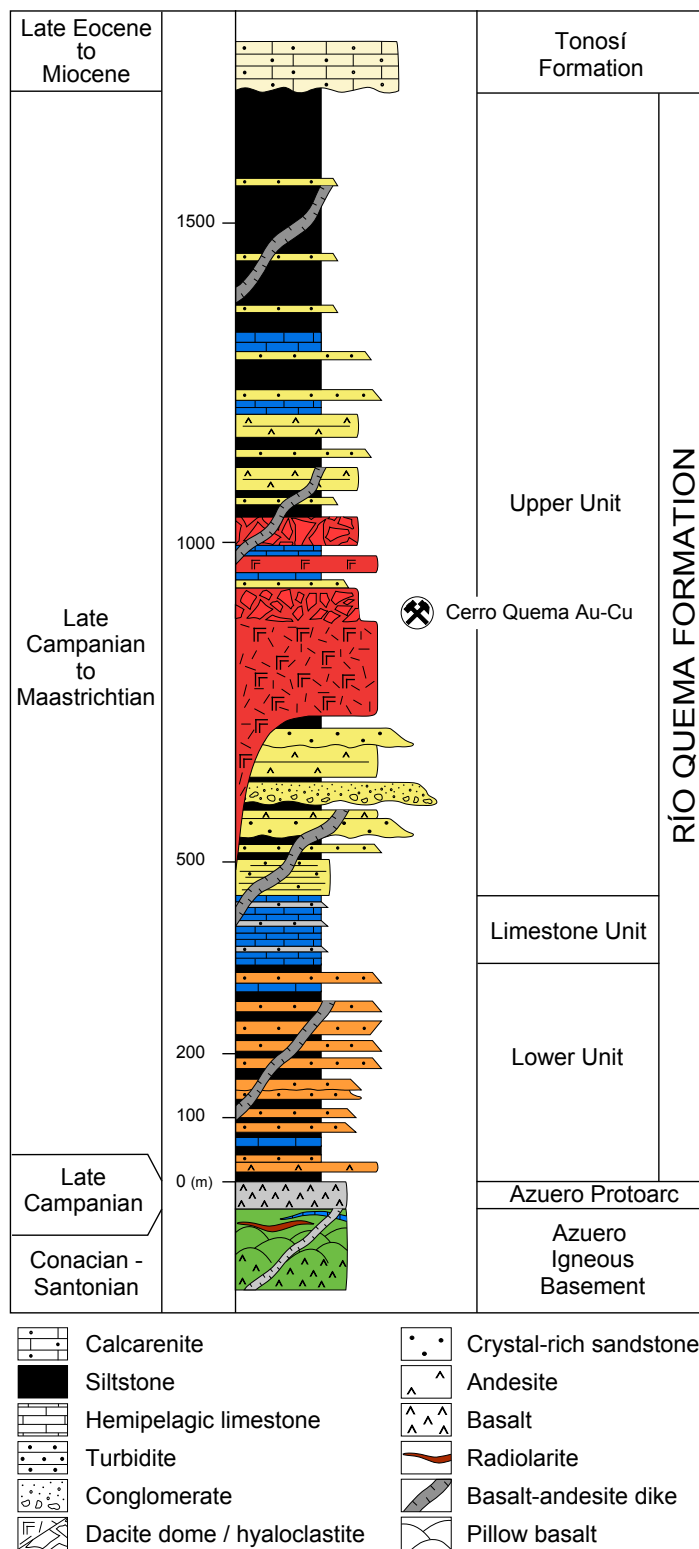


Figure 1 Stratigraphic section of the Río Quema Formation showing the emplacement of the Cerro Quema Au-Cu deposit (modified from Corral *et al.*, 2016).

