Using Platinum Group Elements to Identify Sulfide Saturation in a Porphyry Cu System: the El Abra Porphyry Cu Deposit, Northern Chile

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Received September 30, 2014; Accepted November 27, 2015

ABSTRACT

Geochronological and geochemical studies, including platinum group element (PGE) analyses, were undertaken on samples from the El Abra–Pajonal igneous complex, northern Chile, to investigate the magmatic evolution of the suite. Special attention was paid to identifying the onset of sulfide saturation and to documenting how it influenced the geochemistry of the chalcophile elements and the formation of the El Abra porphyry Cu deposit. The PGE have extreme sulfide melt–silicate melt partition coefficients, making them sensitive indicators of the timing of sulfide saturation in an evolving magmatic system. In arc-related intermediate to felsic magmatic systems, which have the potential to produce porphyry deposits, the timing and extent of sulfide saturation relative to ore-fluid saturation may control the capacity of these systems to produce economic mineralization and, if they do, whether the deposits are Cu-only or Cu–Au. This study incorporates the first comprehensive analysis of PGE in a felsic magmatic suite associated with an economic porphyry system. The suite comprises a series of quartz monzodiorite to granite intrusions with U–Pb zircon ages between 43 and 35 Ma. Their petrography and major element chemistry, including increasing Sr/Y ratios and rare earth element patterns, suggest that crystal fractionation and crustal assimilation were the key magmatic processes governing the evolution of the El Abra–Pajonal suite. Plagioclase fractionation dominated the oldest intrusions, and their associated granites and aplites. Following the injection of a more primitive, wetter, mafic magma at 41–40 Ma, plagioclase fractionation became suppressed and amphibole became the dominant fractionating phase, leading to the formation of the El Abra porphyry intrusion and Cu deposit. Abundances of Pt and Pd in felsic rocks from the El Abra–Pajonal intrusive complex drop rapidly in samples with MgO values below 2.5 wt %, following sulfide saturation of the magmas, which occurred slightly before ore-fluid saturation and formation of the Cu deposit. Modeling suggests that the amount of sulfide formed was very small, enough to strip the PGE and Au from the magma but not Cu, because of the lower partition coefficient of Cu relative to the precious metals, which explains why the mineralization at El Abra is a Cu-only porphyry deposit, rather than a Cu–Au deposit.

Key words: El Abra; platinum group elements; porphyry copper deposits; sulfide saturation; U–Pb dating
INTRODUCTION

Porphyry systems

The majority of the world’s Cu production comes from porphyry Cu deposits, making an understanding of their genesis a critical factor in Cu exploration. Porphyry deposits are typically large-tonnage, low- to medium-grade deposits. They are frequently associated with other intrusion-related hydrothermal mineralization systems such as skarn and epithermal deposits (Mudd et al., 2013). Characteristics of porphyry deposits, including associated magmatic and hydrothermal processes, have been summarized in numerous recent review papers including those by Seedorff et al. (2005), Sillitoe (2010), Audet & Simon (2012) and Kouzmanov & Pokrovski (2012), and in references therein.

Porphyry Cu systems typically develop in association with magmatic arcs above subduction zones. The ascending magmas form intermediate to felsic intrusions of ‘calc-alkaline to alkaline’ composition that are relatively oxidized and hydrous. The deposits are associated with shallow intrusive porphyry stocks, which are interpreted to originate from deeper parent magma bodies (Dilles, 1987; Seedorff et al., 2005, 2008; Sillitoe, 2010). The shallow ore-associated intrusions exsolve magmatic fluids, which, along with circulating meteoric water, hydrothermally alter the host-rock and deposit ore minerals. There are many different aspects of porphyry formation that influence porphyry mineralization. These include the composition of the magma, oxidation state, timing of magmatic processes (including sulfide and ore-fluid saturation), depth of emplacement, and geodynamic setting (Candela, 1997; Cooke et al., 2005; Seedorff et al., 2005; Sillitoe, 2010). The interplay among these factors controls the quantity and type of porphyry mineralization that will form.

El Abra, northern Chile (Fig. 1), is a classic example of a porphyry copper deposit with excellent exposures of a complete suite of weakly altered plutonic rocks that are directly associated with the ore body. It is therefore an ideal natural laboratory in which to examine the magmatic processes that lead to the formation of porphyry Cu deposits, by addressing two key questions: How did the El Abra–Pajonal magmatic suite evolve though time? What influenced and controlled the porphyry mineralization? This study focuses on understanding the connection between the magmatic processes involved in the evolution of the El Abra–Pajonal suite intrusions and the El Abra porphyry Cu mineralization being mined today. Therefore, the nature of the deposit itself, in terms of mineralization, alteration, and veining style for example, has not been studied, but rather we have focused on the temporal and chemical development of the intrusions directly associated with the mineralization, using petrographic, geochemical, and geochronological analytical techniques. Special emphasis has been placed on the role of the timing of sulfide saturation relative to ore-fluid saturation, using the platinum group elements (PGE) to pinpoint the onset of sulfide saturation.

Sulfide saturation

The PGE have been successfully used to identify sulfide saturation in mafic systems (e.g. Keays & Lightfoot, 2007) but analytical difficulties have limited their application in felsic systems. Recent advances in the inductively coupled plasma mass spectrometry (ICP-MS)–NiS fire assay–isotope dilution method (Park et al., 2012) now make it possible to measure the PGE at the 1–20 ppt level, so that they can now be analyzed in rocks with very low abundances, including felsic suites. As a consequence, PGE geochemistry can be now used to identify the onset of sulfide saturation in evolving felsic magmas, which can potentially be used to distinguish between Cu- and/or Au-bearing and barren felsic systems. The initial hypothesis we set out to test is that if a fractionating magmatic system becomes sulfide saturated before it becomes ore-fluid saturated most of the Cu and Au will be trapped within sulfides in a deep parent magma chamber and be unavailable to enter a hydrothermal fluid, which emanates from one of the shallow daughter intrusions, the El Abra porphyry. Alternatively, if ore-fluid saturation occurs before sulfide saturation most of the Cu and Au will be available to partition into the magmatic hydrothermal fluid,
which could lead to the formation of an economic Cu and/or Au deposit.

The PGE are preferred to Au and Cu for identifying sulfide saturation in evolving silicate melts for two reasons. First, the partition coefficients for Pt and Pd into an immiscible sulfide melt are approximately two orders of magnitude higher than those for Au and Cu (Mungall & Brenan, 2014). As a consequence, Pd and Pt orders of magnitude higher than those for Au and Cu are not uncommon. Second, the original Cu and Au content of the rocks can be overprinted by secondary Cu and/or Au mineralization, making it impossible to obtain the primary concentration of these elements in samples. Although the ore-forming fluid can carry Pd, the amount is trivial compared with Cu and Au. For example, the Au/Pd ratio of the primitive mantle (McDonough & Sun, 1995) and basaltic magmas, prior to sulfide saturation (Park et al., 2013a, 2015), is typically 0.25–0.8 but it averages over 90 for a wide range of Pd-rich porphyries analyzed by Tarkian & Stribny (1999). Bearing in mind that the Pd content of many of the analyzed samples was below their detection limit of 8 ppb, the high Au/Pd ratio of porphyry ore implies that Au is at least 100 times more soluble than Pd in the ore-forming fluid.

Sulfide saturation in the evolution of porphyry systems has been discussed in the recent literature but pertains to either hypothetical suppositions or analysis of silicate and sulfide melt inclusions and typically entails later breakdown of the sulfides to release the chalcopyrite elements into the ore fluid for deposit formation (Keith et al., 1997; Halter et al., 2002, 2005; Richards, 2009; Audet & Simon, 2012; Wilkinson, 2013). In this study the whole-rock abundances of Pt and Pd are used to identify the occurrence and timing of sulfide saturation, relative to ore-fluid saturation, in an evolving magmatic system that produced a porphyry Cu deposit. The identification of sulfide saturation in arc-related magmatic systems using PGE abundances has been previously demonstrated and discussed by Park et al. (2013a, 2013b, 2015) but the method has not been applied to porphyry mineralization. This study presents the first use of PGE to identify sulfide saturation in a felsic ore system associated with a significant porphyry Cu deposit. The El Abra deposit and associated El Abra–Pajonal intrusive complex makes an ideal study area because it is a well-exposed suite that exhibits a range of chemical compositions (quartz monzodiorite to granite), leading up to the formation of a porphyry Cu deposit. A secondary aim of this study is to determine why El Abra is a Cu-only system and to determine its place in a continuum of Cu ± Au ± (± PGE-enriched) systems for a discussion of PGE enrichment in porphyry systems see Tarkian & Stribny (1999) and Economou-Eliopoulos (2005)). It does not aim to address all of the different types of porphyry systems, such as Cu ± Au ± Mo, but instead attempts to understand how sulfide saturation in a crustal magmatic system controls Cu ± Au porphyry mineralization.

