

# Zircon petrochronological evidence for a plutonic-volcanic connection in porphyry copper deposits

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## ABSTRACT

**Bridging the gap between the plutonic and volcanic realms is essential for understanding a variety of magmatic processes from caldera-forming eruptions to the formation of magmatic-hydrothermal ore deposits. Porphyry copper deposits are commonly associated with large and long-lived volcanic centers, but the temporal and dynamic link between mineralized intrusions and volcanic eruptions has remained controversial. Based on the combination of (1) high-precision zircon U-Pb geochronology and trace element geochemistry with (2) plagioclase textures, we discovered an intimate connection between an ignimbrite eruption and a nearby world-class porphyry deposit (Bajo de la Alumbrera in the late Miocene Farallón Negro Volcanic Complex of Argentina). Our results indicate that the magmatic-hydrothermal deposit and explosive volcanism were derived from a common magma reservoir that evolved over a minimum duration of  $217 \pm 25$  k.y. before the final eruption. We show that the volcanic pile represents the inverted magma reservoir, recording systematic differences in plagioclase textures and juvenile clast content from bottom to top. This tight temporal and geochemical link suggests that deposit formation and volcanic eruption were both triggered by the same injection of a volatile-saturated primitive magma into the base of the magma chamber. A time gap of  $19 \pm 12$  k.y. between porphyry mineralization and the onset of explosive volcanism indicates a minimum duration of magma reservoir rejuvenation that led to the explosive eruptive event. Catastrophic loss of volatiles by explosive volcanism terminated the ore-forming capacity of the upper-crustal magma chamber, as evidenced by the intrusion of a syn-eruptive barren quartz-feldspar porphyry. Our results demonstrate that porphyry copper deposits provide critical information to understand how volatiles control the fate of hydrous magmas between pluton formation and explosive volcanism.**

## INTRODUCTION

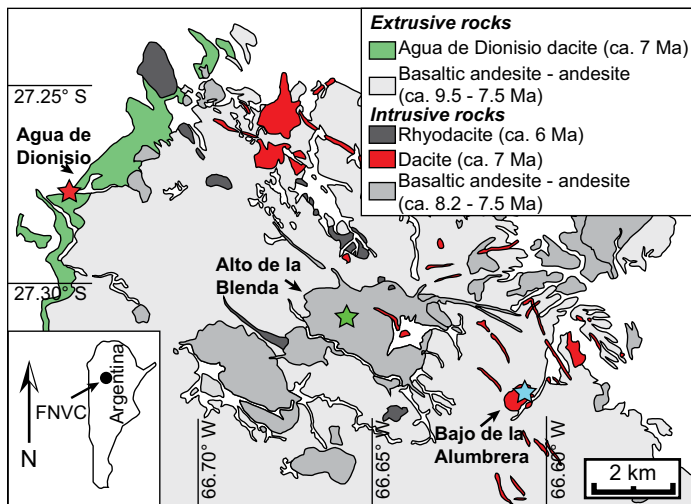
Large andesitic stratovolcanoes are the source of hazardous eruptions, but the dissected edifices of ancient volcanic centers also host some of the most valuable economic ore deposits. Hydrothermal copper mineralization commonly occurs as porphyry copper deposits (PCDs), which form through superposition of several small magmatic intrusions and associated hydrothermal fluid pulses within the base of volcanoes (Sillitoe, 1973, 2010; Proffett, 2003). Mass balance demands that these magmatic-hydrothermal bodies are sourced from larger, upper-crustal magma reservoirs (Burnham and Ohmoto, 1980; Dilles, 1987; Sillitoe, 2010; Chelle-Michou et al., 2014). However, the nature of these magma reservoirs during the lead-up to PCD formation remains a topic of contention. Traditional models suggest that PCD formation occurs as the result of a cooling upper-crustal magma reservoir, which exsolves and focuses the metal-charged fluids toward the upper parts of the magma chamber (Dilles, 1987; Sillitoe, 2010). This contradicts an increasing body of evidence that upper-crustal magma chambers in arc settings are stored at near-solidus temperatures as highly crystalline bodies that remain rheologically immobile throughout most of their lifetime before rejuvenation through the injection of