3. Age of the Cerro Quema host rock

Several hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ spectra should be considered to cogently constrain the age of the Cerro Quema host rock (Figure 2). The dacite dome complex of the Río Quema Formation is the main mineralization host rock (Leach, 1992; Horlacher and Lehmann, 1993; Torrey and Keenan, 1994; Nelson, 1995; Corral *et al.*, 2011, 2016; Perelló *et al.*, 2020). The volcanic domes have been dated at Cerro Quema by Corral *et al.*, (2016; hornblende $^{40}\text{Ar}/^{39}\text{Ar}$) obtaining a weighted average date of 66.5 ± 1.6 Ma (Table 1, Figure 2). The Corral *et al.*, (2016) hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ total gas age was not included in the calculation as it was considered less reliable than plateau ages. Two

amphibole-bearing dacitic rocks located 10 and 5 km from Cerro Quema were dated by Wegner *et al.*, (2011; hornblende $^{40}\text{Ar}/^{39}\text{Ar}$) yielding a 71.0 ± 2.5 Ma weighted average date and a 67.5 ± 1.9 Ma plateau date, respectively (Table 1). Although the sample PAN-05-017A studied by Wegner *et al.*, (2011) shows a bumpy spectrum between 20 – 40% of cumulative ^{39}Ar fraction that compromises the age, a plateau date of 72.3 ± 2.5 Ma was calculated (Figure 2A). A duplicate sample (PAN-05-017B; Figure 2B) has a disturbed spectrum between 10 – 30% of cumulative ^{39}Ar fraction with no apparent plateau that compromises the reported plateau date of 68.9 ± 3.3 Ma. The final reported age of this sample is an average of the two plateau dates, which is questionable

