



Boletín de la Sociedad Geológica Mexicana

ISSN: 1405-3322

Sociedad Geológica Mexicana A.C.

Perelló, José; Creaser, Robert A.; García, Alfredo
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Boletín de la Sociedad Geológica Mexicana, vol. 73, no. 1, 00019, 2021
Sociedad Geológica Mexicana A.C.

DOI: <https://doi.org/10.18268/BSGM2021v73n1a101220>

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Reply to “Porphyry-related high-sulfidation mineralization early in Central American Arc development: Cerro Quema deposit, Azuero Peninsula, Panama” by Corral (2021)

Respuesta 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 Corral (2021)

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How to cite this article:

Perelló, J., Creaser, R. A., García, A., 2021, Reply to “Porphyry-related high-sulfidation mineralization early in Central American Arc development: Cerro Quema deposit, Azuero Peninsula, Panama” by Corral (2021): Boletín de la Sociedad Geológica Mexicana, 73 (1), A101220. <http://dx.doi.org/10.18268/BSGM2021v73n1a101220>

Manuscript received: September 25, 2020
Corrected manuscript received: November 15, 2020
Manuscript accepted: November 20, 2020

Peer Reviewing under the responsibility of Universidad Nacional Autónoma de México.

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ABSTRACT

Dear Editor, we thank Corral (2020) for his anticipated interest in our paper on the timing of the porphyry-related high-sulfidation epithermal mineralization at Cerro Quema in the Azuero peninsula of southwestern Panama. Our study, based on three Re-Os ages for molybdenite intimately associated with Cu-bearing sulfide minerals from the hypogene roots of the La Pava center (Figure 1), shows that the main event of high-sulfidation Cu mineralization took place during the earliest Maastrichtian at ~71 Ma. The reported ages, together with the geologic relationships described in our paper (Perelló *et al.*, 2020), plus a series of regional geologic, structural, petrochemical, and geotectonic considerations, not only precisely date the porphyry-related nature of the Cerro Quema high-sulfidation mineralization, but are also significant in that they confirm the rapid evolution of the earliest stages of the Central American Arc – from subduction initiation at 75-73 Ma to arc stability and maturation at 71 Ma (*e.g.*, Buchs *et al.*, 2011a and references therein) – and place the mineralization in a regional geodynamic setting. Irrespective of the regional geologic arguments reiterated by Corral (2020) in support of his previous genetic interpretation (*e.g.*, Corral *et al.*, 2016) and to invalidate our conclusions, Corral’s real concern is the reliability of our molybdenite ages, which are much older than his preferred age of mineralization for Cerro Quema. We believe that many of the points raised by Corral (2020), including the regional and local geologic backgrounds of the deposit and the dated samples, were properly addressed in Perelló *et al.* (2020), and that it would be redundant to repeat them here. Additional petrochemical evidence in support can be found in Whattam and Stern (2015, 2020) and Whatam (2018).

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

RESUMEN

Estimado Editor, agradecemos a Corral (2020) por su interés anticipado en nuestro artículo sobre el momento de la mineralización epitermal de alta sulfuración en relación con el pórfido en el Cerro Quema en la península de Azuero, al suroeste de Panamá. Nuestro estudio, basado en tres edades Re-Os para la molibdenita, íntimamente asociadas con minerales de sulfuro que contienen Cu de las raíces hipógenas del centro de La Pava (Figura 1), muestra que el evento principal de la mineralización de alta sulfuración de Cu tuvo lugar durante la primera Maastrichtiense en ~71 Ma. Las edades reportadas, junto con la relación geológica descrita en nuestro artículo, (Perelló *et al.*, 2020), además de una serie de consideraciones geológicas, estructurales, petroquímicas y geotectónicas regionales, no solo datan con precisión la naturaleza de la alta sulfuración en relación con el pórfido del Cerro Quema, sino que, además, son significativas porque confirman la rápida evolución de las primeras etapas del Arco Centroamericano- desde la iniciación de la subducción a 75-73 Ma hasta la estabilidad del arco y la maduración a 71 Ma (por ejemplo, Buchs *et al.*, 2011a y referencias en él) - y situar la mineralización en un entorno geodinámico regional. Independientemente de los argumentos geológicos regionales reiterados por Corral (2020) en apoyo a su interpretación genética previa (por ejemplo, Corral *et al.*, 2016) y para invalidar nuestras conclusiones, la verdadera preocupación de Corral es la confiabilidad de nuestras edades de molibdenita, las cuales son mucho más antiguas que su edad preferida de mineralización para el Cerro Quema. Creemos que muchos de los puntos planteados por Corral (2020), incluidos los antecedentes geológicos locales y regionales del depósito y las muestras fechadas, se abordaron adecuadamente en Perelló *et al.* (2020), por lo que repetirlos aquí sería redundante. Pueden encontrarse pruebas petroquímicas adicionales en Whattam y Stern (2015, 2020) y Whatam (2018).