more-primitive magma into the base of the reservoir (Bachmann et al., 2002; Wotzlaw et al., 2013; Cooper and Kent, 2014). These findings are consistent with recent studies suggesting that much of the ore-forming volatiles is derived from mafic magma that is injected into a cooler felsic magma chamber (Tapster et al., 2016; Buret et al., 2016) and with geochemical evidence from explosive volcanism in ancient and modern settings (Hattori and Keith, 2001; Nadeau et al., 2016). These observations suggest a plutonic-volcanic connection in PCDs, contributing to the general question of how plutonic and volcanic regimes are linked (Bachmann et al., 2007; Keller et al., 2015). It is generally thought that volcanism prevents the formation of PCDs due to volatile dispersion into the atmosphere (e.g., Pasteris, 1996) and that ore formation occurs well after the termination of extensive volcanism (Halter et al., 2004; Sillitoe, 2010). However, the temporal separation between PCD formation and volcanism may have been overestimated due to dating uncertainties and because any coeval volcanic materials above exposed porphyry deposits are usually eroded.

In this study, we discovered an unexpected temporal and genetic link between PCD formation and explosive volcanism, by combination of field geology with high-precision zircon dating using chemical abrasion–isotope dilution–thermal ionization mass spectrometry (CA-ID-TIMS) and zircon trace element compositions obtained by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS). We demonstrate a direct link between explosive volcanism and PCD formation and show that both processes are triggered by the same event of mafic recharge into a large upper-crustal magma chamber.

