Triggers for the formation of porphyry ore deposits in magmatic arcs: predisposition or perfect storm?

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Porphyry ore deposits source much of the copper, molybdenum, gold and silver utilized by humankind. They typically form in magmatic arcs above subduction zones via a series of linked processes, beginning with magma generation in the mantle and ending with the precipitation of metals from hydrous fluids in the shallow crust. A hierarchy of four key "triggers" involved in the formation of porphyry deposits is outlined. Trigger 1 (10^2-10^3 km scale) is a process of cyclic refertilization of magmas in the deep crust. Trigger 2 (10^1-10^2 km scale) is the process of sulfide saturation in magmas that can both enhance and destroy ore-forming potential. Trigger 3 (10^0-10^1 km scale) relates to the efficient transfer of metals into hydrothermal fluids exsolving from porphyry magmas. Trigger 4 (~10^0 km scale) identifies processes that lead to the final precipitation of ore minerals. Although all processes are required to a greater or lesser degree, it is argued that trigger 3, as an over-riding mechanism, can best explain the restriction of large deposits to specific arc segments and time periods. Consequently, recognition of the fingerprint of sulfide saturation in igneous rocks may help mineral exploration companies to identify parts of magmatic arcs particularly predisposed to ore formation.

Ore deposits are scarce. Their discovery consumes considerable time and resources and only about one in every one thousand prospects explored by companies is eventually developed into a mine. Deposits often occur in clusters and formed within specific time intervals. This non-uniform pattern provides keys to understanding how and why metals accumulate in some places and not in others and its explanation is fundamental for mineral exploration.

The most important metalliferous ore deposits are hydrothermal deposits, formed from hot waters circulating in Earth's crust. Such deposits represent a highly efficient trap where fluids were focused into a limited volume of rock, became supersaturated and precipitated ore minerals. In theory, this does not require unusual fluid compositions[1,2] as long as fluid focusing, sufficient fluid flux and efficient precipitation conditions can be maintained. Recently, this paradigm has been challenged by the recognition that ore fluids in sediment-hosted[3-5], epithermal[6,7] and porphyry-related[8-10] hydrothermal deposits can carry orders of magnitude more metal than previously considered probable, or measured in modern fluid samples. This suggests that our understanding of metal extraction and transport processes is incomplete.

Here, this theme is explored by consideration of porphyry ore deposits[11-15], remarkable geochemical anomalies that can contain up to 1 Gt of sulphur[16], 200 Mt copper, 2.5 Mt molybdenum and 2600 t gold[17]. The most copper-rich examples include the 4-5 million-year old El Teniente and Rio Blanco-Los Bronces deposits in Central Chile, and the most gold-rich is the 3 million-year old Grasberg deposit in Irian Jaya, Papua New Guinea[17].

Porphyry deposits typically form in oceanic or continental arcs above subduction zones (Fig. 1). As the oceanic plate and overlying sediment subduct, increasing pressures expel water from the sediment, and hydrous minerals in the oceanic plate start to break down. Fluids are released into the overlying mantle wedge causing it to melt (Fig. 1). The magmas produced migrate up into the continental crust and crystallize to form plutons or erupt at the surface to form volcanic rocks[18]. Somewhere along the way, some of these magmas are transformed, and become capable of generating porphyry ore deposits.

Porphyry deposits form at several kilometres depth in the crust, associated with pipe- or dyke-like porphyritic intrusions[11-15,19-22] (See Supplementary Information). Ore-forming fluids are thought

to be released from an underlying magma chamber, deriving metals from either the magma itself[19,20,23] or by leaching them from surrounding rocks. Fractures above the intrusion allow volatiles to separate and escape from the magma[14,19,24] and depressurization causes the fluids to undergo phase separation into coexisting hypersaline brine and vapour. These fluids then migrate upwards and outwards, cooling and possibly mixing with circulating ground waters, resulting in precipitation of metal sulfides.

Although there is a convergence of opinion on ore-forming processes, it is unclear what makes some systems *fertile*, i.e. capable of generating large ore deposits[25,26]. Many systems that appear to have very similar geology to ore deposits produce altered rocks that are only weakly mineralized or barren. Explaining the rarity of large deposits is a challenging scientific problem. The search for such deposits often requires companies to use costly techniques to probe beneath up to a kilometre of barren rock so a clearer understanding of what controls their localization is a pre-requisite for more efficient and environmentally-friendly exploration. This is particularly pertinent given current concerns over mineral-resource supply and the potential conflicts between the need to secure the resources required for socio-economic and clean technology development, and the impacts of resource extraction on the Earth's environment and climate.