GEOLOGICAL SETTING

El Abra is an economic porphyry Cu-only deposit in northern Chile associated with the El Abra–Pajonal complex, a suite of intermediate to felsic intrusive rocks (Fig. 2; Ambrus, 1977; Dilles et al., 1997). The initial Cu-oxide reserve for the El Abra deposit at the commencement of mining in 1995 was 798 million tons at 0.54 wt % Cu (Gerwe, 2005) whereas the Cu-sulfide ore reserve was 452 million tons at 0.64 wt % Cu (Graichen et al., 1995). The deposit occurs within a deep-seated, NW-trending shear zone that is linked to the West Fissure Fault Zone (Graichen et al., 1995; Barrett, 2004; Gerwe, 2005), a major fault that is part of the Domeyko Fault system and is associated with many other porphyry Cu deposits in the region, including, from north to south, Collahuasi District, Chuquicamata, La Escondida and El Salvador (Fig. 1; Ambrus, 1977; Reutter et al., 1996; Cornejo et al., 1997; Garza et al., 2001; Ossandon et al., 2001; Richards et al., 2001; Masterman et al., 2005; Urqueta et al., 2009).

Copper ± molybdenum mineralization is centered on an El Abra porphyry stock that crosscuts the El Abra-Pajonal suite of intrusions, which range in composition from alkali feldspar granite to quartz monzodiorite (Ambrus, 1977; Graichen et al., 1995; Barrett, 2004; Gerwe, 2005). These intrusions delineate a southwards younging trend from the Cerro de Pajonal Mountain. The active mining area lies within a potassic alteration zone that extends up to 1600 m radially from the host El Abra porphyry stock (Graichen et al., 1995; Barrett, 2004; Gerwe, 2005). The deposit is characterized by high-grade Cu (±Mo and Zn), low-S mineralization, with Cu grades decreasing radially from the core of the deposit (Ambrus, 1977; Graichen et al., 1995; Barrett, 2004; Gerwe, 2005). High-grade Cu mineralization is associated with K-feldspar-dominated potassic alteration (Ambrus, 1977); however, the highest Cu grades occur along NW-trending fissures and veins within the potassic alteration zone (Graichen et al., 1995; Barrett, 2004; Gerwe, 2005). The lowest Cu grades occur within the propylitic alteration zone (Ambrus, 1977; Graichen et al., 1995; Barrett, 2004; Gerwe, 2005). Hypogene mineralization is observed to extend to depths >900 m (Graichen et al., 1995; Barrett, 2004) and is generally characterized by chalcopyrite, either intergrown with bornite (Ambrus, 1977) or rimmed by bornite and chalcosite (Graichen et al., 1995; Barrett, 2004). Molybdenite is a minor accessory phase that occurs peripheral to the Cu-rich core of the deposit (Ambrus, 1977; Graichen et al., 1995; Barrett, 2004), such that molybdenite grades increase with decreasing Cu grades (Ambrus, 1977). Galena and sphalerite mineralization are found in the youngest veins within the El Abra deposit (Ambrus, 1977; Gerwe, 2005). Supergene mineralization is coincident with an oxide cap that overlies the hypogene mineralization and this cap extends to a maximum depth of 600 m (Graichen et al., 1995; Barrett, 2004). Chrysocolla is the dominant oxide mineral mined; however,
Fig. 2. (a) Geological map of the El Abra region showing location of the samples used in this study. The area within the dashed rectangle is shown enlarged in (b). Grid references for each sample are included in Table 2. Those samples labeled with numbers (with the ANU07 prefix omitted) refer to samples that were chosen for PGE and Re analysis. Simplified geological map modified from Tomlinson et al. (1995) and Barrett (1997). Post-El Abra–Pajonal units of Tertiary to Quaternary age include the Carcote ignimbrite and Tertiary and Quaternary gravels. Pre-El Abra–Pajonal units of Palaeozoic to Tertiary age include the Icanche Formation, Saturno fanglomerate, Cerro Colorado Complex, Tolar Formation, and Collahuasi Formation. Projection UTM 19K, datum South America Provisional 1956.
turquoise, tenorite, antlerite, brochantite, Cu-wad and Cu-rich clays are also observed within the oxide zone (Graichen et al., 1995; Barrett, 2004). Native Cu and cuprite are commonly found along the irregular and gradational oxide (supergene–hypogene contact (Graichen et al., 1995; Barrett, 2004).

SAMPLES AND METHODS

Samples were collected from all units of the El Abra–Pajonal intrusive complex including the El Abra porphyry. Fresh to weakly altered samples were chosen where possible to avoid mineralization, although some weakly altered samples have small amounts of disseminated hydrothermal sulfide.

U–Pb zircon dating, combined with zircon trace element analyses, was carried out on 26 samples previously analyzed for whole-rock chemistry. The dating technique used in this study is similar to that of Harris et al. (2004) and Campbell et al. (2006). Zircons were separated from 2 kg samples by a combination of standard crushing, magnetic separation and heavy liquid techniques. Epoxy mounts containing zircons from up to four samples of unknown age and three standards [Temora-2 (Black et al., 2004); NIST610 (Kane, 1998); 521-Los Picos (Ballard, 2001)] were set and polished.

Cathodoluminescence (CL) images and optical photography were used to assist with the selection of ablation sites. Laser ablation (LA) was conducted using a pulsed ArF LambdaPhysik LPX 120i UV Excimer Laser at 5 Hz with an operating voltage varying between 20 and 23 kV and a spot size of 32 μm. Particular attention was paid to the selection of rims versus cores as inherited cores are common in zircons from the nearby Chuquicamata region (Zentilli et al., 1994; Ballard, 2001). Ablated material was transported from the laser sample cell via a mixture of c. 70% Ar, 29% He and <1% H2 gas to an Agilent 7500s ICP-MS system for analysis. Counts for 29Si, 91Zr, 31P, 206Pb, 207Pb, 208Pb, 232Th, 235U and 238U were collected in time-resolved mode. Additional isotopes: 49Ti, 89Y, 139La, 140Ce, 144Sm, 153Eu, 163Dy, 175Lu and 177Hf were also collected. As the carrier gas contains 204Hg, it impossible to measure 204Pb owing to the direct isobaric interference. Following the procedure described by Campbell et al. (2006) the raw data were corrected for instrumental mass bias drift, isotopic fractionation, depth-dependent elemental fractionation and common Pb, using the glass NIST610 and zircons from the Temora-2 standard. The zircon standard 521-Los Picos was processed in the same manner as unknown samples and used for quality control. The corrections were applied on an ablation-time (depth) basis. The Temora-2 standard was also used to correct for depth-dependent, inter-element fractionation of 207Pb/206Pb, 208Pb/232Th, 206Pb/238U and 207Pb/235U, by using the known ratios from Black et al. (2004). 235U was calculated from 239U assuming 236U = 238U/137.88, except in extremely U-rich samples where mass 236U was measured directly. The average 208Pb/238U correction factor applied to each mass scan for unknown zircons was based on the ratio between the measured Temora-2 206Pb/238U ratio value (for multiple Temora-2 measurements over the course of an analytical session) to the Black et al. (2004) 206Pb/238U ratio value. Applying this method to correct for depth-dependent fractionation assumes that variation in the fractionation factor with ablation depth is similar in the unknown zircon and Temora-2 standard. The glass standard, NIST610, was used to determine concentrations for all elements following a procedure similar to that described for the isotope ratios. Two methods, the 207Pb and 208Pb correction methods, were used to correct for common Pb [see Campbell et al. (2006) for details]. The 208Pb method to correct for common Pb is preferred to the 207Pb method and has been used in this study. Both methods give dates that, with rare exceptions, agree within analytical error. Zircons were considered to be discordant if their 207Pb-corrected or 208Pb-corrected 206Pb/238U age divided by their 207Pb-corrected or 208Pb-corrected 207Pb/235U age, was greater than 1 ± 0.1, including errors. Discordant zircons were rejected from the age calculation. The quoted 2 SE for the U–Pb zircon age for a single zircon is the error derived from two components: the analytical uncertainty of the zircon measurement, and the uncertainty in the measurement of the standards. The standard deviation for Temora-2 was used to measure the uncertainty of the standards for each analytical session (Supplementary Data Table A1; supplementary data for this paper are available at http://www.petrology.oxfordjournals.org). The data were processed using the ISOPLOT software of Ludwig (2012) to generate weighted average 238U/206Pb ages.