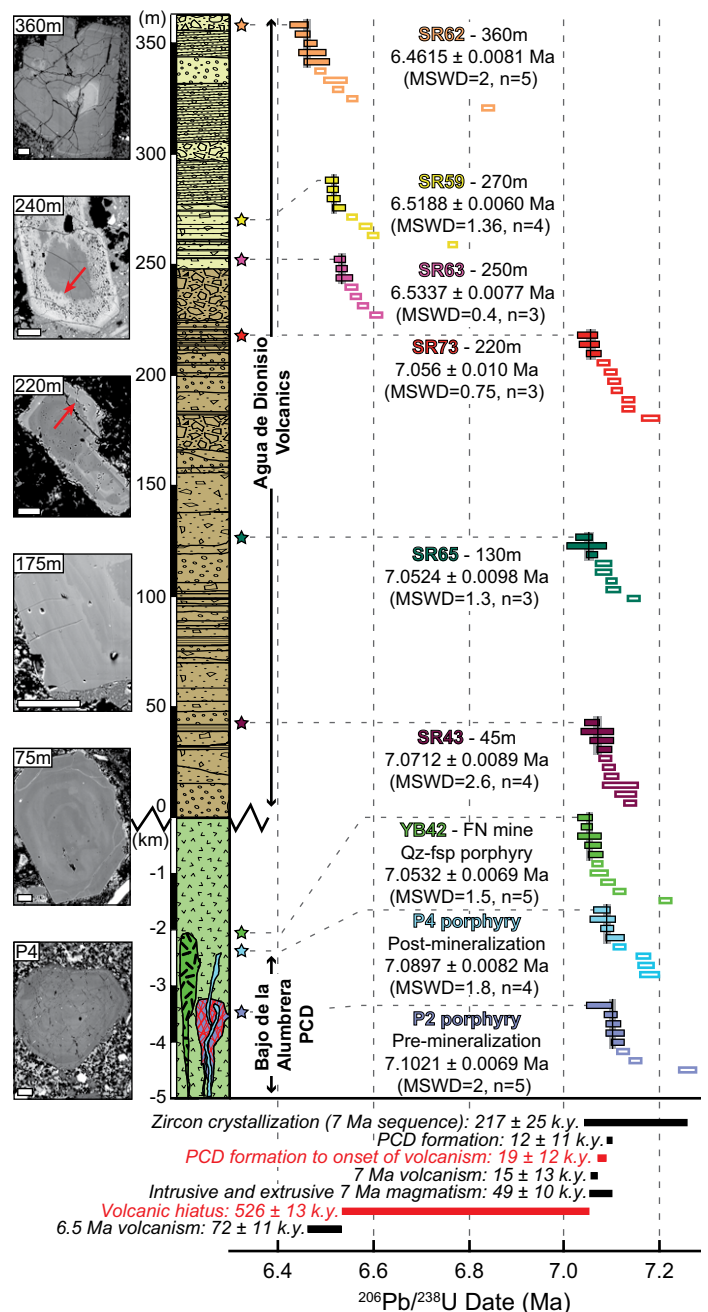
## GEOLOGIC SETTING

The Farallón Negro Volcanic Complex (FNVC) in northwest Argentina (Fig. 1) is an ancient stratovolcano constructed over >3 m.y. (Llambías, 1972; Sasso and Clark, 1998; Halter et al., 2004) mainly through basaltic-andesitic to andesitic lava flows and breccias. This eruptive sequence was intruded by sub-volcanic intrusions between 9 Ma and 6 Ma, including the ca. 7.1 Ma Bajo de la Alumbrera porphyry stock where mineralization occurred between  $7.1102 \pm 0.0093$  Ma and  $7.0994 \pm 0.0063$  Ma (von Quadt et al., 2011; Buret et al., 2016). During later stages of the volcanic complex evolution, the magmatic activity became more silicic, with dacitic compositions at ca. 7 Ma and rhyodacitic magmatism at ca. 6 Ma (Halter et al., 2004). Previous studies suggested that the explosive eruption of a thick sequence of dacitic tuff at Agua de Dionisio, in the northwestern segment of the complex, resulted in partial caldera collapse (Halter et al., 2004). This eruption was previously dated at  $7.35 \pm 0.25$  Ma using biotite <sup>40</sup>Ar/<sup>39</sup>Ar geochronology, implying that the latest volcanic activity preceded PCD formation at Bajo de la Alumbrera by 350 k.y. (Halter et al., 2004). The Agua de Dionisio tuff represents a series of explosive andesitic to dacitic volcanic events and is perfectly exposed as a 300-m-thick sequence (Figs. 1 and 2). Juvenile pumice clasts throughout the Agua de Dionisio eruptive sequence contain phenocrysts of plagioclase, biotite, and amphibole, lesser amounts of quartz, pyroxene, and sanidine, as well as accessory zircon, titanite, and apatite. These clasts contain 25%–50% crystals and a micro-lithic devitrified matrix. The lower 125 m (Fig. 2) of the section comprises



**Figure 1.** Simplified geologic map of Farallón Negro Volcanic Complex (FNVC), Argentina, modified after Llambías (1972). Geochronological constraints are from Sasso and Clark (1998) and Halter et al. (2004). Sample locations given by stars (blue, Bajo de la Alumbrera porphyries; green, quartz-feldspar porphyry intruding into the Alto de la Blenda stock; red, Agua de Dionisio volcanic section).