Here, four key stages in the formation of porphyry deposits are outlined. It is argued that one of these, sulfide saturation in silicate magmas, leads to a critical pre-enrichment in metals without which large porphyry deposits cannot form, and that this process can account for the heterogeneity in the spatial and temporal distribution of these ores.

Mantle origins of porphyry magmas

The magmas that crystallize to generate porphyry orebodies have their origins in the sub-arc mantle (Fig. 1). Melt generation in this region is linked to dehydration and/or melting of the subducting oceanic crust and its veneer of sediment[27], and melting of the overlying mantle wedge triggered by the infiltration of slab-derived fluids. The nature of these fluids and how they may vary with depth are still a matter of debate[28], but conventionally it is believed that dehydration of the slab is a principal mechanism for transfer of water-soluble components into the wedge in the shallower parts, whereas melting of the slab sediment, and the basaltic crust itself, may be increasingly important behind the volcanic front[29,30]. This picture has been complicated by the recognition from experimental studies that a continuum exists between silicate melts and aqueous liquids under subduction zone conditions[31]. The chemical and physical properties of these hydrosilicate fluids are controlled by the polymerization of solutes into melt-like species and they provide an alternative mechanism for transfer of components from the subducting slab to the mantle[32]. Direct evidence of fluids of this kind in nature is provided by unusual silica- and volatile-rich inclusions in diamond[33] and mantle xenoliths[34,35].

To explain the oxidized nature of arc magmas, transfer from the subducting slab to the mantle of oxidizing components such as H_2O, CO_2 and possibly ferric iron[36] has been proposed. Other mobile species are the large ion lithophile (e.g. Sr, Pb) and high field strength elements (U, Th)[32], and components derived from subducted sediment (B and Be)[29,30], sulfate[37], and possibly chlorine[38]. It is not thought likely that the downgoing slab contributes significant copper or gold[39].

Parental arc magmas are mostly thought to be produced by partial melting of the altered mantle wedge above the subducting plate (Fig. 1). In order to concentrate metals during partial melting they must preferentially partition into this melt. The minerals present in the mantle source comprise silicates (98%), spinel (2%), sulphides (0.07%) and possibly metal alloys (<0.05%)[26] and it is likely that

the behaviour of copper, silver, gold and other chalcophile or siderophile metals will be controlled by sulfides. It has been postulated that around 25% partial melting of "normal" mantle would be required to extract all the sulfides present[40] although less (~6%) melting may be required if the mantle has been oxidized by subduction zone fluids[41]. Melting also occurs at lower temperatures if the mantle has been oxidized and hydrated by volatile species derived from the downgoing slab; this is potentially one of the reasons why subduction-related arc magmatism favours the formation of ore deposits in contrast to other parts of the Earth. However, a recent study has suggested that the source region for typical arc magmas is not unusually oxidized, nor enriched in economic elements of interest like copper[42]. Consequently, there is, as yet, little evidence to suggest that selective metal enrichment to form fertile porphyry magmas occurs in the mantle.

Stewing up magmas in the deep crust

The melts produced in the mantle wedge are high alumina, hydrous basalts. Interaction of these melts with the continental crust produces the more silica-rich, typically andesitic to dacitic, magmas that form porphyry deposits and build arc volcanoes. This interaction is thought to occur primarily in "hot zones" in the lower crust of the over-riding plate (Fig. 1) where underplating and/or intrusion of the basaltic melts takes place. In these zones, melting and assimilation of lower crustal rocks and differentiation of the magmas by fractional crystallization produce more silica-rich compositions[43-45]. Further modifications to magma composition may occur on ascent, but it is thought that the base level geochemical signature is established primarily in this zone[44], and it is possibly here that the fertility of magmas that go on to form porphyry deposits is established (Box 1).