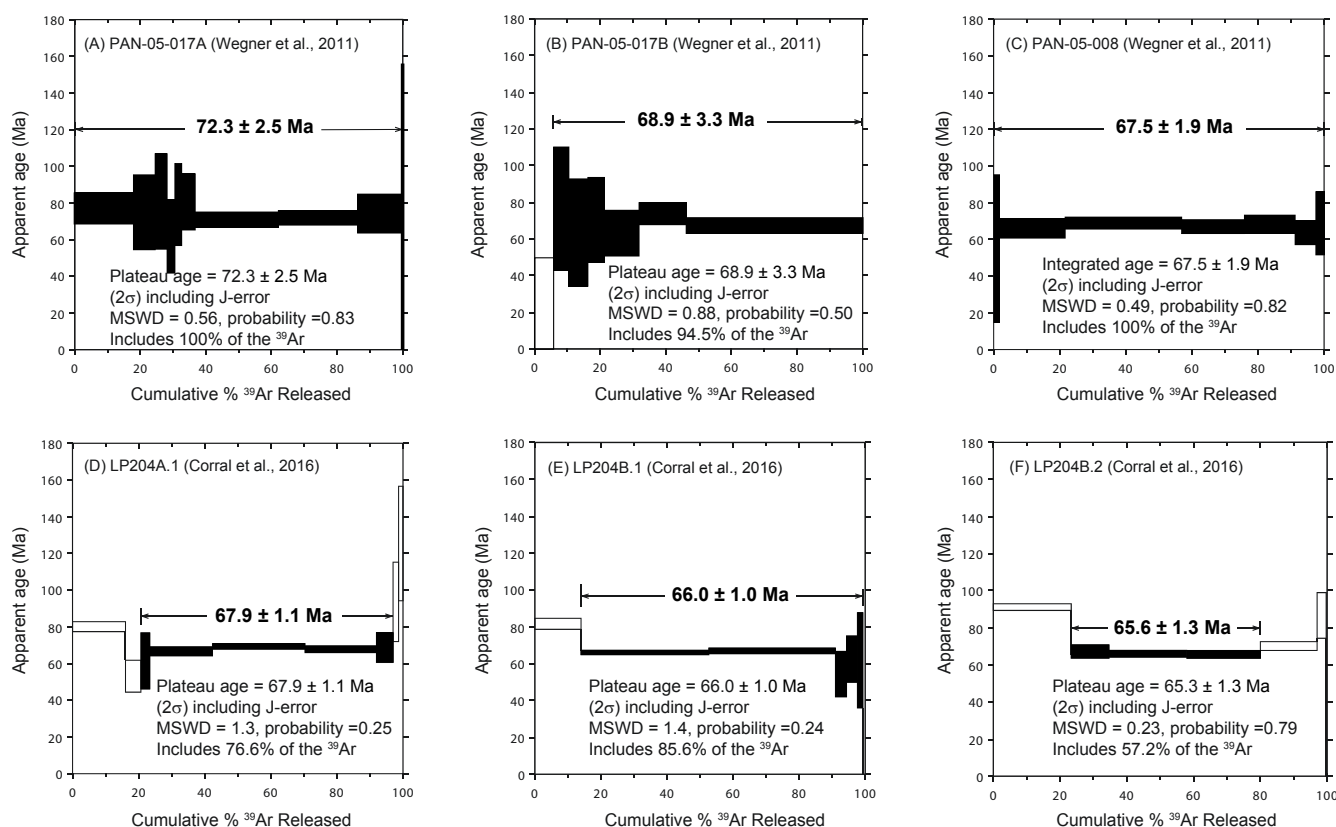


Figure 2 Summary of the hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the Río Quema Formation dacite domes and equivalent rocks from the Azuero Peninsula (Corral, 2021). A – C: Samples from Wegner *et al.* (2011) collected at 10 and 5 km away from Cerro Quema, respectively. D – F: Samples from Corral *et al.* (2016) collected at La Pava orebody. Plateau ages of A and B have been discarded, and C to F are the representative ages of the Río Quema Formation (as discussed in the text).

Table 1. Summary of the available geochronological data of the El Montuoso batholith, Valle Rico batholith and dacites from the Río Quema Formation.

	Dating	Rock	Mineral	Results		
	method			El Montuoso	Valle Rico	Río Quema Fm.
Del Giudice and Recchi (1969)	K/Ar	Qd	hornblende	69 ± 10 Ma		
		Qd	hornblende		53 ± 3 Ma	
Kesler <i>et al.</i> , (1977)	K/Ar	Qd	hornblende	64.87 ± 1.34 Ma		
		Qd	feldspar		52.58 ± 0.63 Ma	
Lissinna, (2005)	Ar/Ar	Gd	plagioclase		49.5 ± 0.2 Ma	
		Gr	plagioclase	-	50.6 ± 0.3 Ma	
Wegner <i>et al.</i> , (2011)	Ar/Ar	Dac	hornblende			67.5 ± 1.9 Ma*
		Dac	hornblende			71.0 ± 2.0 Ma*, **
Montes <i>et al.</i> , (2012)	U/Pb	Gd	zircon	67.6 ± 1.4 Ma		
		Ton	zircon	66.0 ± 1.0 Ma		
		Ton	zircon	67.6 ± 1.0 Ma		
		Ton	zircon		49.2 ± 0.9 Ma	
Corral <i>et al.</i> , (2016)	Ar/Ar	Qd	hornblende	65.7 ± 1.0 Ma		
		Qd	hornblende	67.5 ± 1.1 Ma		
		Qd	hornblende		54.8 ± 1.2 Ma	
		Dac	hornblende			67.9 ± 1.1 Ma
		Dac	hornblende			66.0 ± 1.0 Ma
		Dac	hornblende			65.6 ± 1.3 Ma
		Dac	hornblende			69.7 ± 1.2 Ma***
		Dac	hornblende			
Ramírez <i>et al.</i> , (2016)	U/Pb	Ton	zircon	66.4 ± 0.3 Ma		

Dac : dacite, Gd : granodiorite, Gr : granite, Qd : quartz-diorite, Ton : tonalite.

* = Assigned to the Río Quema Formation due to textural, geochemical and geochronological similarities.

** = Not considered to calculate the age of Cerro Quema host rock as described in the text.

*** = Not considered as it is not a plateau age.

given the nature of their spectra. Therefore, the dacite sample reported by Wegner *et al.*, (2011; PAN-05-008) and the samples of Corral *et al.*, (2016; Figure 2C to 2F) dated by $^{40}\text{Ar}/^{39}\text{Ar}$ 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).