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

1. Age of the Cerro Quema dacite dome complex

There is ample evidence in the geologic literature of the region to suspect that the available Ar-based geochronological data should be treated cautiously (*e.g.*, Lissinna, 2005; Wegner *et al.*, 2011; Buchs *et al.*, 2011a, b; Corral *et al.*, 2016), a situation that finds further support in the analysis conducted by Corral (2020, Figure 3). Our selection of 71 Ma as the age of the Cerro Quema dacite dome was not arbitrary, but rather based on the recommendation by Wegner *et al.* (2011) for hornblende-bearing dacite rocks in the vicinity of the prospect area. This date has also been amply used in the literature to record one of the first vestiges of arc magmatism in the Central American Arc (*e.g.*, Wörner *et al.*, 2009; Wegner *et al.*, 2011; Buchs *et al.*, 2010, 2011a; Whattam *et al.*, 2020 and references therein), including Corral *et al.* (2016).

Corral (2020) argues that this date is dubious and unreliable on analytical grounds, and that the age of the dome complex is younger, between ~65 and 68 Ma. However, his Figure 3 shows a wider range of acceptable ages, from 64 to ~70 Ma, and Corral *et al.* (2016) also accepted a ~71–66-Ma range for the same unit. According to Corral (2020), his new preferred range, and the U-Pb zircon ages of 68 to 66 Ma for the El Montuoso batholith (Montes *et al.*, 2012; Ramírez *et al.*, 2016), would make both the Cerro Quema domes and the El Montuoso batholith coeval with and part of the Azuero Arc volcano-plutonic complex. Although this interpretation may be correct in broad terms, regional geologic maps show the El Montuoso batholith to be transgressive to lower Azuero Arc stratigraphy, including the Río Quema Formation, and its structural grain (Buchs *et al.*, 2011a; Corral *et al.*, 2016), making such correlation unlikely. A simple alternative explanation for the similar ^{40}Ar - ^{39}Ar and U-Pb dates referred to by Corral (2020) would be that all ^{40}Ar - ^{39}Ar ages are compromised by the heating of the El Montuoso and the younger Valle Rico batholiths, as suggested in our paper and in consideration of

the regional evidence, noting that single-mineral, Ar-based chronometers reflect the closure of the clock of the dated mineral at specific temperatures, rather than primary crystallization (*e.g.*, Stein, 2014 and references therein). In this respect, given the high sensitivity of the ^{40}Ar - ^{39}Ar clock to thermal metamorphism, the younger ^{40}Ar - ^{39}Ar ages can be better interpreted in the context of the thermal and uplift history of the region during emplacement of the El Montuoso batholith (*e.g.*, Lee, 2009). Clearly, precise U-Pb zircon dates for the Cerro Quema dacite domes are required, an aspect with which we fully agree with Corral (2020).

2. Age of the Cerro Quema mineralization

Corral (2020) states that our Re-Os molybdenite dates of 70.74 ± 0.29 , 70.70 ± 0.29 , and 70.66 ± 0.29 Ma for La Pava are older than his preferred age of 66.6 ± 1.8 Ma for the Cerro Quema dacite domes that host the mineralization, and claims that our molybdenite data can be compromised by: 1) thermal resetting; 2) alteration due to low-salinity and low-temperature hydrothermal fluids; and 3) the action of supergene fluids related to near-surface weathering processes.