It is generally believed that copper and gold are likely to be derived from the mantle, although an anomalously enriched lower crust due to the presence of pre-existing ore deposits[46] or copper-rich cumulates from an earlier subduction cycle[42] would have a major impact on the fertility of the magmas formed. Although molybdenum is generally considered to have a crustal origin[47], derivation from lithospheric mantle (Fig. 1) with a long history of pre-enrichment has also been proposed[48].

Ascent of magmas and volatile saturation

Ultimately, separation of a magmatic volatile phase (MVP) enriched in H_2O, CO_2, HCl, H_2S, SO_2 and other volatile components is a key step in the transfer of metals from arc magmas into the highly mobile and buoyant hydrothermal fluids from which porphyry and related epithermal orebodies form[19,23]. Significant advances in understanding this complex process have been made in the past two decades via experimental studies, e.g.[49], but the large number of variables involved in natural systems hinders a complete understanding of all the potential interactions.

Saturation of a melt with a volatile phase, normally primarily composed of H_2O, occurs in response to changes in crystallization state, temperature, and most importantly pressure of the magma. These parameters, in buoyant magmas, are controlled largely by ascent through the crust. Assuming an andesitic melt derived from a deep crustal hot zone initially contains ~10 wt% H_2O[45], then it would saturate at about 14 km depth in the crust. At this point, bubbles of aqueous fluid would begin to exsolve and, due to their low density, would start to percolate towards the upper parts of the melt body. Crystallization would begin at around 7-8 km depth by which point the melt would have lost about half of its dissolved water[45]. The likely presence of CO_2 in the melt[50] would increase the depth of the onset of degassing with the earliest fluids released being the most CO_2- and possibly also SO_2-rich, with an evolution toward H_2O-rich compositions on ascent. Other

chemical modifications will be limited because little crystallization will occur and viscosity and density will remain low and approximately constant[45].

The fate and metallogenic significance of volatiles lost at this stage of magma evolution remains a major unknown. Early exsolution of carbonic fluids may have important implications for metal availability in the later stages of porphyry formation. This is because covalently-bonded sulfur complexes of "soft" metals such as copper or gold may be unusually stable in a weakly ionized H_2O-CO_2 solvent[51]. Such fluids could help to defertilize a melt by stripping it of metals. However, if large faults focus the flow of these fluids to shallower crustal levels, they could play a role in the transfer of metals to form pre-ore enrichments in rocks subsequently intruded by porphyry systems, or to form mesothermal or epithermal gold deposits. For example, the degassing of copper-rich fluids from a deep magma chamber (>15 km) was recently suggested based on a study of the Pleistocene Pilavo volcano in Ecuador[52]. In addition, some of the near-surface intense alteration of rocks that occurs when acidic magmatic volatiles dissolve in groundwaters could have formed from fluids released early from rising magmas. These alteration zones are important for exploration because they are typically spatially associated with porphyry systems and may host epithermal ores.

Crustal staging chambers for porphyry magmas

Magmas that source porphyry intrusions are thought to be derived from crustal magma chambers located at 4-10 km depth where, subject primarily to initial water content, andesitic magmas are likely to stall[45]. The lifespan of these chambers, in which magmas fractionate and crystallize to form granitic plutons, is probably from 100,000 to >5 million years based on dating of plutonic phases[53-55] and the age range of associated overlying porphyry and/or volcanic systems[56-58]. This longevity is not possible without thermal rejuvenation, implying that the chambers grow by input of multiple batches of andesitic and/or more mafic magma from the deep crustal melt reservoir[59]. This can lead to complex evolution pathways, reflected in the variety of volcanic rocks observed at surface. It is in this environment that sulfide saturation could occur (Box 2) leading to the production of metal-enriched regions within the chamber that could later be cannibalized by exsolving aqueous fluids.

Episodically, magma can escape from apophyses on the top of the magma chamber to form cylindrical intrusions and dyke swarms that rise to depths of 1-4 km. It is at these depths that porphyry-related mineralization develops (see Supplementary Information). It is possible that these escape events are triggered by hotter mafic intrusions into the chamber, e.g.[60] which could cause volatile saturation in the chamber and the rise of plumes of low-density, bubble-rich magma[61]. If such an event should coincide with a region of prior sulfide saturation, conditions may be optimized for porphyry ore formation.