Whole-rock major element concentrations of 47 El Abra–Pajonal suite samples were measured by X-ray fluorescence (XRF) on fused-glass disks using a Philips PW2400 XRF spectrometer at the University of Otago. Whole-rock trace element concentrations were analyzed at the Australian National University by laser ablation (LA)-ICP-MS on the same glass disks that were used for the XRF analyses. The system used was a pulsed ArF LambdaPhysik LPX 120i UV excimer laser connected to an Agilent 7500s ICP-MS system operated at 5 Hz with a voltage varying between 20 and 23 kV, with a pit diameter of 70 μm and ablation depth of c. 20 μm in 40 s. NIST612 was used as the primary standard and BCR-2 was used to monitor quality control.

Whole-rock PGE and Re abundances in 21 selected samples were determined by the modified NiS fire assay isotope dilution method described by Park et al. (2012). Only intrusions directly related to the magmatic evolution of the El Abra porphyry (mineralizing event) were included for PGE analysis. The Antena aplite, Rojo Grande granite and Apolo granite were excluded because their geochemistry precludes them being part of the suite that evolved to form the ore-associated El Abra porphyry. Duplicate analyses were also run with a Te co-precipitation step, following a method based on that of Jackson et al. (1990) and Savard et al. (2010). The Te and Sn solutions were, however, diluted to 1% of the concentrations described by Savard et al. (2010) to reduce the blank in the PGE
solutions to acceptable levels. A single-collector Agilent 7700 ICP-MS system at the Australian National University was used to analyze the final solutions. A detailed description of the methods used and all of the data for the whole-rock samples analyzed in this study, procedural blanks and reference material samples are given in the Supplementary Data (Tables A2 and A3). The method limits of detection, taken as three standard deviations of the procedural blanks, were 0.5 ppt for Ir, 1.3 ppt for Ru, 1.4 ppt for Rh, 19.7 ppt for Pt, 9.5 ppt for Pd, and 8.2 ppt for Re. Total uncertainties in the data primarily result from uncertainty in the blank subtraction and ICP-MS counting statistics. The reference material TDB-1 (CCRM-PANET diabase) was used to assess the accuracy and precision of the measurements. Our analyses of the PGE and Re abundances in TDB-1 and error measurements are reported in Table A3 in the Supplementary Data and are consistent with the previously reported values of Plessen & Erzinger (1998), Peucker-Ehrenbrink et al. (2003), Meisel & Moser (2004) and Savard et al. (2010).

Ce⁴⁺/Ce³⁺ ratios in zircon were calculated using the whole-rock and zircon Ce concentrations determined by LA-ICP-MS of XRF fused disks and zircons, respectively. The zircon Ce⁴⁺/Ce³⁺ ratio values are based on the preferential partitioning of Ce⁴⁺ into the zircon structure over Ce³⁺. Calculation of the ratios follows the method of Ballard et al. (2002) using the following equation:

\[
(\text{Ce}^{4+}/\text{Ce}^{3+})_{\text{zircon}} = \frac{\text{Ce}_\text{melt} - \text{Ce}_\text{zircon}}{\text{Ce}_\text{zircon} - \text{Ce}_\text{melt}}
\]

where the whole-rock (Ce_melt) concentrations of Ce and Ce in zircon (Ce_zircon) are from this study and the partition coefficients for Ce⁴⁺ and Ce³⁺ are estimated from plots of distribution coefficients of tetravalent and trivalent cations (Ballard et al., 2002).

PETROGRAPHY

Descriptions of each of the intrusive units of the El Abra–Pajonal suite are given below in order of youngest to oldest, based on their U–Pb zircon ages in conjunction with field and drill core observations. A comparison to oldest, based on their U–Pb zircon ages in conjunction with field and drill core observations. A comparison to the El Abra–Pajonal suite, excluding the Lagarto porphyry and Pajonal quartz monzonite. The El Abra porphyry is a moderately porphyritic dacite with phenocrysts ranging in size from 0.5 to 2 mm and groundmass microlites from 0.01 to 0.1 mm. Thin-section microscopy shows that the phenocryst mineralogy is dominated by plagioclase and amphibole, with later-forming biotite, orthoclase and quartz. The groundmass mineralogy consists of Ti-magnetite, quartz, orthoclase, plagioclase and accessory phases including apatite, zircon, and orange- and lemon-colored titanite. Plagioclase crystals occasionally show oscillatory zoning and some crystals do not have distinct cores and rims. Amphibole and titanite are common inclusions in plagioclase. Amphibole phenocrysts feature abundant inclusions including quartz, apatite, chalcopyrite, titanite and magnetite. Smaller-sized amphibole phenocrysts are often zoned, with the euhedral cores and rims resorbed.

Apolo granite

The Apolo granite (and aplite) is a leucocratic granite containing a maximum of 5% mafic minerals (biotite and magnetite) with a coarse (1–5 mm) holocrystalline texture. The mineralogy includes anhedral to euhedral quartz, orthoclase and minor plagioclase, biotite and Ti-magnetite, with accessory minerals including rutile, apatite, and zircon. The Apolo granitic and aplitic stocks crosscut the Clara granodiorite.

Clara granodiorite

The Clara granodiorite is a coarse-grained, holocrystalline rock (grain size varies from 0.2 to 2 mm, with an average size of 1 mm). Mineral shapes range from subhedral to euhedral and the paragenesis is amphibole (with rare quartz or plagioclase inclusions), weakly oscillatory-zoned plagioclase, quartz, Ti-magnetite, biotite, microcline and orthoclase. Accessory minerals include orange- and lemon-colored titanite, apatite (often very coarse grained, up to 0.1 mm in size) and zircon. Accessory chalcopyrite occurs as inclusions in amphibole and plagioclase. Previously, the Clara
granodiorite has been mapped and subdivided into two sub-members, the Mafic Clara granodiorite and Leucocratic Clara granodiorite (Ambrus, 1977; Tomlinson et al., 1995). No crosscutting igneous relationships or chilled margins were observed in the field between the two sub-members of the Clara granodiorite and there is no difference in the major element chemistry of these two sub-units. Furthermore, the dating work completed for this study showed that all samples from the Clara granodiorite have the same age within analytical error. These observations support the view of Dilles et al. (1997) that the Clara granodiorite represents one intrusive event.

Rojo Grande granite
The Rojo Grande granite is distinguished from the Apolo granite by containing on average 5 wt % less SiO2 than the Apolo granite and having a greater abundance of mafic minerals (10–15%). The Rojo Grande granite has a coarse (1–5 mm) holocrystalline texture; its principal minerals are anhedral to euhedral biotite (up to 10%), quartz, orthoclase and plagioclase, with trace amounts of amphibole (magnesio-hornblende and actinolite) and Ti-magnetite. Accessory minerals include orange- and lemon-colored titanite, apatite, zircon, and trace rutile.

Llareta quartz monzodiorite
The Llareta quartz monzodiorite is an equigranular, medium- to coarse-grained (0.5–2 mm) unit composed of amphibole, biotite, Ti-magnetite, orthoclase, plagioclase and quartz. Accessory minerals include apatite, zircon, lemon-colored titanite and trace rutile are the accessory minerals.