Corral (2020) suggests that the three overlapping Re-Os molybdenite ages of 70.7 Ma are anomalously old as a result of weathering processes affecting the Re-Os system in molybdenite. Independently of the fact that our samples are entirely devoid of supergene sulfide and silicate mineralogy (Perelló *et al.*, 2020; Figure 1), and that these younger events would have to remove an exact amount of Re from each sample to yield three identical inaccurate ages, this suggestion is counter to the current understanding of the Re-Os system in molybdenite, which is well summarized by Stein (2014). The salient points regarding development, testing and calibration of the Re-Os molybdenite geochronometer are that, prior to a series of major advances from ~1997

to 2007, Re-Os dating of molybdenite generally yielded erratic and imprecise ages resulting from low-precision isotopic analysis using ICP-MS and lack of knowledge regarding ‘decoupling’ of Re from radiogenic Os internally within molybdenite (*e.g.*, Stein, 2014). As an example, using the same analytical methods employed by Suzuki *et al.* (2000, as cited by Corral (2020) as support for anomalous Re-Os ages), Suzuki *et al.* (2001) concluded that inaccurate and imprecise Re-Os molybdenite ages from the Galway Granite in Ireland resulted from younger hydrothermal fluid interaction. However, Selby *et al.* (2004) showed that using different analytical protocols, reproduc-

ible and geologically plausible Re-Os molybdenite ages were produced from the same molybdenite samples. The citation for Re-loss in molybdenite by McCandless *et al.* (1993) similarly suffers from the issues noted above, as does the assumption that comparison ages, mostly K-Ar, are correct (*e.g.*, Stein, 2014). Georgiev *et al.* (2012) studied Re and Os release from organic-rich shales, in which Re is hosted almost exclusively in organic matter, and is known to be readily leached during laboratory experiments (Selby and Creaser, 2003), but this topic is not relevant to Re-Os geochronology in molybdenite. Modern Re-Os molybdenite geochronology in porphyry systems typically yields

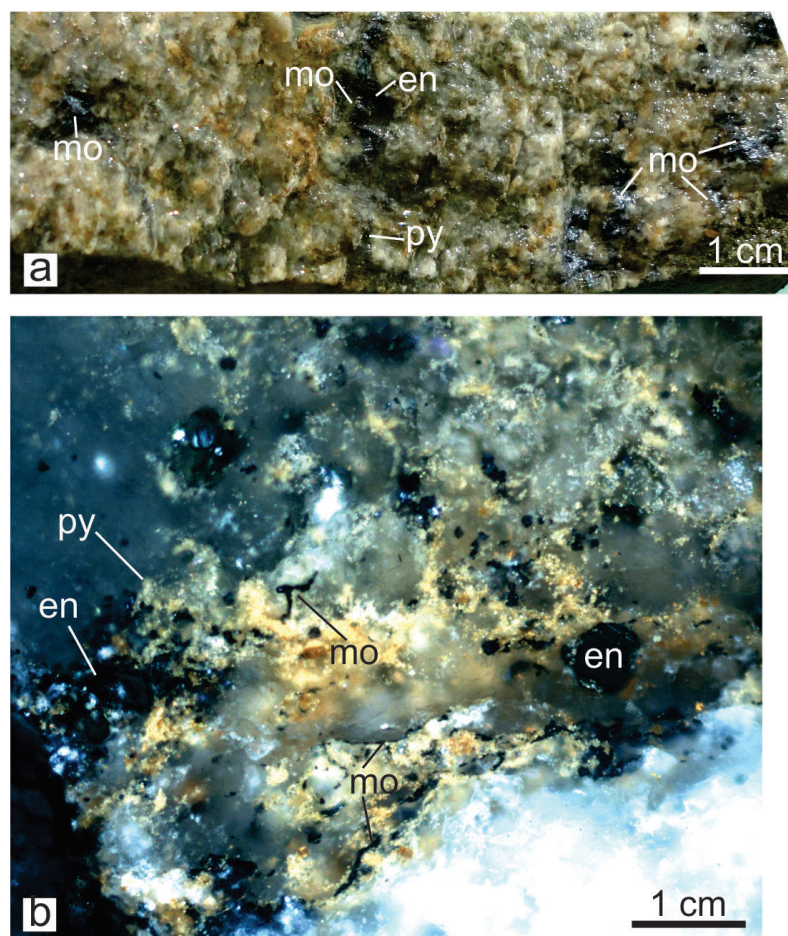


Figure 1 Textural aspects of the molybdenite-bearing mineralization from the La Pava area at Cerro Quema. a. Hand specimen showing intensely sericite-pyrophyllite altered Cerro Quema dacite with ill-defined veinlets of pyrite, enargite and molybdenite plus disseminations of molybdenite. b. Binocular view of an internal face of a veinlet with quartz, sericite, and pyrophyllite plus pyrite, molybdenite, and enargite. Note the complete absence of supergene silicate and sulfide mineralogy in these samples. Abbreviations: en: enargite; mo: molybdenite; py: pyrite.