**Figure 2.** Stratigraphy and geochronology of Agua de Dionisio tuff and porphyry intrusions of Farallón Negro Volcanic Complex (FNVC), Argentina. Pre- and post-mineralization (P2 and P4) Bajo de la Alumbrera porphyries were intruded at minimum depth of 3 km (Ulrich and Heinrich, 2002) into undifferentiated andesites, and unmineralized quartz-feldspar (Qz-fsp) porphyry (YB42) was intruded into Alto de la Blenda stock. Back-scattered electron (BSE) images show representative plagioclase phenocrysts from various stratigraphic levels (scale bars are 50  $\mu$ m). Red arrows point to dissolution features overgrown by high-An, sieve-textured rims. Chemical abrasion–isotope dilution–thermal ionization mass spectrometry (CA-ID-TIMS) U-Pb dates from single zircons are color-coded to corresponding stratigraphic level and porphyry intrusion as indicated by stars. Eruption or intrusion ages of each sample are calculated using youngest statistically equivalent population (indicated by filled bars) of zircon crystallization ages. Empty bars are not included in age calculation. Geochronological data are summarized in lower panel with process durations indicated by black bars and time gaps denoted by red bars. Duration of zircon crystallization is calculated as age difference between oldest and youngest single-crystal U-Pb dates from the 7 Ma sequence. Window of porphyry copper deposit (PCD) mineralization is based on age difference between P2 and P4 porphyries. Time gap between PCD formation and onset of volcanism is the age difference between P4 porphyry and the oldest volcanic sample SR43. Duration of the 7 Ma volcanism is age difference between samples SR43 and SR73. Total duration of intrusive and extrusive 7 Ma magmatism is age difference between P2 porphyry and barren quartz-feldspar porphyry, YB42. Volcanic hiatus is age difference between samples SR73 and SR63. Duration of the 6.5 Ma volcanism is age difference between samples SR63 and SR62. All uncertainties are  $2\sigma$ . MSWD—mean square of weighted deviates.



laterally discontinuous 0.1–2-m-thick horizons of ash-supported volcanic tuff breccia with most clasts ranging in size from several centimeters to tens of centimeters. In the interval between 125 and 225 m, thick monotonous clast-supported breccias become common. A 20-m-thick package containing juvenile clasts of less-evolved compositions (amphibole rich, biotite poor) marks the end of this sequence. The upper part of the section (245–360 m) is composed of more-evolved tuffs with intercalated conglomerates in channels filling fluvial incisions. A more comprehensive geological review of the FNVC is given in Halter et al. (2004).

## SAMPLES AND METHODS

We report a comprehensive high-precision zircon U-Pb geochronology data set comprising 80 single-crystal dates obtained by CA-ID-TIMS at the Institute of Geochemistry and Petrology, ETH Zurich (von Quadt et

al., 2016). Prior to CA-ID-TIMS analyses, internal textures of all zircon crystals were characterized by cathodoluminescence imaging, and trace element concentrations were measured by LA-ICP-MS (Fig. DR1 in the GSA Data Repository<sup>1</sup>). Selected crystals were subsequently extracted from the grain mount for CA-ID-TIMS analyses (see Tables DR1 and DR2 in the Data Repository). U-Pb dates were obtained from nine samples of the FNVC, including six pumice clasts sampled at various stratigraphic levels of the Agua de Dionisio tuff (Fig. 2); two dacitic intrusions (the P2 and P4 porphyries) from Bajo de la Alumbrera PCD, which bracket the Cu mineralization based on cross-cutting relationships (previously dated

<sup>1</sup>GSA Data Repository item 2017203, details of analytical procedures and full data tables (Tables DR1 and DR2), is available online at <http://www.geosociety.org/datarepository/2017/> or on request from [editing@geosociety.org](mailto:editing@geosociety.org)

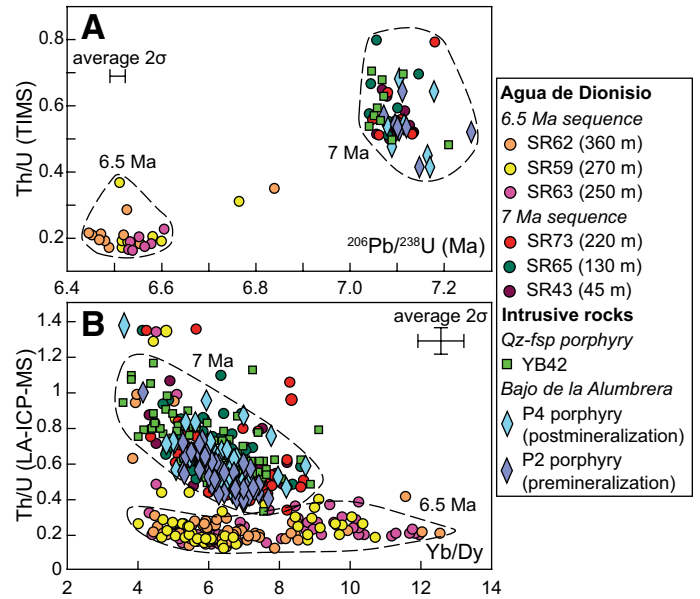
by Buret et al., 2016); and a quartz-feldspar porphyry with no associated Cu mineralization (YB42) that intruded the Alto de la Blenda stock and is cross-cut by ca. 6.6 Ma epithermal veins in the Farallón Negro mine (Márquez-Zavalía and Heinrich, 2016; Figs. 1 and 2). Detailed sample locations and analytical methods are given in the Data Repository.

