Porphyry copper enrichment linked to excess aluminium in plagioclase

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Porphyry copper deposits provide around 75%, 50% and 20% of world copper, molybdenum and gold, respectively[1]. The deposits are mainly centred on calc-alkaline porphyry magmatic systems[2,3] in subduction zone settings[1]. Although calc-alkaline magmas are relatively common, large porphyry copper deposits are extremely rare and increasingly difficult to discover. Here, we compile existing geochemical data for magmatic plagioclase, a dominant mineral in calc-alkaline rocks, from fertile and barren magmatic systems worldwide, barren examples having no associated porphyry deposit. We show that plagioclase from fertile systems is distinct in containing 'excess' aluminium. This signature is clearly demonstrated in a case study carried out on plagioclase from the fertile La Paloma and Los Sulfatos copper porphyry systems in Chile. Further, the presence of concentric zones of high 'excess' aluminium in case study plagioclase suggests incorporation as a result of magmatic processes. As 'excess' aluminium has been linked to high melt water contents, the concentric zones may record injections of hydrous fluid or fluid-rich melts into the sub-porphyry magma chamber. We propose that 'excess' aluminium may exclude copper from plagioclase so enriching remaining melts. Furthermore, this chemical signature can be used as an exploration indicator for copper porphyry deposits.