Dark quartz monzodiorite
The Dark quartz monzodiorite is distinctive and is the most mafic unit in the El Abra–Pajonal suite. It is equigranular in texture and fine grained (0.1–0.5 mm). The mineralogy includes subhedral to euhedral amphibole, biotite, Ti-magnetite, orthoclase, microcline, oscillatory-zoned plagioclase, and quartz. Accessory minerals are apatite, zircon, chalcopyrite (as inclusions in amphibole) and lemon-colored titanite.

Central granodiorite
The Central granodiorite is one of the major rock units in the active mining area. Texturally it is equigranular and medium to coarse grained (0.5–2 mm). The mineralogy includes amphibole, biotite, Ti-magnetite, orthoclase, plagioclase, and quartz. The accessory minerals are apatite, zircon, chalcopyrite (as inclusions in amphibole), orange-colored titanite and rutile.

Equis monzogranite
The Equis monzogranite is a major rock unit in the active mining area. Texturally it is equigranular and medium to coarse grained (0.5–2 mm). The mineralogy includes amphibole, biotite, Ti-magnetite, orthoclase, plagioclase and quartz. Apatite, zircon, orange-colored titanite, chalcopyrite (as inclusions in amphibole) and rutile are present as accessory minerals.

Pajonal quartz monzonite
Outcrop of the Pajonal quartz monzonite is confined to north of the pit area, on the Cerro de Pajonal Mountain. Texturally it is equigranular and medium to coarse grained (0.5–2 mm); its mineralogy includes orthoclase, plagioclase, quartz, amphibole, biotite, Ti-magnetite and trace amounts of clinopyroxene. Accessory minerals include apatite, zircon and lemon-colored titanite, with trace amounts of ilmenite.

RESULTS

U–Pb zircon ages
The 208Pb-corrected 206Pb–238U emplacement ages for the dated samples from the El Abra–Pajonal igneous complex are listed in Table 1. The order of emplacement of the intrusions based on their U–Pb ages is as follows: Pajonal quartz monzonite, 43.2 ± 0.21 Ma; Antena aplite, 42.83 ± 0.22 Ma; Equis monzogranite, 41.73 ± 0.19 Ma; Dark quartz monzodiorite, 40.83 ± 0.33 Central granodiorite, 40.64 ± 0.24 Ma; Llareta quartz monzodiorite, 40.10 ± 0.40 Ma; Rojo Grande granite, 39.21 ± 0.2 Ma; Clara granodiorite, 37.83 ± 0.19 Ma; Apolo granite, 37.55 ± 0.26 Ma; El Abra porphyry, 36.89 ± 0.30 Ma; Lagarto porphyry, 35.53 ± 0.47 Ma. Uncertainties are quoted at the 95% confidence level. A number of the intrusions were emplaced at the same time within the analytical uncertainty of the LA-ICP-MS U–Pb zircon dating method; in these cases, field and drill-core relationships were used to resolve the intrusion order. However, the order of emplacement of the intrusions at c. 40–41 Ma (Central granodiorite, Dark quartz monzodiorite, and Llareta quartz monzodiorite) remains unclear. Figure 3 shows weighted average U–Pb ages for single samples, as well as the weighted
average from the total zircon population for each intrusion.

Whole-rock major and trace element geochemistry

Whole-rock major and trace element data for representative samples of each intrusive unit are reported in Table 2. Figures 4 and 5 show the variation of selected whole-rock major and trace elements. The intrusions have been divided into two series: a Plagioclase series and an Amphibole series. There is a general trend of decreasing TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MgO, CaO and P$_2$O$_5$ with increasing SiO$_2$ (Table 2; Fig. 4a and b). Fe$_2$O$_3$ decreases with decreasing MgO, as is typical of ‘calc-alkaline’ arc suites (Fig. 4d). Al$_2$O$_3$, Na$_2$O and K$_2$O show two distinct trends related to the different Plagioclase and Amphibole fractionation series (Fig. 4a, c and e). The Amphibole series shows little variation in Al$_2$O$_3$ with SiO$_2$ or K$_2$O with MgO, and only a gradual increase in Na$_2$O with decreasing MgO. In contrast, the Plagioclase series samples show decreasing Al$_2$O$_3$ with increasing SiO$_2$, and decreasing Na$_2$O and increasing K$_2$O with decreasing MgO. The MgO and Ni contents of the most primitive Amphibole series samples are higher than those of the most primitive Plagioclase series samples and the most fractionated Amphibole series samples have lower SiO$_2$ (Fig. 4b). Many trace elements (e.g. Y, La, Dy, Cr, Cu, Ba) show considerable scatter and are weakly correlated or show no correlation with SiO$_2$; this may also be partly due to weak alteration of the samples. TiO$_2$ and Ni decrease with decreasing MgO (Figs 4f and 5a); however, Fig. 4f shows two decreasing TiO$_2$ trends. Samples from the Plagioclase series that are older than 41 Ma (Pajonal quartz monzonite, Antena aplite, Equis monzogranite) have higher TiO$_2$ concentrations than those from the Amphibole series at similar MgO concentrations. In contrast, Cu plotted against MgO shows no trend (Fig. 5b). A plot of Sr/Y against Eu/Eu* (Fig. 5c), where Eu/Eu* = Eu$_{Eu}/(Sm_{Eu}/Gd_{Eu})$, shows further differences between the Amphibole and Plagioclase series. Samples from the Plagioclase series show a steady decrease in Sr/Y with decreasing Eu/Eu* whereas those from the Amphibole series plot in two clusters with a distinct gap between them. Amphibole series samples with the highest Sr/Y also have the highest Eu/Eu* but the decrease in Eu/Eu* is appreciably less than for the Plagioclase series.

Chondrite-normalized (Palme & O’Neill, 2014) rare earth element (REE) plots are shown in Fig. 6 and show distinct differences between the Amphibole and Plagioclase series. Members of the Amphibole series, which include the Dark quartz monzodiorite, Central granodiorite, Llareta quartz monzodiorite, Clara granodiorite, and the El Abra and Lagarto porphyries, are plotted in Fig. 6a. They are characterized by Eu anomalies that are small or absent and that tend to decrease with increased fractionation. The heavy REE (HREE) also decrease with fractionation whereas the light REE (LREE) change little or increase slightly. The most evolved samples (e.g. the El Abra porphyry) have
usual spoon-shaped or concave-up HREE patterns. Samples from the Plagioclase series, which are older than 41 Ma, are plotted in Fig. 6b. They include the Pajonal quartz monzonite, Antena aplite and Equis monzogranite and are characterized by pronounced Eu anomalies, which increase with fractionation, as do all of the REE, such that the patterns remain subparallel as the concentrations of the REE increase. The patterns for the HREE are again slightly spoon shaped. Figure 6c shows the patterns for the Rojo Grande and Apolo granites. The Rojo Grande granite is geochemically similar to the suite plotted in Fig. 6b but is distinctively younger. The Apolo granite is also younger than the intrusions plotted in Fig. 6b and has strong Eu anomalies that can be positive or negative; the concentrations of the REE are lower than in the other suites. This combination suggests that cumulate processes dominate the geochemistry of the Apolo granite.

### Whole-rock PGE and Re results

Whole-rock Pt and Pd abundances are reported for 21 El Abra–Pajonal suite samples in Table 3; all PGE and Re values are blank subtracted. The other analyzed PGE were below or close to the limit of detection and are therefore not considered further. Re abundances were measurable in 20 samples and range from <8.2 ppt to 46.7 ppb, but show no clear trend.