## HIGH-PRECISION ZIRCON U-Pb DATES AND TRACE ELEMENTS

All samples exhibit resolvable durations of zircon crystallization ranging from  $67 \pm 36$  k.y. to  $185 \pm 31$  k.y. (Fig. 2) recording prolonged crystallization in an evolving magma reservoir (e.g., Miller et al., 2007). We estimate the eruption or emplacement age of each sample based on the youngest statistically equivalent population of dated zircon crystals. Our data suggest that the stratigraphic section at Agua de Dionisio records two distinct eruptive phases separated by  $526 \pm 13$  k.y. at a stratigraphic height of 245 m above the base of the section (Fig. 2). The three samples from the first phase of volcanism suggest that the lower ~245 m of the Agua de Dionisio sequence was erupted between  $7.0712 \pm 0.0089$  Ma and  $7.056 \pm 0.010$  Ma, corresponding to a duration of  $15 \pm 13$  k.y. (Fig. 2) but likely representing a single eruptive cycle. Zircons from this part of the sequence exhibit overlapping trace element geochemistry, reflecting the co-crystallization of zircon with titanite  $\pm$  amphibole and apatite (e.g., Wotzlav et al., 2013; Fig. 3). The second stage of volcanism, recorded in the upper 115 m of the Agua de Dionisio sequence, is accompanied by a pronounced shift in zircon geochemistry reflecting changes in melt chemistry due to allanite crystallization (Fig. 3). This second eruptive cycle commenced at  $6.5337 \pm 0.0077$  Ma and continued intermittently for  $72 \pm 11$  k.y. until the last eruptive event at  $6.4615 \pm 0.0081$  Ma (Fig. 2). New zircon dates from two porphyries bracketing hydrothermal ore formation at Bajo de la Alumbraera yielded weighted means of  $7.1021 \pm 0.0069$  Ma and  $7.0897 \pm 0.0082$  Ma (Fig. 2), confirming a maximum duration of mineralization of  $12 \pm 11$  k.y. (Fig. 2; Buret et al., 2016). The difference between the intrusion age of the post-mineralization P4 porphyry intrusion at Bajo de la Alumbraera and the eruption age of the oldest dated volcanic sample suggests that explosive volcanism began  $19 \pm 12$  k.y. after the termination of copper mineralization (Fig. 2). The barren quartz-feldspar porphyry at Alto de la Blenda was emplaced at  $7.0532 \pm 0.0069$  Ma, coeval with the youngest volcanic sample of the 7 Ma eruptive phase. These data demonstrate that this phase of magmatism, which included porphyry copper mineralization and the entire sequence of explosive volcanism, occurred within a short time window of  $<49 \pm 10$  k.y., indicating a strong temporal and genetic link between the plutonic and volcanic regimes (Fig. 2).