Plagioclase provides a unique window into the genesis of calc-alkaline rocks being little affected by subsolidus re-equilibration[4] and recording subtle changes in magma composition[5]. Here, we compare published major element data for plagioclase, from electron probe micro-analyses (EPMA), from fertile and barren calc-alkaline rocks. We restrict data to I-type, medium- (to low-)K calc-alkaline systems that most commonly host porphyry copper deposits (PCDs)[1]. Plagioclase from fertile and barren systems can be effectively discriminated on a diagram of anorthite An% vs Al/(Ca+Na+K) (calculated on
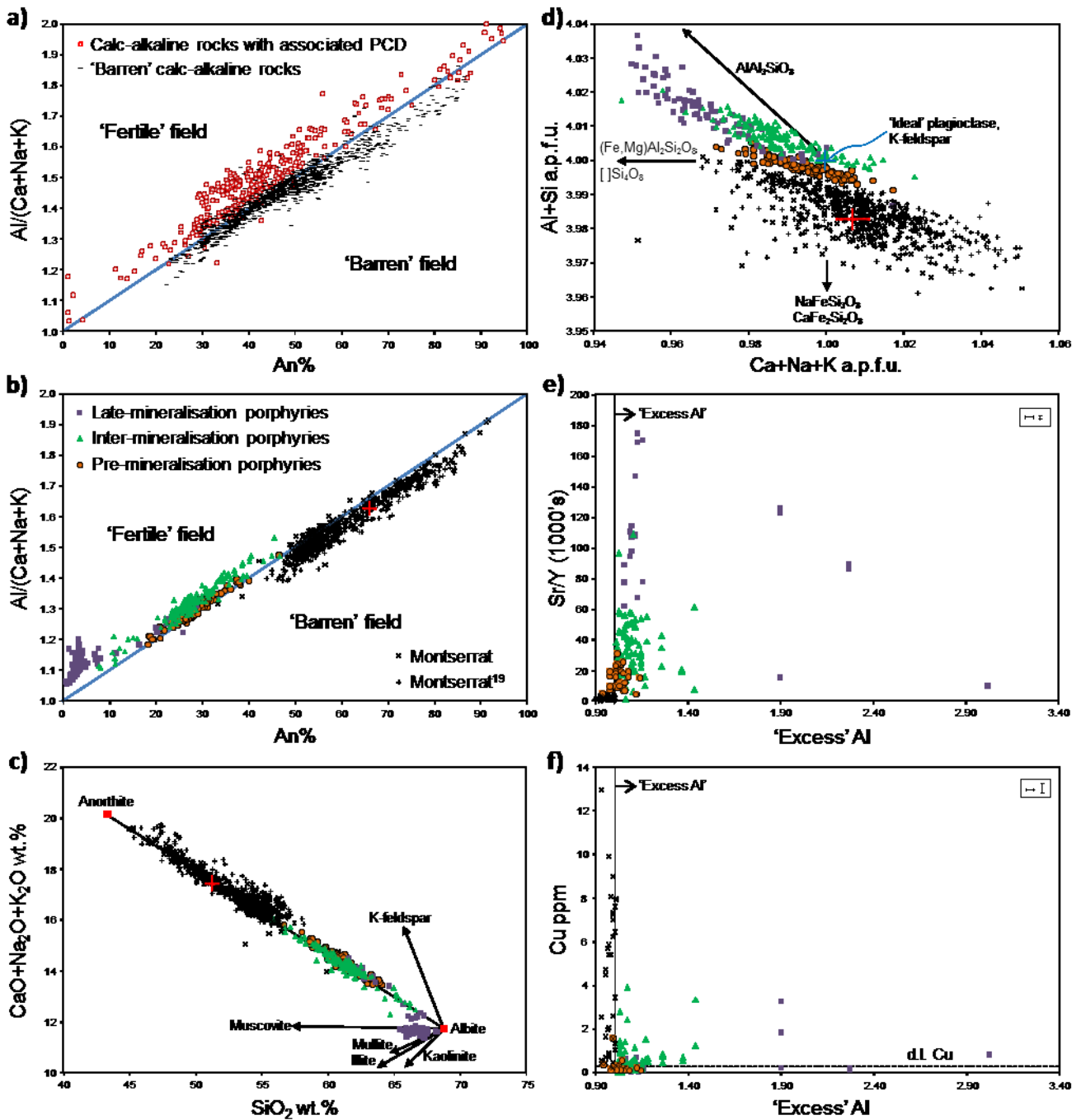
Fig. 1 Geochemical data for plagioclase: a) An% versus Al/(Ca+Na+K) from 11 and 14 published data sets from fertile and barren systems, respectively (Supplementary Table 1). The blue line joins albite and anorthite endmembers; b) Diagram for case study plagioclase and Montserrat plagioclase for comparison; c) SiO$_2$ versus CaO+Na$_2$O+K$_2$O wt% showing trajectories towards common plagioclase alteration phases; d) Ca+Na+K versus Al+Si (a.p.f.u.) showing trajectories towards plagioclase endmembers. Blue cross indicates the ideal plagioclase and K-feldspar. Error bars (red crosses) in b–d are 1 s.d. (n=10); e) Excess Al versus Sr/Y; f) Excess Al versus Cu ppm. Error bars in e,f are 2 s.d. (n=48). Data determined by EPMA, except that for Sr, Y and Cu which were measured by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

