

# Using PGE geochemistry to assess magma fertility in the Polo Sur and Penacho Blanco porphyry copper deposits, Centinela District, Northern Chile

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**Abstract.** The Centinela District is host to several mineralized porphyries, including both Cu-only and Cu-Au deposits. This study focusses on the known Polo Sur and Penacho Blanco porphyry Cu±Mo deposits as cases of study to assess their Cu-Au fertility.

PGE are sensitive indicators of sulphide saturation in silicate melts due to their strong partitioning into sulphide melts. They also have relatively low mobility in hydrothermal fluids, minimizing any effects of addition during hydrothermal alteration. If a parent magma reaches sulphide saturation early in its history, an immiscible sulfide melt will extract chalcophile metals trapping them at depth, potentially preventing them from entering the volatile ore-forming phase. In contrast, if sulphide saturation occurs close to the time of volatile saturation, or does not occur, then metals will be available to enter the fluid phase to form a deposit.

Thirty igneous rock samples from both deposits were analysed for major and trace elements. A subset of these samples were analysed to determine their PGE concentrations. Preliminary results suggest that sulphide saturation may occur before the MgO content of magmas at Penacho Blanco fell below 3.5 wt.% but the timing of sulfide saturation, if it occurred at all, at Polo Sur is unclear.

Zircon geochemical data from thirteenth samples indicate that the oxidation state of the magmas of the are increased as the samples became younger.

Keywords: porphyry copper deposits, Centinela District, platinum group elements

## 1 Introduction

Copper is one of the most widely used metals in our society and it is essential in electronics, vehicles, telecommunications, electrical power generation and distribution systems, industrial and domestic piping, chemicals, currency and general infrastructure (Mudd and Jowitt 2018). The main source of this metal is porphyry copper deposits which provide nearly three-quarters of the world's copper and a fifth of its gold (Sillitoe 2010; Mudd and Jowitt 2018). It is estimated that the demand for metals doubles every 20-30 years, but, in contrast, the average discovery rate of economic deposits is falling each year (Schodde 2017). For this reason, it is important to reach a better understanding of the processes that form these deposits, which can help us sustain the copper supply in future decades.

Porphyry ore deposits are related to igneous rocks, usually of dioritic to granitic composition, that form in

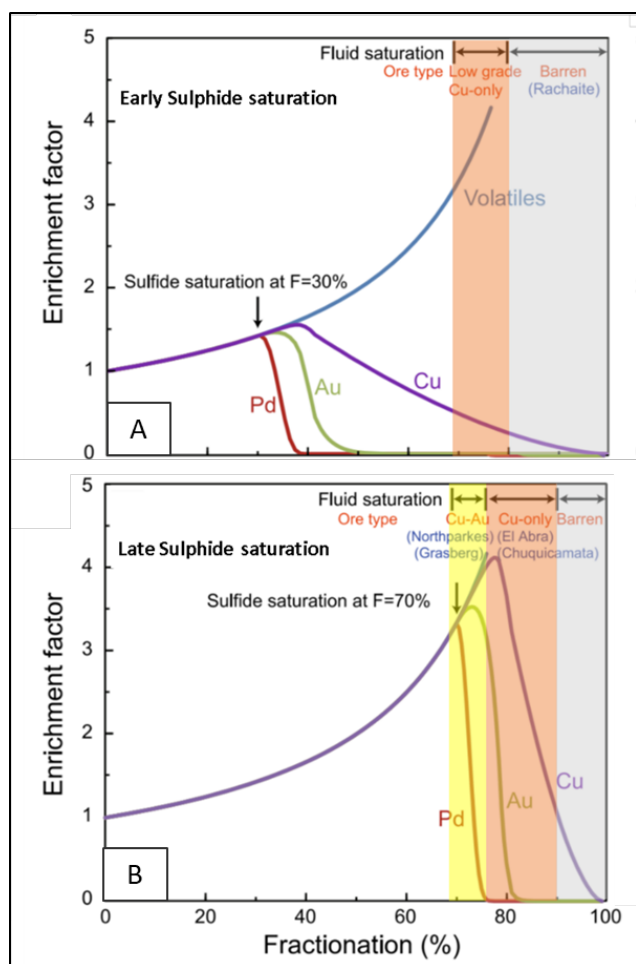
magmatic belts above subduction zones (Richards 2003; Seedorff et al. 2005; Sillitoe 2010; Audétat and Simon 2012; Wilkinson 2013). The magmas produced in this setting are usually of basaltic composition, hydrated and oxidized, and ascend until they reach the base of the crust where they stagnate due to the contrast of density (Richards 2003). Here, they evolve to more felsic compositions that are able to ascend to upper crustal levels where a decrease in temperature and pressure can lead to the exsolution of a volatile phase (Wilkinson 2013, and references therein). These fluids can transport metals and have the potential to develop ore systems, known as porphyry copper deposits. However, not all porphyry systems contain economic concentrations of metals, and 'barren' systems share many features with fertile ones. Although there is an understanding of the general processes that can lead to a mineralized system, the factors that control the fertility of porphyry systems remain unclear (Wilkinson 2013, and references therein).