These data and geochronological studies of the El Montuoso batholith (e.g., U-Pb in zircon, $^{40}\text{Ar}/^{39}\text{Ar}$ in hornblende and plagioclase; Table 1; Figure 3), indicate that they were coeval and represent the Late Cretaceous magmatic arc.

On the contrary, Perelló *et al.*, (2020) assumed the 71.0 ± 2.5 Ma date of Wegner *et al.*, (2011) as the age of the Cerro Quema host rock. They discarded the younger dacite dome complex ages (Figure 2C to 2F; Wegner *et al.*, 2011; Corral *et al.*, 2016) interpreting them to be likely compromised by disturbed isotopic systems, including the presence of excess argon and partial to complete resetting and neocrystallization during younger heating events. However, samples from Figure 2C to 2F used to calculate the age of the dacite dome complex of the Río Quema Formation do not reflect any of the abovementioned processes.

4. Age of the Cerro Quema deposit

Perelló *et al.*, (2020) performed Re-Os dating on molybdenite samples from La Pava orebody. Four samples were analyzed yielding dates of 70.74 ± 0.29 , 70.70 ± 0.29 , 70.66 ± 0.29 and 68.72 ± 0.29 Ma being the youngest date discarded by the presence of significant common Os.

They presented a good and consistent data establishing ~ 71 Ma as the age of the Cerro Quema mineralization. However, their results conflict with the age range of 55 – 49 Ma proposed in Corral *et al.*, (2016), and the ~ 49 Ma alunite $^{40}\text{Ar}/^{39}\text{Ar}$ date of Corral (2021). Considering the 66.6 ± 1.8 Ma age of the Cerro Quema host rock,

the molybdenite Re-Os age of ~ 71 Ma is considerable older than the host rocks (Figure 3).

If as mentioned in Perelló *et al.*, (2020), the younger hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ dates of Wegner *et al.*, (2011) and Corral *et al.*, (2016) are compromised by resetting, their molybdenite Re-Os ages would also be compromised by the same process as the closure temperature of hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ and molybdenite Re-Os isotopic systems is the same, ~ 500 °C (Harrison, 1982; Suzuki *et al.*, 1996). Other processes that may compromise the Re-Os systematics are surface weathering (e.g., oxidation) and alteration by low salinity ($< 1\%$ NaCl eq.) and low temperature ($\sim 180^\circ\text{C}$) hydrothermal fluids containing NaCl and/or CO_2 (McCandless *et*