Volatile exsolution and ore formation

The extraction of metals from the melt into a separating volatile phase is a key stage in the evolution of mineralized porphyry systems[62]. The efficiency of this process could make the difference between systems that generate highly metalliferous ore fluids and ultimately form large ore deposits, and those that just produce weak mineralization (Box 3). Many experimental studies have investigated partitioning behaviour of metals[49] and sulfur[63] between melt and MVP but the number of competing variables makes it difficult to establish the most important factors. Melt reduction is a potentially important trigger process that may significantly enhance transfer of metals into exsolving

aqueous, sulfur-bearing fluids, assuming that the bulk of copper and gold are transported by reduced sulfur species[8,10], rather than halogens[11,62].

The final step in the formation of porphyry ore deposits involves the escape of magmatic-hydrothermal fluids upwards and/or outwards from the lithostatically-pressured magmatic source[24], primarily through fractures, where they undergo cooling, depressurization and react with surrounding wall rocks. The processes involved are complex[64]. Recent models have proposed that cooling and expansion of vapour-like fluids is the primary control of ore deposition[65] as solubility of sulfides is strongly related to temperature and the density of transporting fluids[66,67]. Numerical modeling suggests that the dynamic evolution of permeability in the fracture network that develops above a porphyry intrusion is probably an important control on the localization of the precipitation front[68]. An additional sulfide precipitation mechanism, particularly in the later stages of hydrothermal evolution, is related to the neutralization of acidity in increasingly dissociated, cooling magmatic fluids by reaction with feldspars to form fine-grained white mica, illite and clays[69]. In order to form an economically exploitable porphyry orebody, fluids must be channelled through a relatively small volume of rock and the precipitation of metal sulfides must be very efficient within this volume (Box 4).

Episodicity and rarity of ore formation

The conventional view of the hydrothermal ore deposit as a zone of highly efficient precipitation from unexceptional fluids poses an interesting mass balance conundrum for ore deposit modellers because low metal concentrations require very large fluid fluxes for the formation of giant deposits. This typically requires the existence of stable flow systems over hundreds of thousands to millions of years, for which there is rarely good evidence. In the case of porphyry systems, numerical models and detailed geochronology suggest that an individual hydrothermal system linked to an intrusion is likely to be active for no more than 50-100 ky[58,70]. The recognition that porphyry ore fluids commonly contain up to 1 wt% copper (and possibly several times more than this in some cases), means that the mass of fluid required to form giant deposits is actually rather modest. If the source magma contained around 5 wt% fluid by mass, only ~50 km^3 of magma in the crustal chamber, equivalent to a sphere of radius ~2.3 km, is all that would be needed to provide the requisite metal-rich fluid for a giant (10 million tonnes of Cu metal) orebody.

Here, it is suggested that certain hydrothermal systems have what is referred to as *a predisposition to form ore* – the enrichment of a system in metals at depth that leads to a subsequent evolutionary path towards ore formation, involving a not unusual sequence of crustal processes. This focuses attention on the processes by which metals are enriched in hydrothermal fluids, and, in the case of porphyry systems, in their precursor magmas. In order to understand the rarity of large ore deposits, it is argued that the key step is the process by which the predisposition is developed, in the fluid / metal source region. This could either be by derivation of fluids (or melts) from a pre-enriched source (the source rock paradigm, e.g.[46]); or by unusually efficient extraction from an un-enriched source[4]. The alternative argument, that large deposits are rare because they require the random coincidence of multiple, coincident, not atypical factors[26,71] – the "perfect storm" of ore formation – is hard to disprove, but does not satisfactorily explain the clustering of deposits in certain belts and at certain periods of time. It is clearly necessary for all the ingredients of ore formation to be in place, yet the existence of a dominant, overriding trigger process that switches on or off ore-forming predisposition is a simpler explanation for deposit clustering and is supported by emerging melt and fluid compositional data[10,72,73].

For porphyry deposits, only two of the triggers discussed above can lead to exceptional metal endowment on the scale required to form the major porphyry belts. Trigger 1 (Box 1) can potentially generate fertile melts that then exsolve fertile ore fluids, predisposed to form large and/or high grade ore deposits when they encounter the suitable trap conditions that may be intrinsic to most porphyry systems. However, this mechanism does not easily explain the barren or low grade intrusions that are commonly observed within fertile systems, predicting instead an evolution from lower to higher fertility through time. The lower crustal hot zone as currently envisaged involves chemical variations on quite a broad scale such as are recognized along segments of the Andean arc[44]. Consequently, it is considered more likely that melt fertilization, if it occurs, takes place in the mid- to shallow crustal magma chambers.