accurate, precise ages which are well-correlated to the U-Pb ages of causative intrusions (Selby *et al.*, 2007; Rosera *et al.*, 2013; Li *et al.*, 2017), and in many cases older than local and regional ^{40}Ar - ^{39}Ar and K-Ar ages (*e.g.*, Selby *et al.*, 2002).

Similarly, the problems associated with thermal resetting are nearly irrelevant to Re-Os molybdenite geochronology (Stein, 2014), while the complexities of the temperature-dependent ^{40}Ar - ^{39}Ar method in the ore-forming environment were clearly evidenced by the work of Arribas *et al.* (2011) at Pueblo Viejo, Dominican Republic (see also Nelson *et al.*, 2015 and Torró *et al.*, 2017). Corral (2020) defends a new single ^{40}Ar - ^{39}Ar alunite date of ~ 49 Ma obtained by him from a pyrite-alunite cemented breccia at Cerro Quema, and claims he did not detect any evidence of resetting in his samples. However, neither did Arribas *et al.* (2011), despite their ultra-detailed work on hypogene alunite at Pueblo Viejo and neighboring alteration zones. Furthermore, Arribas *et al.* (2011) concluded that the wide variability of the obtained ages, ranging from 70 to 40 Ma, was independent of the many textural and compositional features of the dated alunite, but it rather seemed to depend on “the actual ^{40}Ar - ^{39}Ar geochemistry of the alunite, with individual alunite crystals or crystal groupings yielding different ages” (Arribas *et al.*, 2011, p. 1965).

Interestingly, the wide variability of hypogene alunite ages determined at Pueblo Viejo and many other deposits and prospects (*e.g.*, Arribas *et al.*, 2011 and references therein), can also be anticipated to constitute a problem at Cerro Quema, where three alunite separates from a high-sulfidation vein of coarse-grained alunite intimately intergrown with pyrite and enargite from La Pava yielded K-Ar ages of 62 ± 2 , 58.0 ± 1.9 , and 62 ± 3 Ma (J. Perelló, unpub. data). Irrespective of the Ar-based method, these and Corral's new data imply an age range from ~ 65 to 49 Ma for Cerro Quema hypogene alunite, and further confirm the complicated nature of the Ar systematics of alunite and support the interpretation of a complex thermal history for the region.

Rocks of the Azuero peninsula expose a complicated pattern of accretion, magmatism, and subduction during the development of the Central American margin (*e.g.*, Buchs, 2008), hence major regional thermal events that may have played a role in the formation and resetting of alunite at Cerro Quema are numerous. These include not only the thermal heating associated with the intrusion of the El Montuoso and Valle Rico batholiths mentioned above, but also additional post-mineralization arc magmatism, the ~ 2 km stratigraphic load of volcano-sedimentary and sedimentary sequences that once must have covered the prospect area and the region, regional events of tectonic accretion and associated metamorphism, tectonically induced uplift and erosion, and far-field strain accommodation associated with large-scale subcontinental collisions (Kolarsky *et al.*, 1995; Wörner *et al.*, 2009; Buchs *et al.*, 2010, 2011a, b; Montes *et al.*, 2012; Ramírez *et al.*, 2016; Andjić *et al.*, 2018; Perelló *et al.*, 2020).

3. Conclusion

In conclusion, we interpret the ~ 71 Ma age of our 3 molybdenite samples as meaningful and that the Re-Os molybdenite method accurately dates the hypogene ore-stage mineralization at Cerro Quema. Both the Re-Os and Ar-based methods point to a more complex magmatic and mineralization history at Cerro Quema that is either currently understood, or as presented by Corral (2020). In this context, the ~ 71 -Ma age of the hypogene mineralization at Cerro Quema effectively constrains the metallogenic birth of the Central American Arc.

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