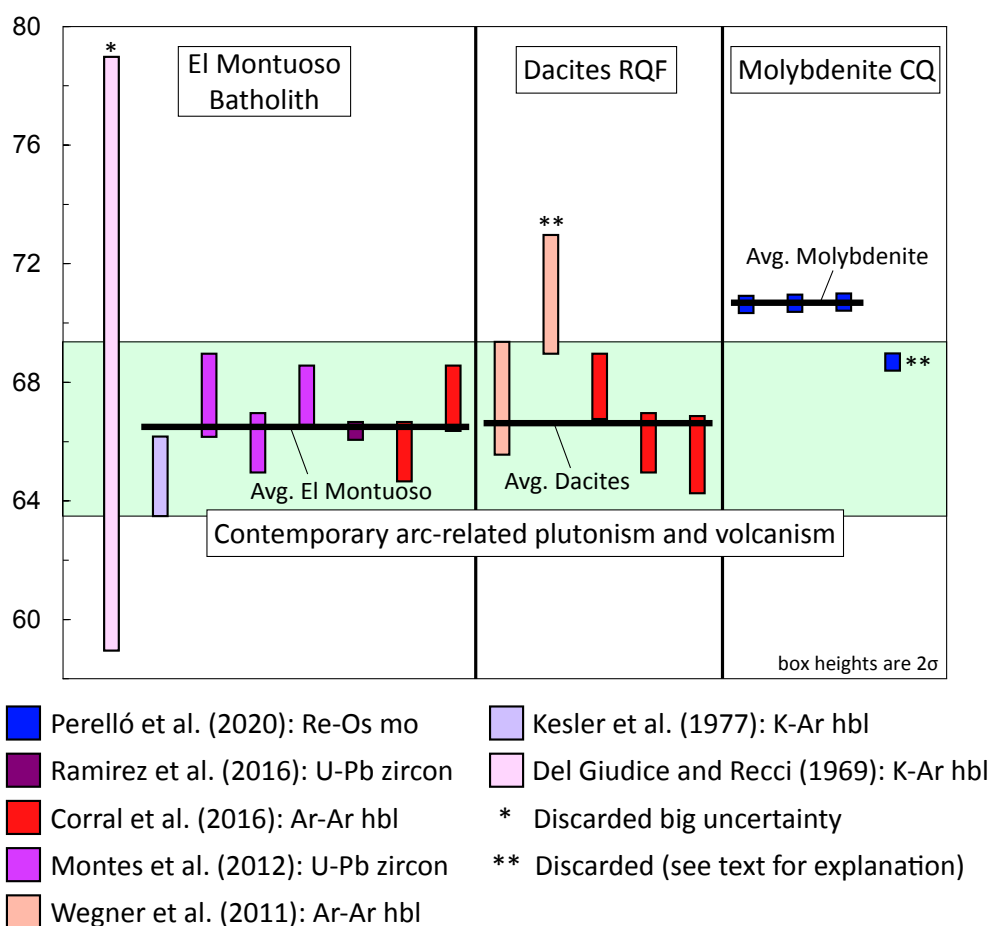


Figure 3 Comparative diagram showing the geochronological data of the El Montuoso batholith, the dacites of the Río Quema Formation and the Re-Os molybdenite ages (Corral, 2021). Avg. = average, CQ = Cerro Quema, hbl = hornblende, mo = molybdenite, RQF = Río Quema Formation.

al., 1992; Suzuki *et al.*, 2000; Georgiev *et al.*, 2012; Stein and Hannah, 2014). According to the location of molybdenite samples studied by Perelló *et al.*, (2020), some of them are likely to be affected by weathering processes as they are in the range of the weathering profile that has affected Cerro Quema to depths of 150 m (Corral *et al.*, 2011, 2016, 2018).

However, no further speculation can be done to explain the anomalous old molybdenite Re-Os ages as molybdenite occurrence at Cerro Quema is only documented by two pictures of the same hand sample, with no supporting optical microscope or SEM-BSE images by Perelló *et al.*, (2020).

Although most of the alunite $^{40}\text{Ar}/^{39}\text{Ar}$ dating studies considered the obtained age as representative of the age of hypogene mineral precipitation (Rye *et al.*, 1992; Itaya *et al.*, 1996; Bissig *et al.*, 2001; Holley *et al.*, 2016; Sahlström *et al.*, 2018), alunite dating 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). However, Corral (2021) could not prove the hypothesis of resetting. If resetting could be proven, the obtained alunite $^{40}\text{Ar}/^{39}\text{Ar}$ age would be interpreted as a minimum age of Cerro Quema.

In this case, the maximum age of Cerro Quema is that of the host rocks: 66.6 ± 1.8 Ma (Wegner *et al.*, 2011; Corral *et al.*, 2016). Therefore, the ~ 49 Ma alunite $^{40}\text{Ar}/^{39}\text{Ar}$ date of Corral (2021) is interpreted as representative of the age of hypogene mineral precipitation (at ~ 240 °C; Corral *et al.*, 2017).

5. Alternative genetic model for Cerro Quema

Subduction initiation of the Farallon plate beneath the Caribbean plate and ensuing protoarc volcanism are dated at $\sim 75 - 73$ Ma (i.e., late Campanian; Buchs *et al.*, 2010). From Late Cretaceous to middle Eocene (68 – 40 Ma), the first stage of magmatism occurred within the Caribbean plate.