Trigger 2 (Box 2) is a highly effective process for scavenging and enriching a system in metals and sulfur at the same time; indeed this process is known to be the fundamental trigger for the formation of magmatic nickel-copper-platinum deposits in mafic igneous rocks. The problem with porphyry systems is that this will result in depletion of the remaining silicate melt, so a later remobilization process is necessary, e.g.[56]. Nonetheless, this process will generate highly enriched – but heterogeneously distributed – sources that could be scavenged later, and on the right scale to account for observed ore deposit distributions. Unlike the mafic magmas hosting nickel-copper-platinum sulfide deposits, the water-rich nature of arc magmas makes this later volatile-driven extraction process potentially viable.

Trigger 3 (Box 3) involves processes operating at scales between that of the crustal staging chamber and the deposit itself. Although unusually efficient extraction of metals into the hydrothermal fluid may play a role in governing ore-forming potential, the requirement of specific geology means that it is unlikely to represent a universal control of fertility. Trigger 4 (Box 4), as argued above, may be innate to intrusion-centred hydrothermal systems and so does not distinguish between fertile and barren systems; it does not matter how efficient precipitation processes are if the fluids involved contain low concentrations of metals and/or sulfur. It should be noted, however, that the roles of fluid flux and focusing as controls of deposit size are relatively poorly constrained.

In conclusion, it is considered likely that sulfide saturation is a key step that heterogenizes melts in the mid- to shallow crust and thereby produces regions on the scale of tens to hundreds of km that are both enriched and depleted in ore metals. Cannibalization of sulfide-rich domains should be traceable using a range of geochemical proxies which would only be observed within systems that are fertile. The process by which cannibalization occurs may be related to injections of more primitive, mafic melts into the crustal chamber; the presence of such magmas has been noted in many porphyry systems but their role in ore formation has remained enigmatic. It is suggested here that such intrusions, and release of their contained volatiles, may trigger sudden, local sulfide undersaturation in the chamber, producing a flush of metalliferous, sulphur-rich volatiles and, at the same time, initiating emplacement of a porphyry intrusion[60,74]. A number of previous workers have proposed that such mafic intrusions could themselves add sulfur and metals during such a process[61,74-79].

Implications for exploration

So where do these ideas take us with regard to our understanding of hydrothermal systems in general and porphyry ore deposits in particular? The proposal for the generation of a predisposition to form ore in crustal magma chambers as an explanation for large porphyry ore deposits remains speculative, although similar conclusions have been drawn for the development of major

hydrothermal gold deposits[80]. It is hoped that the synthesis of research ideas from many authors summarized here provides some pointers to where further work will help us to better understand the heterogeneous distribution of porphyry and their associated epithermal ore deposits in time and space. The potential exists to use this science in a practical way because the identification of a predisposition represents a key step in the evaluation of belts within the Earth that may be more or less fertile for mineralization. In theory, it should be possible to identify geochemical tracers of the process or processes that have enriched a certain arc segment in metals. The perfect storm paradigm implies that large ore deposits are inherently unpredictable and can only be located by exploration that detects the direct effects of the associated hydrothermal system. The development of geochemical or isotopic tools that can identify fertilization signatures would appear to be a key objective that may provide companies with a greater predictive capacity to identify prospective parts of the Earth's crust sooner and therefore at lower economic and environmental cost.