Abundances of Pd and Pt are plotted versus whole-rock MgO contents for each of the El Abra–Pajonal suite samples in Fig. 7a and b, and are compared with those for samples from Pual Ridge and Niutahi–Motutahi in Fig. 7c and d. As in previous figures the samples are divided into the Amphibole and Plagioclase series. The plot of Pd versus MgO shows no clear trend for the Amphibole series samples with MgO above 2 wt %; Pd decreases at a similar rate in the Amphibole series samples with MgO above 2.5 wt % (Fig. 7a), but Pd falls rapidly once the MgO content falls below this value. The abundance of Pt decreases continuously with decreasing MgO but the rate of decrease becomes more rapid once MgO drops below 2 wt %. Both Pd and Pt decrease with decreasing MgO for these samples; Pd decreases at a similar rate in the Amphibole series samples with MgO above 2.5 wt % (Fig. 7b). Samples from the ore-bearing El Abra porphyry have both low MgO values and low Pt and Pd abundances, with the exception of the sample with the lowest MgO content, which has an anomalously high Pt abundance. The Plagioclase series samples all have MgO <2.5 wt %. Both Pd and Pt decrease with decreasing MgO for these samples; Pd decreases at a similar rate in the Amphibole series samples with MgO above 2.5 wt % MgO; Pt overall decreases more gradually than in the Amphibole series samples below 2.5 wt % MgO. The El Abra–Pajonal suite samples run in duplicate are shown

### Table 1: U-Pb zircon age results for samples from the El Abra-Pajonal igneous complex showing 208Pb-corrected 206Pb/238U emplacement ages (Ma).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intrusive unit</th>
<th>208Pb corrected, 206Pb/238U emplacement age (Ma)</th>
<th>2σ</th>
<th>MSWD</th>
<th>n</th>
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<td>ANU07-118</td>
<td>Lagarto porphyry</td>
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<td>0.47</td>
<td>1.03</td>
<td>10</td>
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<tr>
<td>ANU07-094</td>
<td>El Abra porphyry</td>
<td>36.80</td>
<td>0.32</td>
<td>0.72</td>
<td>22</td>
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<td>ANU07-107</td>
<td>El Abra porphyry</td>
<td>37.50</td>
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<td>ANU07-081</td>
<td>Apolo granite</td>
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<td>Apolo granite</td>
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<td>1.30</td>
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<td>Rojo Grande granite</td>
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</table>

1All uncertainties are standard error at 95% confidence limits.
with filled symbols. In some cases the duplicates lie within plotting error and only a single point is plotted. Where there is a distinct difference between duplicates a connecting line has been drawn between them. Samples with MgO >2.5 wt % (Amphibole series) show greater scatter in Pt than Pd, which shows no significant variation between duplicates, whereas for samples with MgO <2.5 wt % both Pt and Pd show similar scatter.

When plotted against age, there is a distinct spike in several elements, for example MgO and Pd abundances at 40–41 Ma (Fig. 8a and c), which correspond to the employment of the Dark quartz monzodiorite and

<table>
<thead>
<tr>
<th>Sample:</th>
<th>ANU 07-116</th>
<th>ANU 07-115</th>
<th>ANU 07-094</th>
<th>ANU 07-107</th>
<th>ANU 07-081</th>
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<th>ANU 07-095</th>
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<td>El Abra porphyry</td>
<td>El Abra porphyry</td>
<td>Apolo granite</td>
<td>Clara granodiorite</td>
<td>Clara granodiorite</td>
<td>Clara granodiorite</td>
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wt %

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<th>Al₂O₃</th>
<th>Fe₂O₃</th>
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<th>CaO</th>
<th>Na₂O</th>
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<td>65.46</td>
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<td>ppm</td>
<td>3</td>
<td>67.77</td>
<td>65.83</td>
<td>65.46</td>
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<td>63.94</td>
<td>70.60</td>
<td>5.09</td>
<td>4.68</td>
<td>5.09</td>
<td>80.0</td>
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</tbody>
</table>

(continued)
Central granodiorite intrusions. The Dark quartz monzodiorite is the most mafic of the El Abra–Pajonal suite intrusions. Samples from the Amphibole series show an increase in Sr/Y ratios versus decreasing U–Pb age, whereas those from the Plagioclase series show no clear trend (Fig. 8b).

**Cerium ratios**

Zircon $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratios were measured to monitor variations in the relative oxidation state of the melt and the median, upper and lower quartiles of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratios are plotted against the average age for each of the El Abra–Pajonal intrusions used for PGE
analysis in Fig. 8d. There is a general trend in the median ratio values of increasing Ce$^{4+}$/Ce$^{3+}$ with increasing magmatic fractionation for samples from the Amphibole series, which implies that the suite became more oxidized with time. This is important because the oxidation state of the melt has a controlling influence on the solubility of sulfur in the melt as will be discussed further below. Samples from the Plagioclase series show little or no increase in Ce$^{4+}$/Ce$^{3+}$ with time (Fig. 8d).

**DISCUSSION**

**Zircon age correlations**

The majority of the average ages for the intrusive units of the El Abra–Pajonal igneous complex from this study
agree, within analytical error, with those of samples dated by Ambrus (1977), Dilles et al. (1997) and Campbell et al. (2006). The ages of the inherited zircons show that the magmas of the El Abra–Pajonal suite sample known stratigraphic and intrusive units in the area. These inherited populations can be correlated with the Eocene Icanche Formation, which consists of andesitic flows and tuffs (Maksaev, 1990; Maksaev et al., 1994; Tomlinson et al., 1995; Ireland, 2010), and the Permian–Triassic Collahuasi Group, which is predominantly made up of interbedded intermediate–felsic volcanic rocks and sedimentary units of sandstone and limestone (Maksaev, 1990; Munizaga et al., 2008).

Magmatic evolution
Although the intrusions that make up the El Abra–Pajonal suite have many similar geochemical characteristics, it is unclear if they have formed predominantly from a single, deeper parent magma that experienced the injection of a more primitive, wetter melt followed by mixing of these magmas, or from separate parent magmas that followed different fractionation trends. As noted above, two distinct series can be recognized, a Plagioclase- and an Amphibole-dominant series. Both evolved through a combination of fractional crystallization and assimilation. New magma batches, originating from the deeper magma chamber(s), were periodically...
injected into a series of short-lived shallow-crustal magma chambers, from which our samples were collected. Evidence of assimilation, which comes from zircon inheritance and the presence of xenoliths in the intrusions, has been discussed in more detail by Valente (2008).

The older Plagioclase series, which includes the Pajonal quartz monzonite, Equis monzogranite and Antena aplite, shows all the characteristics of plagioclase-dominated fractionation: REE patterns with negative Eu anomalies (i.e. decreasing Eu/Eu*) that correlate with decreasing Sr/Y (Figs 5c and 6b), REE abundances that increase with increasing fractionation, with little change in La/Lu, and Al$_2$O$_3$ contents that decrease with increasing SiO$_2$ (Fig. 4a). Major and trace element modeling by Valente (2008) suggests that pyroxene was the dominant ferromagnesian phase. The Plagioclase series is interpreted to have formed from a relatively dry magma (Annen et al., 2006).

The younger Amphibole series includes the Dark quartz monzodiorite, Central granodiorite, Llareta quartz monzodiorite, Clara granodiorite, El Abra porphyry and Lagarto porphyry. It is characterized by HREE contents that decrease and La/Lu ratios that increase with fractionation, small Eu anomalies that decrease with fractionation (Figs 5c and 6a), and Al$_2$O$_3$ that varies little with increasing SiO$_2$ (Fig. 4a). This type of fractionation is attributed to amphibole-dominated fractionation with little to no plagioclase fractionation from a relatively wet magma (Annen et al., 2006; Richards, 2011a; Chiaradia et al., 2012). The spoon-shaped (concave) HREE patterns displayed by these samples are characteristic of amphibole ± titanite fractionation (Ballard, 2001; Valente, 2008).

The exceptions are the Rojo Grande and the Apolo granites, which are clearly the product of plagioclase fractionation but are distinctly younger than the other members of the Plagioclase series. Furthermore, they have the distinctive spoon-shaped HREE patterns of the Amphibole series and clearly belong to that series. Valente (2008) suggested that the fractionation seen in these samples took place in the upper crustal intrusions from which the samples were collected, to explain the compositional variation of samples from the same intrusion, which is appreciably greater than for other members of that series. A drop in pressure, accompanied by loss of water, may explain why plagioclase replaced amphibole as the dominant crystallizing phase. The Apolo granite samples (Fig. 6c) have lower REE abundances and show a wider range of positive and negative Eu anomalies than all other samples, reflecting a combination of plagioclase fractionation and cumulate processes.