the basis of atoms per formula unit (a.p.f.u.; Fig. 1a), where the blue line joins 'pure'

compositions between albite (NaAlSi$_3$O$_8$) and anorthite (CaAl$_2$Si$_2$O$_8$) end-members.

Importantly, the blue line, denoting $Al*=((Al/(Ca+Na+K)-1)/0.01An)=1$, separates analyses from fertile systems, which contain 'excess' Al ($Al*>1$), from those which are barren ($Al*<1$).

To test for potential bias in the published data, we carried out EPMA analyses of plagioclase phenocrysts from inter- to late-mineralisation porphyries at La Paloma and Los Sulfatos, central Chile. Here "inter-" and "late-" refer to porphyry emplacement either during or relatively late in the multiple-intrusion–mineralisation system. The porphyries in the case study form part of the Los Bronces-Río Blanco district, the most richly Cu-endowed PCD 'cluster' in the world[6]. Porphyry melts were emplaced into the pre-mineralisation San Francisco batholith. The magmatic parts of La Paloma and Los Sulfatos porphyries are fairly typical of PCDs, being associated with vein-type and disseminated mineralisation, however, like many of the world's largest deposits (e.g. El Teniente), much of their copper is also contained within genetically-related tourmaline- and biotite-breccias.

The vast majority of magmatic plagioclase from the case study contains 'excess' Al, whereas that from the barren Soufrière Hills volcano, Montserrat, analysed alongside as a comparator, mostly has $Al*<1$ (Fig. 1b). Taken together with the data from Fig. 1a, this strongly suggests that 'excess' Al in plagioclase can be used to discriminate fertile from barren calc-alkaline systems. In practice, surface or sub-surface (drilled) calc-alkaline rocks could be individually assessed for plagioclase 'excess' Al as a low cost exploration tool.

The cause of 'excess' Al provides important constraints on PCD formation. To rule out alteration, we searched for microcrystalline alteration phases within the excitation volume

of EPMA analyses by plotting SiO_2 versus $CaO+Na_2O+K_2O$ wt.% (Fig. 1c). Data from the case study mostly fall along the tie-line between albite and anorthite, with very little shift towards common alteration phases in porphyry systems, except for two groups of data from the late-mineralisation porphyries (with >65 wt.% SiO_2) which appear to show partial alteration to muscovite; these points also show low An values (<10%) probably indicating additional albitization. 'Excess' Al in most data is therefore unlikely to result from alteration. Additional support for this is that plagioclase alteration, in most rock types, is patchy, along cleavages or concentrated in high-An regions. From X-ray maps in Fig. 2, high 'excess' Al occurs within discrete (relatively low An) concentric zones strongly suggesting formation by magmatic processes.

We believe that a more compelling explanation for 'excess' Al is substitution of $AlAl_3SiO_8$, with co-substitution of $[\ ]Si_4O_8$ ($[\ ]$ = defect on M site), as suggested for Rb feldspars[7]. There are three lines of evidence to support this in the case study: 1) compositions mainly lie above the maximum tetrahedral T-site occupancy of 4 a.p.f.u. (Si+Al), implying that Al must also be contained within large cation (M-)sites (Fig. 1d); 2) there is a trend of decreasing Ca+Na+K with increasing Si+Al, suggesting substitution of Al for Ca and Na in M-sites (Fig. 1d); 3) pre- to late-mineralisation porphyries form well-defined trends between $AlAl_3SiO_8$ and $[\ ]Si_4O_8$ (Supplementary Fig. 1a), with an indicated incorporation of up to 2.5 mol.% $AlAl_3SiO_8$ and 3 mol.% $[\ ]Si_4O_8$, similar to levels in anorthite megacrysts from island arc basalts in Japan (≤ 2 mol.% $AlAl_3SiO_8$ and ≤ 1.4 mol.% $[\ ]Si_4O_8$[8]).

Why $AlAl_3SiO_8$ and $[\ ]Si_4O_8$ are incorporated in feldspars is not entirely clear. From the work of Kyono and Kimata[7], large vacancies in $[\ ]Si_4O_8$ are commonly occupied by H_2O, which suggests that high PH_2O (partial pressure of water) is the driver. Evidence to support this is that literature data for hydrothermal plagioclase (i.e. crystallised from H_2O-dominated

fluids) also contain 'excess' Al, e.g. from El Teniente[9,10]. In addition, 'excess' Al increases with Sr/Y in plagioclase from the pre- to late-mineralisation porphyries (Fig. 1e); high melt (whole-rock) Sr/Y (inherited by plagioclase) is thought to result from elevated PH$_2$O which reduces Y via amphibole fractionation (± garnet) and increases Sr due to the initial suppression[2] and then enhanced late stage crystallisation of plagioclase. Collectively, we propose that these lines of evidence indicate that 'excess' Al results from high melt PH$_2$O, and that this is the reason for the discrimination between barren and fertile systems (Fig. 1a,b). It should be noted, however, that the discrimination does not appear to hold for plagioclase containing relatively high Fe (usually >0.02 a.p.f.u. and >An$_{70}$). In such plagioclase crystallised experimentally in H$_2$O-saturated calc-alkaline melts (mostly buffered at NNO)[11], only 2 out of 22 data points contained 'excess' Al. On a diagram of Ca+Na+K versus Al+Si a.p.f.u. (Supplementary Fig. 1b), the data fall to low Al+Si likely indicating incorporation of CaFe$_2$Si$_2$O$_8$ or NaFeSi$_3$O$_8$ end members, rather than AlAl$_3$SiO$_8$. It is also notable that plagioclase from high-K calc-alkaline rocks does not conform to the discrimination, probably because K out-competes Al for incorporation in M-sites.