This stage is characterized by the development of the Soná-Azuero (Western Panama) and the Chagres-Bayano (Eastern Panama) arcs, which record abundant tholeiitic to calc-alkaline arc magmatism and emplaced on an oceanic plateau crust (Lissina, 2005; Buchs *et al.*, 2010; Wörner *et al.*, 2009; Wegner *et al.*, 2011; Corral *et al.*, 2011; Montes *et al.*, 2012). El Montuoso batholith constitutes the main arc-related plutonic rocks of the Soná-Azuero arc, whereas the dacite domes of the Río Quema Formation emplaced in its forearc basin at ~ 67 Ma (Del Giudice and Recchi, 1969; Kesler *et al.*, 1977; Wegner *et al.*, 2011; Montes *et al.*, 2012; Corral *et al.*, 2013, 2016; Ramírez *et al.*, 2016). During the lower Eocene ($\sim 55 - 49$ Ma), diorites and quartz-diorites associated with the Valle Rico batholith intruded the Soná-Azuero arc along E-trending regional faults (Del Giudice and Recchi, 1969; Lissina, 2005; Montes *et al.*, 2012; Corral *et al.*, 2016). These E-trending structures and contacts around the dacite dome complex probably served as conduits for magmatic-hydrothermal fluids derived from porphyry copper-like intrusions associated with the Valle Rico batholith to form the Cerro Quema Au-Cu deposit (Corral *et al.*, 2011, 2016; Corral, 2021).

The dacite domes played a key role on the Au-Cu mineralization as they are the most permeable and porous rocks cropping out in the area, facilitating the mineralizing fluid flow preferentially through this lithology (permeability: $2.0 \cdot 10^{-11}$ kg/s*m Pa; porosity: 10.8%; Corral *et al.*, 2017). After this tectono-magmatic event, the magmatic arc migrated ~ 50 km to the north, where it is represented by the Parita batholith (48 – 36 Ma; Lissina, 2005; Montes *et al.*, 2012; Corral *et al.*, 2016; Ramírez *et al.*, 2016). Additionally, this genetic model mirrors the metallogenic evolution of the Chagres-Bayano arc (Eastern Panama) where diorites and quartz-diorites intruded Cretaceous volcanosedimentary sequences at ~ 49 Ma forming the Río Pito porphyry copper deposit (Kesler *et al.*, 1977; Nelson, 1995).

This alternative model is consistent with the Azuero Peninsula geology and geochemistry, as

well as with previous geochronological studies (U-Pb zircon, Montes *et al.*, 2012; Ramirez *et al.*, 2016; $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende and plagioclase, Lissinna, 2005; Corral *et al.*, 2016; K-Ar hornblende and plagioclase, Del Giudice and Recchi, 1969; Kesler *et al.*, 1977). It differs from the genetic model proposed by Perelló *et al.*, (2020) that invokes a previously unrecognized regional-scale magmatic event to explain the mineralization at Cerro Quema based on their molybdenite Re-Os ages.

6. Reinforcement of the Cerro Quema genetic model

Further geochronological work would help to improve the Cerro Quema genetic model. U-Pb dating of zircons from the Cerro Quema host rock (e.g., LP-204; Corral *et al.*, 2016) will help to better constrain its age and therefore, provide insightful information to validate the proposed genetic models. This is an opportunity for a collaborative work between the two groups that worked on the Cerro Quema deposit to propose a more robust genetic model based on further geochronological data.

7. Conclusions

After a thorough review of the geologic, geochemical and geochronological data from the Cerro Quema area, it is concluded that the Re-Os molybdenite dates reported by Perelló *et al.*, (2020) are not representative of the formational age of Cerro Quema. The geology interpreted by Perelló *et al.*, (2020) differs from the geology reported by field-based studies, especially when describing the stratigraphic relationship between the Azuero Protoarc unit and the dacite dome complex of the Río Quema Formation. They also invoke a previously unrecognized regional-scale magmatic event based on their molybdenite Re-Os ages. Furthermore, their proposed formational age at ~71 Ma is significantly older than the age of the hosting

dacite dome complex (~67 Ma). Instead, the Cerro Quema formational model discussed here, in which magmatic-hydrothermal fluids derived from porphyry copper-like intrusions associated with the Valle Rico batholith produced the Au-Cu mineralization at ~49 Ma, is consistent with the geology, geochemistry and geochronology of the Azuero Peninsula.

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