The most primitive magma in the El Abra–Pajonal suite is the Dark quartz monzodiorite, which belongs to the Amphibole series. We attribute the Dark quartz monzodiorite to the entry of a new pulse of magma into the system. It is not clear whether this new pulse entered a deep chamber, which contained magma of the Plagioclase series that had been previously been crystallizing plagioclase, and mixed with that magma to produce a magma with an intermediate Eu anomaly, or

![Fig. 5. Selected whole-rock trace element results for El Abra–Pajonal suite samples. (a, b) Ni and 1000Cu vs MgO; (c) Sr/Y vs Eu/Eu*. Symbols as in Fig. 4.](http://petrology.oxfordjournals.org/)


whether the Amphibole series developed in a deeper chamber that was independent of the first series. The observation that the most primitive magma of the Amphibole series has the strongest Eu anomaly is most simply explained by the former hypothesis. On the other hand, the range of REE concentrations seen in each of the intrusions of the Plagioclase series shows that much of the fractionation occurred within the

![Graph](image)

**Fig. 6.** CI-normalized whole-rock rare earth element patterns for El Abra–Pajonal intrusion samples. (a) El Abra–Pajonal intrusions that are younger than 41 Ma, excluding granites. (b) El Abra–Pajonal intrusions that are older than 41 Ma. (c) Granite intrusions of the El Abra–Pajonal suite that are younger than 41 Ma.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Intrusive unit</th>
<th>MgO (wt %)</th>
<th>Cu (ppm)</th>
<th>Ir (ppt)</th>
<th>Ru (ppt)</th>
<th>Rh (ppt)</th>
<th>Pt (ppt)</th>
<th>Pd (ppt)</th>
<th>Re (ppt)</th>
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<td>52 ± 7.3</td>
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<td>89</td>
<td>&lt;0.5</td>
<td>&lt;1.3</td>
<td>&lt;1.4</td>
<td>46 ± 7.2</td>
<td>151 ± 5.5</td>
<td>20 ± 3.3</td>
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<td>El Abra porphyry</td>
<td>1.5</td>
<td>1688</td>
<td>&lt;0.5</td>
<td>16.62 ± 1.17</td>
<td>&lt;1.4</td>
<td>59 ± 7.2</td>
<td>&lt;9.5</td>
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<td>&lt;0.5</td>
<td>8.86 ± 2.02</td>
<td>&lt;1.4</td>
<td>55 ± 7.1</td>
<td>&lt;9.5</td>
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<tr>
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<td>1.7</td>
<td>13</td>
<td>&lt;0.5</td>
<td>&lt;1.3</td>
<td>&lt;1.4</td>
<td>55 ± 7.2</td>
<td>123 ± 6.0</td>
<td>&lt;9.2</td>
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<td>&lt;0.5</td>
<td>&lt;1.3</td>
<td>&lt;1.4</td>
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<td>144 ± 4.5</td>
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<td>Pajonal quartz monzonite</td>
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<td>43</td>
<td>1.89 ± 0.24</td>
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<td>408 ± 8.0</td>
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<td>&lt;0.5</td>
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<td>58</td>
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<td>353 ± 9.6</td>
<td>183 ± 5.4</td>
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<td>1.88 ± 0.18</td>
<td>&lt;1.3</td>
<td>9.90 ± 1.56</td>
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<td>808 ± 7.9</td>
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<td>1445</td>
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<td>429 ± 9.3</td>
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<td>2.1</td>
<td>&lt;0.5</td>
<td>1.39 ± 0.67</td>
<td>&lt;1.4</td>
<td>984 ± 15.1</td>
<td>400 ± 10.3</td>
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<td>Equis monzodiorite</td>
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<td>5493</td>
<td>1.73 ± 0.18</td>
<td>2.30 ± 0.53</td>
<td>5.90 ± 0.56</td>
<td>776 ± 10.6</td>
<td>212 ± 5.4</td>
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<td>2.1</td>
<td>1.87 ± 0.26</td>
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<td>3.60 ± 0.84</td>
<td>784 ± 9.9</td>
<td>253 ± 6.1</td>
<td>415 ± 11.8</td>
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*Duplicate samples that also incorporated the Te co-precipitation method.

†MgO and Cu data are from Ballard (2001).

Errors are the total combined uncertainties in the data, which primarily result from uncertainty in the blank subtraction and ICP-MS counting statistics.
sampled upper-level intrusions. As with the Rojo Grande and Apolo intrusions, loss of water during decompression may explain why amphibole crystallization is unimportant or absent in the Plagioclase series. In either case the PGE geochemistry of the two series needs to be treated separately.

Amphibole fractionation can be characterized by depletion of elements such as Fe, Mg, Ti, Al, Ca, Ni and Y, along with depletion of the middle REE (MREE; e.g. Dy) (Table 2; Figs 4, 5 and 6a; Supplementary Data Fig. A1; Bottazzi et al., 1999). Rohrlach (2005) proposed that the Sr/Y ratio can be used to measure the relative importance of plagioclase versus amphibole fractionation in evolving magmas and therefore to establish if the magmas are hydrous or anhydrous because Sr is preferentially partitioned into plagioclase, which is favored by dry magmas, and Y into hornblende, which crystallizes from wet magmas. Therefore magmatic systems in which amphibole fractionation dominates over plagioclase will produce melts with successively higher Sr/Y and La/Yb values (Figs 5c and 8b; Rohrlach, 2005; Richards, 2011a). Amphibole-dominant fractionation in the deeper parent magma chamber, which fed the smaller higher-level chambers of the Amphibole series we have sampled, is marked by continuously increasing La/Dy and La/Yb (Fig. 6) and decreasing Dy, Y, Ni, Fe and Mg concentrations. These observations suggest that amphibole fractionation became increasingly important in the magmatic system from 41.7 Ma, peaking with the emplacement of the Clara granodiorite and the
porphyries, which are depleted in MREE to HREE and have very small or no Eu anomalies compared with the older intrusive units of the Amphibole series (Fig. 6a). We attribute the increasing Eu/Eu* to plagioclase accumulation, which also increases Sr/Y, and the bimodal distribution as discriminating between intrusions that accumulated plagioclase phenocrysts, such as the Clara granodiorite, El Abra porphyry and Lagarto porphyry, and those that did not, such as the Dark quartz monzodiorite and Central granodiorite. The obvious inference of the increasing importance of amphibole in the magma system is that the deep parent magma chamber became increasingly hydrous and thus a greater amount of water exsolved in the shallow-level chambers, leading eventually to the formation of the magmatic hydrothermal fluids that produced the El Abra porphyry mineralization. These trends contrast sharply with those seen in the Plagioclase series, which are produced by relatively dry magmas. It should be noted that the higher Sr/Y seen in the Apolo granite samples (which have corresponding Eu/Eu* > 1) relative to the other granites is due to plagioclase accumulation rather than fractional crystallization. Pyroxene, although seen in only trace amounts in the Pajonal quartz monzodiorite, is also a likely cumulate phase in the plagioclase-dominated parent chamber of the intrusions older than 41 Ma.

PGE-alloy and sulfide saturation
Samples with MgO > 2.5 wt % show a steady decrease in Pt abundance with decreasing MgO content, as is typical of a magma that is saturated with a Pt-rich metal alloy, but not with a sulfide melt (Fig. 7d; Park et al., 2013a). However, there is no clear trend in Pd for samples with MgO > 2.5 wt %, which is different from the well-defined trends seen in the Paul Ridge and Niuatahi–Motutahi data (Fig. 7c). This difference is attributed to the Paul Ridge and Niuatahi–Motutahi samples being fine-grained or glassy lavas, representing melts, whereas those from El Abra–Pajonal are phenocryst-bearing porphyritic to phaneritic plutonic rocks collected from shallow-level intrusions. Evidence of fractionation occurring within single intrusions (Figs 4–6) provides clear indication that cumulate processes were operating in the deep magma chamber. Prior to sulfide saturation, Pd behaves as an incompatible element (Park et al., 2013a) and its concentration in cumulate rocks is controlled by a combination of its concentration in the melt and the fraction of trapped liquid in the cumulate rock. We suggest that the absence of a clear trend in the El Abra–Pajonal Pd data, owing to the expected increase in the Pd content of the melt (compare Fig. 7a and c), is obscured by variations in the amount of trapped liquid in the cumulate rocks. Alternatively, lack of a clear trend in the pre-sulfide Pd data could be due to subtle magma mixing that cannot be unambiguously identified in the major or trace element data. Over the same MgO interval Pt follows a well-defined trend because it is precipitating as a cumulus Pt-rich alloy and is less affected by the amount of trapped liquid in the rocks. Its decline in Fig. 7b and d is controlled mainly by the declining solubility of Pt in the cooling melt.