The results presented here have important implications for determining which calc-alkaline systems host PCDs. Case study plagioclase shows a general increase in AlAl$_3$SiO$_8$ and [ ]Si$_4$O$_8$ (Fig. 1d), and Sr/Y (Fig. 1e), through the sequence from pre- to late-mineralisation porphyries, but no increase in Cu which mostly remains below 1 ppm (Fig. 1f; average of 0.5 ppm), significantly lower than in plagioclase from barren rocks (average 6 ppm[12], and 4.2 ppm for Montserrat). The rare instances of relatively high Cu zones, also showing high An and low Sr/Y and 'excess' Al (white arrows in Fig. 2), likely bear witness to mixing with less evolved melts. Assuming that plagioclase compositions reflect those of surrounding melts, then melt-Cu apparently showed no increase as the system fractionated to higher

Sr/Y. This trend has also been observed in whole-rock data from a large number of calc-alkaline systems[13, 14]; some even show a decline in Cu with fractionation[14].
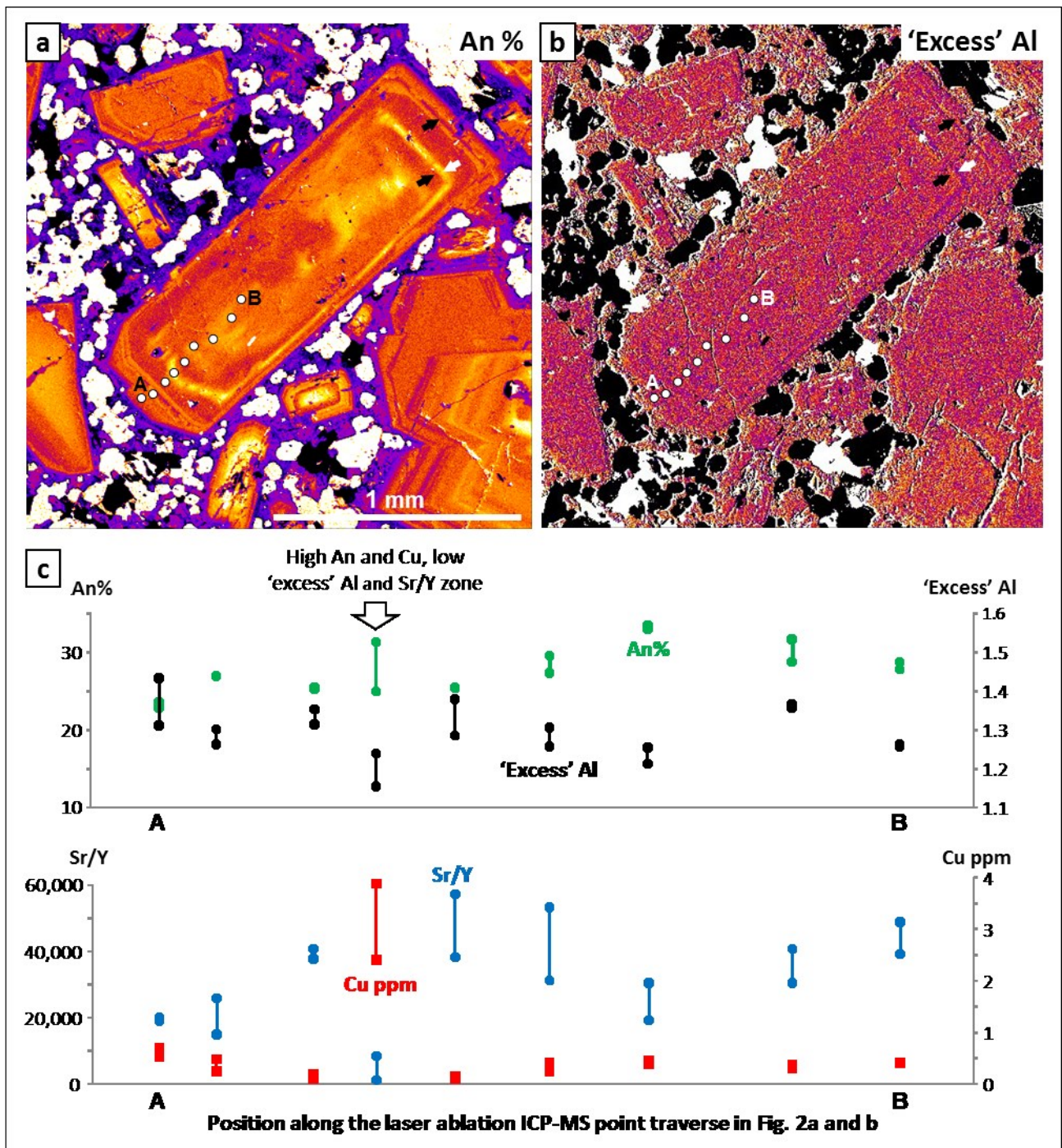