The aim of this project is to test the hypothesis that the timing of sulfide saturation, relative to volatile saturation, is an important factor controlling the type (Cu or Cu-Au) and fertility of porphyry systems from the Centinela District, Northern Chile. If a parent magma reaches sulfide saturation before volatile saturation, an immiscible sulfide melt will form, which will extract chalcophile metals, such as Cu and Au, and may trap them at depth so that they are unable to enter the volatile ore-forming phase (Fig. 1A), potentially resulting in a barren system. In contrast, if volatile saturation occurs before sulfide saturation, if the fraction of immiscible sulfide to form is small, if the time difference between these events is short, or if does not happen, most of the metals will remain in the melt and be available to enter the fluid phase and form an economic Cu or Cu-Au deposit (Fig. 1B). To address this aim, two porphyries from the Centinela District were studied, Penacho Blanco and Polo Sur.

Recent advances in platinum group element (PGE) analysis, developed at the Research School of Earth Sciences (RSES) at the Australian National University (ANU), are allowing analysis of PGE at ultra-low concentrations (Park et al. 2012a). Therefore, it is now possible to study rocks with low abundance of these elements, such as felsic suites, including the rock types associated with porphyry copper deposits. The PGE have been demonstrated to be sensitive indicators of sulfide saturation due to their high partition coefficients into sulfide melts (Mungall and Brennan, 2014). Furthermore, they are substantially less mobile in hydrothermal fluids than Cu and Au (Park et al., 2016) so are less likely to be

impacted by post-magmatic hydrothermal addition .

Recent studies used PGE geochemistry to establish the timing of sulfide saturation in the El Abra porphyry Cu deposit in Northern Chile (Cocker et al. 2015) and in the Cu-Au deposits of the Northparkes region, New South Wales, Australia (Hao et al. 2017). The latter work also included barren suites from the same region allowing the PGE geochemistry of barren rocks to be contrasted with the mineralized bodies. The results suggest that sulfide saturation occurred at earlier stages of magmatic differentiation for the non-mineralized suites than in the Cu-Au porphyries, where sulfide saturation occurred slightly before volatile saturation. Moreover, the results from the El Abra porphyry copper system showed that sulfide saturation occurred earlier than at Northparkes, which is consistent with the former being a Cu-only (gold removed early by limited sulfide saturation) and the latter being a Cu-Au deposit.

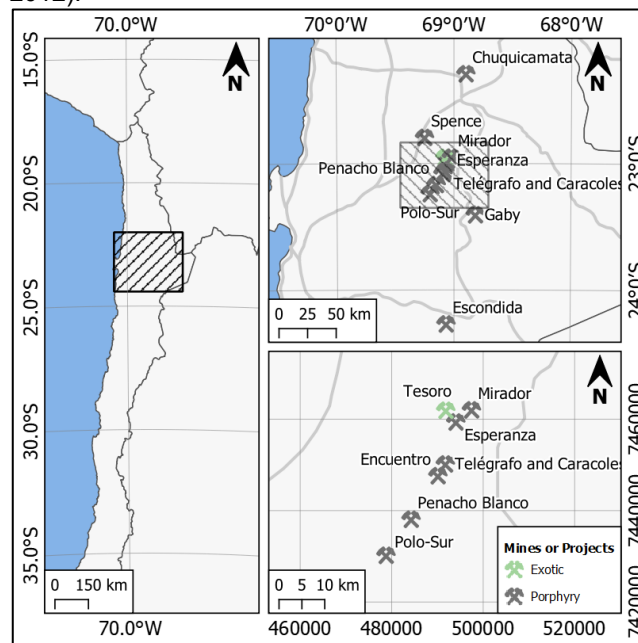


**Figure 1.** Models for Pd, Cu and Au behaviour in a silicate melt for early (A) and late (B) timing of sulfide saturation. Modified from Park et al. (2018).

## 2 Geological Background

The Centinela District, located in northern Chile, is part of the middle Eocene to early Oligocene metallogenetic belt which contains a number of renowned deposits like

Chuquicamata and La Escondida (Sillitoe and Perelló 2005). The Centinela District forms a NE-trending block of approximately 40 km length and 25 km width, limited by the Coastal Cordillera to the west and the Domeyko Cordillera to the east. It is associated with the northern tip of the Sierra de Varas Fault, part of the Domeyko Fault System which is related to most of the mineralization in this belt (Perelló et al. 2010; Mpodozis and Cornejo 2012).