Depletion in Pt, without a corresponding decline in Pd, is attributed to alloy precipitation (Park et al., 2013a, 2015). The fraction required to produce the observed decline in Pt in samples with MgO > 2.5 wt % is very small (Fig. 7b). Because the rate of decline of Pt in the melt is low, the bulk partition coefficient must be only
slightly greater than unity. If we assume that the alloy contains c. 85% Pt, as expected for an alloy precipitating from a felsic melt (Park et al., 2013a), the fraction of alloy needed to produce the observed Pt decline from 700 to 450 ppt (from 4.2 to 2.7 wt % MgO) is c. 8 ppb, assuming that 30% fractionation is required to produce the observed drop in MgO. The scatter in duplicate analyses of samples with MgO contents greater than 2 wt % MgO is greater for Pt than Pd, which is consistent with the existence of a Pt-rich alloy, because the presence of these alloys affects the Pt but not Pd concentrations (see Park et al., 2013a).

Below c. 2.5 wt % MgO the Pt and Pd concentrations in the El Abra samples decrease rapidly, which we attribute to the melts reaching sulfide saturation. This is best seen in the Amphibole series, which gave rise to the ore-associated El Abra porphyry. As noted above, most of the fractional crystallization at El Abra is interpreted to have occurred in a deep parent magma, which underlay the shallow daughter intrusions that were sampled for this study, whereas the ore-forming fluids emanated from one of the shallow daughter intrusions, the El Abra porphyry. As a consequence, the ore-forming fluids did not have access to the cumulate sulfides in the deep parent magma chamber. In this context we note that the cumulus sulfides of the Merensky and Platinoiva Reefs of the Bushveld and Skaergaard intrusions, respectively (Barnes & Campbell, 1988; Keays & Tegner, 2015), and Opirarukaomappu Gabbroic Complex of Japan (Tomkins et al., 2012) preserve their cumulate sulfides at depth with no evidence of having lost either Cu or Au. Furthermore, if magmatic sulfides were contributing to the ore fluid, one might expect a correlation between Cu and Pd. A plot of Cu against Pd for the analyzed El Abra samples (Supplementary Data Fig. A2) shows no such correlation. Plots of Cu (Fig. 5b) and Au (not shown) versus MgO, prior to sulfide saturation (before the appearance of sulfide nuggets), show appreciably more scatter than the PGE plots, which supports the conclusion that Cu and Au are more mobile than the PGE. The decreases in Pt and Pd seen in this series are similar to those seen at Pual Ridge and Niutatai–Motutahi (Fig. 7c and d), which are also attributed to sulfide saturation (Park et al., 2013a, 2015). Once sulfide saturation was reached at 2.5 wt % MgO the Pt concentration of the samples fell below the Pt solubility curve as obtained by projecting the pre-sulfide Pt solubility curve beyond sulfide saturation (Fig. 7b). Prior to sulfide saturation at 2.5 wt % MgO only the Pt data show scatter in the duplicate analyses, whereas for samples with <2.5 wt % MgO both Pt and Pd show scatter. We attribute this difference to the presence of an immiscible sulfide melt, which sequesters both Pt and Pd, replacing the Pt-rich metal alloy as the nugget phase precipitating from the melt.

The presence of nuggets complicates the interpretation of the post-sulfide saturation trend line shown in Fig. 7a and b. This means that the analyzed samples have two components, a solidified melt component and a nugget (or cumulate) component. The post-sulfide saturation melt component is best evaluated by drawing the trend line through the lowest points in Fig. 7a and b to minimize the nugget effect. We have done this, but because there is no certainty that even the low Pt–Pd points contain no nuggets, the trend line may have a slope that is lower than the true liquid fractionation trend.

The disagreement in Pt and Pd values for duplicates from the Plagioclase series samples, which is greater than that seen in the Amphibole series, is attributed to a higher abundance of sulfide nuggets. The absence of clear trends in this series is also attributed to the abundance of nuggets. Although no trends can be recognized, the presence of sulfide nuggets requires all samples from the Plagioclase series intrusions to have crystallized from a sulfide-saturated melt.

Significant and conclusive petrographic evidence of PGE-alloys and sulfide melt in the El Abra–Pajonal suite samples is lacking because the amount of alloy or sulfide required to produce the observed effect is minuscule, which makes them difficult to find by optical microscopy. Furthermore, most of the alloys and sulfide precipitates are postulated to form in an unexposed deeper magma chamber below the sampled shallow intrusions. Sulfide melt blebs associated with sulfide saturation in an evolving magmatic system have been identified in other intrusive suites; for example, the Boggy Plains pluton (Park et al., 2013b). In reflected light, yellow inclusions in phenocrysts of possible primary origin, which are rare and too small to identify with confidence, occur in several of the El Abra–Pajonal suite units (El Abra porphyry, Clara granodiorite, Central granodiorite, Dark quartz monzodiorite, Equis monzogranite). These could be sulfide melt blebs that may have formed in the deeper magma chamber and been incorporated into the sampled high-level intrusions in phenocrysts.

A sample of the El Abra porphyry with 1.1 wt % MgO (Fig. 7b) is anomalous with very high Pt but only slightly elevated Pd, indicating that the anomaly is due to the presence of nuggets of Pt-rich metal alloy and not an immiscible sulfide. This interpretation is consistent with the marked difference in the Pt duplicates. If the anomalous Pt values are due to nuggets they must come from the deep chamber, probably as inclusions in early formed phenocrysts, because the sample that contains them formed well after sulfide saturation. Park et al., (2013a) also noted a correlation between the presence of phenocrysts and metal alloy nuggets at Pual Ridge.

The El Abra porphyry Cu deposit formed towards the end of the magmatic evolution of the intrusive system. Whole-rock MgO values for the El Abra porphyry, which is the unit associated with the mineralizing event, range from 1.05 to 1.54 wt %, which is at least 1.0 wt % MgO less than the MgO content at which sulfide saturation occurred. Despite the occurrence of sulfide saturation prior to ore-fluid saturation, Cu was available to partition into the ore-fluid phase and form the Cu deposit.
This is possible only if the amount of sulfide liquid that formed at sulfide saturation was small. The sulfide melt–silicate melt partition coefficient of Cu ($10^{-2}$–$10^0$) is lower than that of Au ($10^3$–$10^5$) and much lower than that for Pt and Pd (c. $10^8$–$10^{10}$) (Campbell & Barnes, 1984; Ripley et al., 2002; Fonseca et al., 2009; Mungall & Brenan, 2014), allowing the sulfide liquid to strip the magma of Au and PGE but not Cu. Richards (2005) recognized that fractionation of a small amount of sulfide melt would remove Au from the silicate melt but not significantly affect its Cu content; the results of this study are consistent with this hypothesis. Therefore both the timing of sulfide saturation relative to ore-fluid saturation and the amount of sulfide melt are important. Where sulfide saturation preceded ore-fluid saturation it is the amount of sulfide melt that formed that controls the Cu and Au content of the silicate melt and therefore whether the magmatic system has the potential to produce an ore deposit and, if it does, whether the deposit that forms is Cu-only or Cu–Au.