Fig. 2 Quantitative X-ray maps of: a) An% and b) 'excess' Al, for plagioclase phenocrysts from an inter-mineralisation porphyry. Values increase from purple through to orange/yellow. Black and white arrows point to low An-high 'excess' Al, and high An-low 'excess' Al zones, respectively; c) LA-ICP-MS data for points along traverse A-B (data for P6–Circle 2 in Supplementary Table 3). Duplicate analyses are connected by tie-lines.

This is paradoxical since Cu is incompatible in most crystallising phases (mainly plagioclase at high levels) so should increase with fractionation in relatively oxidising porphyry magmatic systems (i.e. with no, or limited sulphide saturation). Dilles[15] explained this by invoking progressive loss of Cu to an exsolving aqueous phase, and Richards[14], additionally, by "minor degrees of sulphide saturation throughout the magmatic cycle". We concur with these explanations but from our data propose an additional mechanism, that the substitution of $AlAl_3SiO_8$, with [ ]Si_4O_8 and H_2O, excludes Cu from plagioclase M-sites. This would enhance Cu incompatibility in plagioclase and so progressively enrich residual melts and exsolving aqueous fluids. Plagioclase is usually the dominant mineral in calc-alkaline rocks (comprising 70% at Los Sulfatos[6]), and therefore low Cu in plagioclase will lead to low Cu in whole-rocks. To demonstrate this further, with an average of 0.5 ppm Cu in plagioclase from the case study, and assuming 50 ppm in porphyry melts, reasonable given that "most arc magmas retain ~50 ppm Cu on average into the andesitic range of compositions"[14], the plagioclase/melt partition coefficient for Cu would be 0.01. This is at the lowest point in the range determined for basaltic andesites (0.07 to 0.38[16]; 0.01 to 0.12[17]). The low value could indicate that the melts contained less than 50 ppm Cu; however this is difficult to envisage given that they went on to form one of the largest porphyry copper districts in the world. Alternatively, we suggest that plagioclase showed enhanced incompatibility for Cu (with lower than published plagioclase/melt partition coefficients) due to the presence of 'excess' Al.

From our data, we can place new constraints on the formation of the La Paloma and Los Sulfatos systems, and other PCDs. Current models for PCD formation generally invoke three regions of magma storage and evolution: a deep/lower crustal chamber, a higher level chamber (4-10 km depth) and porphyry apophyses which rise to 1-4 km from surface[18]; the latter two are depicted for La Paloma - Los Sulfatos in Fig. 3. Due to the

presence of 'excess' Al in plagioclase, Cu was particularly incompatible and therefore highly enriched in late stage melts. In addition, as evident from the presence of low Sr/Y and Al*, and high Cu and An, zones in plagioclase (Fig. 2), the higher chamber was periodically re-fertilised with Cu due to ingress of less evolved melts. Intriguingly, the zones of high An and high Al* are spatially distinct. From this, we propose that the injection of less evolved melts was interspersed with separate intrusions of hydrous fluids, or at least relatively H_2O-rich melts (Fig. 3). Melt-H_2O contents progressively rose, with periods of fluid exsolution to produce conventional porphyry mineralisation, until major decompression events occurred which led to porphyry groundmass crystallisation and breccia formation.