## A COMMON MAGMATIC RESERVOIR FOR PORPHYRY COPPER DEPOSITS AND EXPLOSIVE VOLCANISM

Our U-Pb dated zircons record  $217 \pm 25$  k.y. of crystallization prior to intrusion of the porphyry stock and eruption of the lower part of the Agua de Dionisio tuff (Fig. 2). As small porphyry intrusions cool rapidly upon emplacement, we interpret this age range to reflect zircon crystallization in an upper-crustal magma reservoir, from zircon saturation until the final eruption or intrusion of the respective sample. The similar distribution of zircon crystallization ages and overlapping zircon trace element geochemistry suggest that zircons from the porphyry intrusions and the 7 Ma explosive volcanic sequence were derived from a common magma reservoir (Fig. 3). Despite a common upper-crustal magma reservoir for the explosive volcanism and the PCD, the resolvable age difference between PCD formation and explosive volcanism suggests that Bajo de la Alumbraera was not the conduit for the volcanic activity, which continued for  $34 \pm 13$  k.y. (i.e., the difference between P4 porphyry emplacement and the youngest eruption age from this phase) after the emplacement of the latest Bajo de la Alumbraera porphyry intrusion (P4 porphyry). Emplacement of a barren syn-volcanic quartz-feldspar porphyry into the Alto de la Blenda stock (YB42) at  $7.0532 \pm 0.0069$  Ma



**Figure 3. Zircon trace element compositions fingerprinting magma reservoirs, Farallón Negro Volcanic Complex, Argentina. A: Th/U of dated zircons plotted against their corresponding  $^{206}\text{Pb}/^{238}\text{U}$  date. B: Zircon geochemical compositions obtained by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS). Fields indicate the different magmatic events. Agua de Dionisio sample heights refer to position in volcanic section (see Fig. 2). TIMS—thermal ionization mass spectrometry; Qz-fsp—quartz-feldspar.**

(Fig. 2) suggests that volcanism terminated the ore-forming capacity of the magma reservoir by catastrophic loss of volatiles.

## THE PLUTONIC-VOLCANIC CONNECTION IN PORPHYRY COPPER DEPOSITS

Unlike large-volume eruptive sequences, mineralized porphyries are small magmatic bodies that are most likely extracted from the uppermost part of a larger magma reservoir and thus provide no direct information about lower parts of the reservoir. The overlapping zircon crystallization ages from the porphyry intrusions and the volcanic units suggests that most of the crystal cargo observed in both regimes crystallized in the same magma reservoir. The first phase of the Agua de Dionisio sequence (Fig. 2) records the inverted zonation of an upper-crustal magma reservoir, from which the top erupted first and the lower parts erupted later. Petrographic textures reveal an increasing abundance of resorbed, reversely zoned plagioclase phenocrysts toward the top of the section (Fig. 2). Abundant dissolution features and the sharp transition toward anorthite-rich and sieve-textured rims record injection of more primitive magma into the lower part of the magma chamber (Fig. 2; e.g., Bachmann et al., 2002). The recharge magma is represented by abundant less-evolved juvenile clasts, including gabbroic enclaves, at the very top of the 7 Ma volcanic sequence. The absence of strong dissolution features in the Bajo de la Alumbraera porphyry intrusions and in the lower parts of the Agua de Dionisio section shows that little or no large-scale magma mixing occurred within the dacitic magma reservoir during mafic injection. Furthermore, the resolvable difference between the termination of PCD mineralization and the initiation of explosive volcanism ( $19 \pm 12$  k.y.; Fig. 2) suggests that porphyry emplacement occurred at the beginning of the rejuvenation event, before generation of large volumes of eruptible magma. Numerical models show that a highly crystalline magma mush allows efficient volatile transfer from the underplated mafic magma toward the upper parts of the magma chamber (Bachmann and Bergantz, 2006; Parmigiani et al., 2016), creating fluid overpressure resulting in rapid emplacement of the porphyry deposit. Our estimated time gap of  $19 \pm 12$  k.y. between

ore-deposit formation and explosive volcanism provides a minimum time span for the rejuvenation of the crystal mush that is in excellent agreement with numerical modeling (Huber et al., 2011). Ultimately, volatile loss during evacuation of the magma reservoir terminated its potential for hydrothermal ore formation. In summary, this study shows that the formation of a world-class porphyry copper deposit and a major volcanic eruption can occur in quick succession, and that both can be linked to the same mafic recharge event that rejuvenated a large silicic upper-crustal magma chamber.

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