Sulfide saturation in porphyry systems is suggested to have occurred at other deposits; for example, Bajo de la Alumbrera, Argentina, and Bingham Canyon, Utah (Keith et al., 1997; Halter et al., 2002, 2005). These studies, along with review papers, have proposed that the sulfide droplets that form at sulfide saturation subsequently break down and release chalcophile elements into exsolving fluids that form the porphyry deposits (Richards, 2009, 2011b; Audétat & Simon, 2012; Wilkinson, 2013). However, this does not appear to be the case at El Abra, nor for the magma chambers that are interpreted to underlie the Pual Ridge and Niuatahi–Motutahi volcanic areas (Fig. 7c and d), because in all cases the Pt and Pd abundances fall following sulfide saturation in a deeper magma chamber. In addition, there is no correlation between Cu and Pd at El Abra (Supplementary Data Fig. A2), as would be expected if sulfide droplets broke down and released the chalcophile elements into hydrothermal fluids, because the amount of sulfide melt that formed in the deeper chamber was very small, removing PGE and Au from the melt but not significant Cu, allowing the Cu to partition into the hydrothermal fluids that exsolved to form the El Abra porphyry Cu deposit.

Although there are many factors that can influence the nature of porphyry mineralization, our study focuses on the role of sulfide saturation and its impact on porphyry Cu ± Au deposits. The geodynamic setting and the alkalinity of the magmas may also play a role in determining Cu:Au ratios in some porphyry systems and these have been discussed in more detail by Sillitoe (1997) and Richards (2009). Gold-rich porphyries are typically associated with more alkaline magmas, for example the Cu–Au porphyries in New South Wales, Australia (Wilson et al., 2003; Cooke et al., 2007; Lickfold et al., 2007), which form in post-subduction settings. In contrast, Cu-rich porphyries are often related to intrusions of weakly alkaline to subalkaline affinities that are associated with active subduction (Sillitoe, 2010). The El Abra–Pajonal suite intrusions are subalkaline magmas associated with subduction.

**Relative oxidation state of the magmas**

Changes in the Ce$^{4+}$/Ce$^{3+}$ in zircon suggest that the magmas of the Amphibole series became more oxidized as the suite evolved (Fig. 8d); we estimate the $f_{O_{2}}$ of the suite to be near that of the sulfide–sulfate transition. These results are consistent with those of Ballard et al. (2002) for samples from the same suite (shown as small black crosses in Fig. 8d). As noted above, the oxidation state of the melt has an important influence on the solubility of sulfur. The stable species of sulfur in oxidized magmas is sulfate, which dissolves readily in silicate melts, whereas in reduced melts the stable form is the less soluble sulfide. We suggest that late sulfide saturation in the Amphibole series is due to the magma becoming increasingly oxidized with fractionation, and that this partially offsets the effect of declining temperature in the cooling parent magma chamber that is interpreted to underlie the El Abra suite of intrusions. We note too that the El Abra suite follows a monotonic Fe depletion trend so that there is no ‘magnetite crisis’, which leads to a sudden drop in the oxidation state and precipitation of sulfides, as seen at Pual Ridge (Jenner et al., 2010). For these reasons the increase in the oxidation state of the Amphibole-series melts with fractionation increased the likelihood of them forming an economic Cu deposit.

**Sulfide saturation modeling**

The theoretical effects of sulfide saturation have been modeled using the Rayleigh fractionation equation and assuming that the partition coefficients ($D$) for the partitioning of Cu, Au, and Pt–Pd between immiscible sulfide and silicate melts are $1.5 \times 10^3$, $10^6$, and $2 \times 10^5$, respectively (Ripley et al., 2002; Fonseca et al., 2009; Mungall & Brenan, 2014). The models assume that the rate of sulfide precipitation increases gradually over a 10% interval, as observed by Keays & Tegner (2015) for Skaergaard, starting at 70% fractionation, and are shown in Fig. 9. It should be noted that the rate of decline of Cu, Au, and the PGE is in order of their partition coefficients, as expected. Although there is some uncertainty as to the exact $D$ values, these do not affect the conclusions drawn here, provided the relative order of $D_{Cu} < D_{Au} < D_{PGE}$ is correct, because the differences between them are so large (e.g. order of magnitude variations). If the $D$ values are lower than the assumed values, more sulfide precipitation is needed to produce the bulk $D$ values required to explain our data; if they are higher, less sulfide precipitation is required.

At 80% fractionation, if the sulfide melt makes up 1% of the fractionating phases, the Cu, Au and PGE content of the melt will be small to negligible (Fig. 9). A fluid emanating from such a magma would be barren. Alternatively, if the sulfide melt makes up 0.3% of the fractionating phases most of the Au and PGE will be
removed but only c. 50% of the Cu (Fig. 9). If ore-fluid saturation occurred at 80% fractionation, the mineralizing fluid would be Cu-rich and Au-poor, and would produce Cu-only mineralization. If sulfide fractionation is reduced to 0.1%, the Cu content of the melt falls much more gradually following sulfide saturation. However, the Au content continues to fall rapidly, becoming negligible by 80%. A fluid forming at 80% fractionation is expected to form a deposit that is richer in Cu than the previous case, but still Au poor. We suggest that this is the case at El Abra and can explain why El Abra is a Cu-only deposit. A Cu–Au deposit will develop only if the amount of sulfide melt to form is well below 0.03% or if ore-fluid saturation occurs before or very soon after sulfide saturation. The rate of sulfide melt precipitation is probably controlled by a combination of the cooling rate of the magma and the rate at which its oxidation state changes.

**CONCLUSIONS**

Mean U–Pb zircon ages and whole-rock and mineral chemistry data for the El Abra–Pajonal suite intrusions indicate that the El Abra–Pajonal magmas evolved in a long-lived, mid- to lower-crustal magma chamber over a period from 43 to 35 Ma. New magma batches, originating from this mid-crustal chamber, were periodically injected into a series of short-lived upper-crustal chambers with a periodicity of c. 1 Myr. Fractional crystallization and assimilation, along with injection of mafic magma at 41–40 Ma, were the key magmatic processes governing the evolution of the El Abra–Pajonal suite, producing a suite of alkali feldspar granite to quartz monzodiorite intrusions. The intrusions older than 41 Ma formed by plagioclase-dominant fractionation of relatively dry magmas, whereas the younger intrusions of the Amphibole series formed by amphibole-dominant fractionation of wetter magmas. The oxidation state and water content of the Amphibole series increased with fractionation, the former leading to delayed sulfide saturation and the latter promoting early saturation of a hydrothermal fluid. This combination favored the formation of the fertile magmatic–hydrothermal fluid associated with formation of the El Abra porphyry Cu deposit.

Sulfide saturation occurred before ore-fluid saturation during the evolution of the El Abra–Pajonal igneous complex. However, the system still produced a Cu deposit because the amount of immiscible sulfide melt precipitation was very small, enough to strip most of the PGE and Au from the silicate melt but only a fraction of the Cu. As a consequence, the El Abra–Pajonal igneous complex produced a Cu-rich, Au-poor ore body. The timing and extent of sulfide saturation in a porphyry system not only influences whether ore mineralization occurs but may also affect the type of mineralization that forms, whether it is Cu, Cu–Au or PGE-enriched Cu–Au.

![Fig. 9. Concentrations of Cu (blue), incompatible elements (green), Au (orange), and PGE (red) vs per cent fractionation. Sulfide saturation is assumed to occur at 70% fractionation for various percentages of sulfide melt formed. D$_{\text{sulfide melt/silicate melt}}$ values used are $1.5 \times 10^3$ for Cu, $10^4$ for Au, and $2 \times 10^5$ for PGE (see text for details). Shaded grey band indicates 80–90% fractionation; this is used in the text discussion of ore-fluid saturation.](http://petrology.oxfordjournals.org/)

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**Journal of Petrology, 2016, Vol. 56, No. 12**

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ACKNOWLEDGEMENTS

We would like to thank Andres Molina Hidalgo and Jeff Gerwe from El Abra S.C.M., Chile, for sampling and field assistance, and Charlotte Allen for ICP-MS assistance. We thank Andreas Audetat, Steve Barnes and Marjorie Wilson for their comments in reviewing this paper.

SUPPLEMENTARY DATA

Supplementary data for this paper are available at Journal of Petrology online.

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