**Figure 2.** Map showing the location of the Centinela District and the principal mines and projects.

The district is host to at least seven identified mineralized porphyries, including both Cu-only and Cu-Au deposits, and has accounted for nearly 24.8 Mt of refined copper by 2017 (Antofagasta Minerals plc, 2017). Encuentro (41 Ma) and Esperanza (42 Ma) are currently being mined, together with exotic copper deposits at Tesoro and Mirador (Fig. 2). These features make the district a perfect natural laboratory to test whether the timing of sulfide saturation relative to volatile saturation affects the nature of the mineralization (i.e. Cu or Cu+Au).

The Penacho Blanco (formerly Centinela) and Polo Sur deposits account for the 25% of the resources known in the district, with 1.25 Mt contained Cu in the former and 5.14 Mt in the latter (Perelló et al. 2010; Antofagasta Minerals plc 2017). These are the oldest deposits in the district with dates between 45-44 and 42-41 Ma, respectively, and are classified as Cu-Mo porphyries (Perelló et al. 2010; Mpodozis and Cornejo 2012).

Penacho Blanco comprises subvertical cylindrical bodies of granodioritic composition hosted in volcanic rocks and a pre-mineralization diorite. Its alteration pattern is concentric with a central potassic zone overprinted by sericitic alteration. The main hypogene mineralization is dominated by chalcopyrite with an important and well-developed blanket of secondary sulfides that include chalcocite and covellite. The oxidation zone is not well developed and marginal

(Perelló et al. 2010).

The Polo Sur porphyries are irregular to cylindrical bodies of dacitic composition emplaced in Paleocene to early Eocene volcanic rocks. Its alteration zonation is concentric with a potassic core overprinted by sericitic alteration that grades to propylitic alteration laterally and it is capped by an advanced argillic lithocap. The sulfide mineralization is mainly chalcopyrite with minor bornite and, in contrast to Penacho Blanco, the oxidation zone is well developed (Perelló et al. 2010).

### 3 Samples and Methods

A representative group of samples from the deposits were selected according to two main criteria: i) unmineralized samples with a low intensity of alteration were preferred; ii) to encompass the full compositional range of the igneous rocks. Fifteen samples from Penacho Blanco and thirteen from Polo Sur ranging from diorites to dacite porphyries were studied. Three samples of rhyodacite porphyry from the TYC (Telégrafo and Caracoles, Fig. 2) area, which correspond to the youngest porphyries (39 Ma) in the district, were included to extend the temporal range.

Samples were cleaned of visible veinlets and ground in an in-house hardened case soft iron mill until grit-free. Major elements were determined at Intertek Genanalysis in Perth, Australia, by Li-borate fusion and analysis by XRF. Trace elements were analyzed by LA-ICP-MS in fused glass beads using a Lambda Physic Complex 110 excimer laser coupled with an ANU-designed HelEx ablation cell and an Agilent 7700x ICP-MS.

Twenty-three samples were selected based on composition to span the range from the most mafic member (highest MgO content) to the most felsic (lowest MgO). These were analyzed for PGE using the isotopic dilution, Ni-sulfide fire assay method described by Park et al. (2012). Concentrations of monoisotopic Rh and Au were calculated by the method described by Meisel et al. (2003) and Park et al. (2012b), using the ratio between  $^{103}\text{Rh}$  and  $^{106}\text{Pd}$  and  $^{197}\text{Au}$  and  $^{194}\text{Pt}$ , respectively, assuming that the loss of each element was similar during the analytical procedure. Eighteen duplicate samples were analyzed to evaluate the possible impact of PGE heterogeneity in the samples.