The results contained herein not only provide a new exploration tool for PCDs but have implications for models of the evolution of calc-alkaline systems from which they form. Specifically, our study provides a means for determining whether high-level magma chambers have undergone addition of hydrous fluids, or at least H_2O-rich melts, producing the high PH_2O necessary for PCD formation[2].
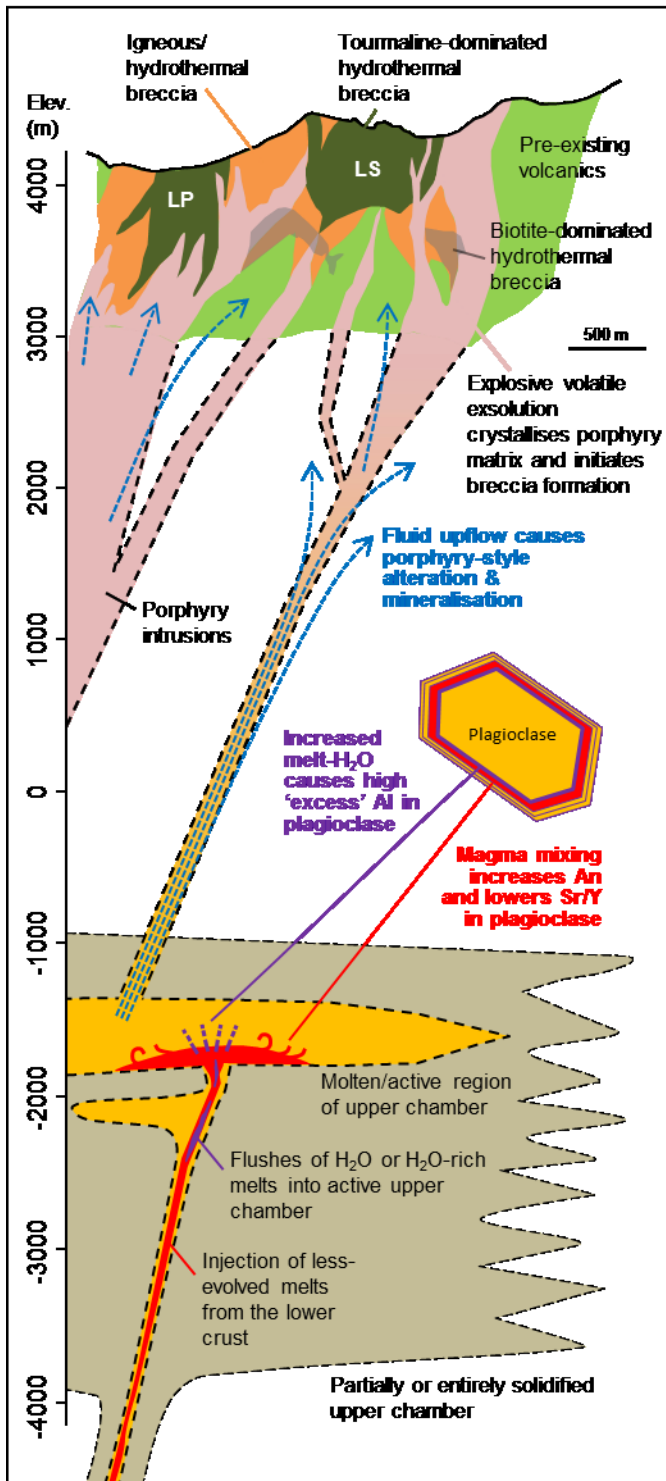
Fig. 3 Section through La Paloma (LP) and Los Sulfatos (LS) breccia-dominated porphyry systems. Section from +3000 to >+4000 m elevation (a.s.l.) is after ref: 6, determined using drill core. Below +3000 m, diagram is largely schematic (based on ref: 20, Fig. 7) showing fluids emanating from a mid-crustal (~5 km depth) magma chamber to form a higher level porphyry-type system. Depth of magma chamber below Los Bronces-Río Blanco district from ref: 21.