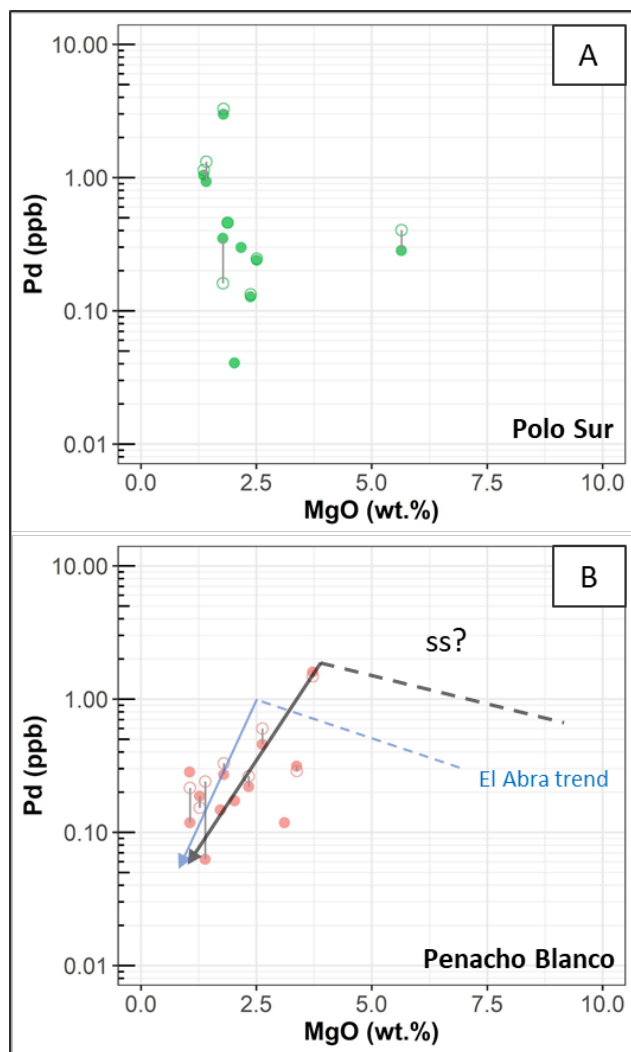
### 4 Results and discussions

The results from major and trace elements indicate that the magmas from Polo Sur and Penacho Blanco are typical calc-alkaline series with a subduction zone signature of Nb depletion and Pb enrichment.

The rare earth element patterns, normalized to chondrite are spoon-shaped, with an enrichment of LREE and depleted in MREE. The europium anomaly varies from slightly positive to slightly negative. The rocks from both deposits present a sub-adakite to adakite-like signature with high values of Sr/Y and La/Yb, especially in the more felsic samples. This signature has been proposed to result from a high water content of the magma (>2%) that suppresses plagioclase crystallization

in early differentiation stages and promotes fractional crystallization dominated by hornblende (Richards and Kerrich 2007, and references therein).

Preliminary results show that the MgO content varies between 0.6 to 3.5 wt. % with one high value at 5.5 wt.% and that Pt and Pd vary from 0.01 to 1.85 and 0.04 to 3.27 ppb, respectively. The results from duplicates yield values that lie close to the corresponding original values (Fig. 3).



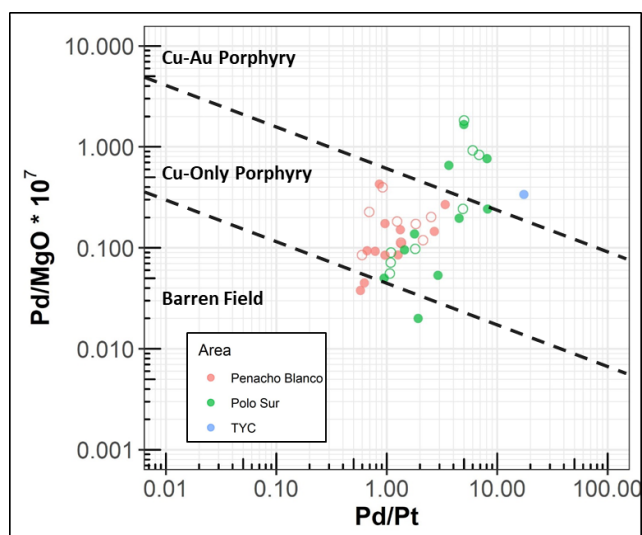
**Figure 3.** Pd vs MgO diagrams for results from Polo Sur (A) and Penacho Blanco (B). Duplicate analyses are linked by a grey line and shown by an open circle.

Pd is the most appropriate element to identify the onset of sulfide saturation because it accumulates in the melt up to sulfide saturation and then drops abruptly following saturation (Park et al. 2013). There is no obvious trend in the Polo Sur data. Thus, it is not possible to identify a sulfide saturation signature in this deposit (Fig. 3A). There is a weak trend of decreasing Pd with decreasing MgO for the Penacho Blanco samples, however, it may be possible to assume that sulfide saturation happened before 3.5 wt.% MgO (Fig. 3B). The trend and values are similar to those observed in the Cu-only El Abra porphyry

deposit (Fig. 3B; Cocker et al. 2015).

Although the samples span dioritic to rhyodacitic compositions, it was not possible to establish evidence for a clear onset of sulfide saturation for these deposits. However, the geochemistry still reflects the nature of the processes involved in the formation of porphyry copper deposits. According to the chalcophile element fertility diagram (Fig. 4) of Park et al. (2018) they are classified as mainly porphyry Cu-Only deposits. A group of Polo Sur samples fall in the Cu-Au area which may be related to small amounts of gold (0.06 g/t) reported in sulfides (Antofagasta Minerals plc 2017)

Finally, the study of the PGE geochemistry of felsic rocks gives us a proxy to better understand how sulfides behave in magmatic systems related to porphyry copper deposits which frequently are overprinted by hydrothermal alteration.



**Figure 4.** Chalcophile element discriminator from Park et al. (2018). Most of the samples fall into the Cu-Only field. Open circles indicate duplicate analyses.

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