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Author Contributions

B.J.W. and R.J.H. wrote the manuscript. A.M. carried out the LA-ICP-MS analyses of the plagioclase at the LODE Facility, Natural History Museum (NHM), London.

Competing financial interests The authors declare no competing financial interests.

Methods

Plagioclase compositional data was collated from available literature sources for magmatic rocks from fertile and barren systems. The number of published datasets was found to be quite low, mainly because authors often give An% for plagioclase rather than full compositional datasets. Where possible, the quality of the data from each publication was checked by assessing the analytical conditions used. Data was only included which had been obtained using EPMA systems with wavelength dispersive detectors; and where the totals for oxides (SiO_2, Al_2O_3, CaO, Na_2O, K_2O and FeO) were between 98.5 and 101.5 wt.%, and K_2O and FeO were <1.2 wt.%. Oxide wt.% were converted to atoms per formula unit (a.p.f.u.), based on 8 oxygen atoms, to facilitate the interpretation of elemental and molecular substitutions. An% values were calculated from the a.p.f.u. data as (Ca/(Na+Ca+K))x100.

Electron probe microanalysis - Selected samples from La Paloma and Los Sulfatos were prepared as polished sections (150 μm thickness suitable for LA-ICP-MS). These sections were carbon coated (~10 nm thickness) and then analysed in a Cameca SX100 wavelength dispersive EPMA system at the Natural History Museum, London. Analyses were carried out at an accelerating voltage of 15 kV and a beam current of 20 nA, with a 10 μm spot size to minimise Na migration. Calibration standards were albite for Si, Al and Na, wollastonite for Ca, synthetic KBr for K, and fayalite for Fe. A ZAF matrix correction routine was automatically applied to the raw data. Smithsonian reference sample Labradorite NMNH115900 was used as a secondary standard. Major element oxides (>3 wt.%) were accurate to within 4.5% (n=10) of the published values[22], except for Na_2O which varied up to 13.5%; values (particularly for Na_2O, <12%) were closer to those published by Straub[23]. Precision, expressed as % relative standard deviation (s.d./average*100) for 10 analyses of NMNH115900 (over 2 analytical runs) was better than 3.6% for major element oxides (>3 wt.%). Data used in this study was restricted to that where oxide totals (SiO_2, Al_2O_3, CaO, Na_2O, K_2O and FeO) were between 98.5 and 101.5 wt.%, and K_2O and FeO were both <1.2 wt.%. Quantitative X-ray element maps were obtained at an accelerating voltage of 15 kV, a beam current of 40 nA, a spot size of 1 μm and a spot interval of 5 μm, giving 512x512 pixel maps for an area of 2 x 2 mm. Peak counts for each point of analysis within the maps were background subtracted, calibrated as for the point analyses and a ZAF matrix correction applied.

Laser ablation inductively coupled plasma mass spectrometry – Analyses were carried out in the LODE facility at the Natural History Museum, London using a New Wave Research (ESI) NWR 193 excimer laser coupled to an Agilent 7700 ICP-MS. The samples were pre-ablated in order to remove any surface contamination before 30 s of background was collected. The samples were then analysed for 60 s using a spot size (diameter) of

between 35 and 50 μm at 10 Hz frequency and with a fluence of between 3.5 and 4.0 Jcm^{-2}. The plasma was operated at 1500 W and the Ar carrier gas flow was 1.1 L min^{-1}. The certified reference glass NIST 612 was used to tune the instrument, to monitor drift and as the primary standard for calibration. Precision and accuracy were determined by analysing a secondary standard (GSD-1g) at the start and end of each run. Accuracy for trace elements given here was better than 10% from the published values, except for Y (11%). Precision for the trace elements shown, expressed as % relative standard deviation, was better than 5%. ^{29}Si was used as the internal standard, Si concentrations having been previously determined by EMPA. Where possible between 2-3 spots were analysed for each zone of each plagioclase, so that the homogeneity of the zone could be investigated. Detection limits for Cu were always better than 0.3 ppm.

References in Methods section

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