Box 1 | Trigger 1 - Cyclic fractionation in deep crustal magma chambers. One of the distinctive characteristics of magmas that are temporally and spatially associated with large porphyry ore deposits is that they are enriched in a specific suite of elements, in particular displaying an unusually high Sr/Y ratio. This chemistry has several proposed origins, but one model is that it is a fingerprint of the crystallization of hornblende ± garnet from water-rich magmas in the deep or mid-crust[52,81-83]. The link between this process and the propensity of magmas to go on to form ore deposits is uncertain[52], but cyclic replenishment of long-lived, deep crustal chambers by mantle-derived basalts has been suggested as a mechanism for ramping up the content of volatiles and metals during amphibole fractionation[81,82]. This potentially generates fertile magmas that can eventually migrate to shallower crustal levels and generate or deposits. Why are these magmas trapped in the lower crust for extended time periods? One key piece of evidence is the link between times when subduction was slowed by the presence of buoyant, topographic features such as ocean ridges on the downgoing plate and the subsequent formation of large ore deposits[17]. The attempt to subduct such features would temporarily put the arc into compression, closing faults that could provide escape pathways, and thereby trapping magmas for unusually long periods in the deep crust. A change in plate motions could eventually release the compressional forces and allow fertile magmas to rise. This model is elegant but two key problems remain. Many fertile porphyry systems evolved over several million years with the emplacement of barren or weakly mineralized intrusions as well as fertile ones[13]. This timescale is significantly shorter than that which relates to the subduction processes discussed above and no consistent links have been established between changing tectonic stress and the emplacement of barren or mineralized intrusions. Furthermore, the earliest pulses of magma in any one cycle are typically most strongly mineralized[13], contrary to the proposal of the model. This seems to point towards a shallower switch, active on a shorter timescale, that could control porphyry ore formation.

Box 2 | Trigger 2 – Magmatic sulfide saturation. There is an increasing awareness of the potential importance of magmatic sulfur in controlling metal enrichment or depletion in porphyry systems, and consequently on their fertility[84]. However, the relationships between sulfur solubility and metal enrichment processes are complex and poorly understood. High magmatic sulfur solubilities would appear to be a pre-requisite for the formation of giant porphyry and related epithermal deposits because these deposits are, first and foremost, sulfur anomalies. Abundant sulfur is required for the voluminous deposition of the sulfide ore minerals themselves and it can also play a role in complexing with copper and gold to enable hydrothermal transport[51,85]. The problem with high sulfide concentrations in the melt is that this may trigger sulfide saturation, resulting in crystallization of sulfide minerals or, at higher temperatures, production of an immiscible sulfide melt. This is particularly likely if the melt becomes reduced which can occur due to the onset of magnetite crystallization[86]. In either case, the strong affinity for the sulfide phase of siderophile metals such as Fe and Au and, to a lesser extent, Cu, will cause them to be stripped very effectively from the silicate melt,

e.g.[56,72,76,87], as long as sufficient interaction between sulfide and silicate melt (such as by convection) occurs. This process may also be expected to deplete more strongly those metals with a greater affinity for the sulfides (e.g. Au relative to Cu, Ag, Zn and Pb). If this process occurs at depth then magmas ascending to shallower levels may be strongly depleted in ore metals[37] and therefore would be de-fertilized and unlikely to form economic deposits. Although sulfide saturation could be viewed as destroying ore potential, the concentration of ore metals by saturation of a sulfide melt may in fact be a highly effective mechanism for converting a magmatic system with a dispersed, low concentration of metals into one with pockets of highly enriched sulfide melt. As long as the sulfide melt, or its crystallized products, are accessible to – and soluble in – fluids that are subsequently exsolved from the magma[72,76,88], then the potential exists to produce anomalously metal-rich hydrothermal fluids[47]. Evidence for the operation of this process has been described from the active Merapi Volcano in Indonesia where it was inferred that the injection of sulfide-saturated mafic magma into a felsic chamber triggered volatile exsolution, dissolution of sulfide into the volatile phase and caused explosive eruptions[75]. Support for this trigger for giant ore deposit formation comes from the very high metal contents reported in porphyry ore fluids in which gold, copper and iron are unusually enriched[10,73,89-91].

Box 3 | Trigger 3 – Melt reduction and enhanced metal partitioning. From experiments on basaltic melts containing geologically reasonable levels of chlorine and sulfur, it was concluded that there was a clear relationship between gold solubility in the melt and its oxidation state[92]. Thus, in a melt saturated with a volatile phase, reduction in the oxygen activity and the increased formation of reduced sulfur species in the MVP would be likely to result in effective gold and copper extraction. The crystallization of magnetite can reduce magmas by sequestering oxidized iron. This process was invoked to account for abrupt decreases in copper and gold with progressive fractionation in lavas from the Manus Basin, offshore Papua New Guinea[93] although the link between magnetite crystallization and metal depletion could also be due to the triggering of sulfide saturation in the melt[86]. The apparently constant redox state of the Manus Basin magmas, also observed in other volcanic suites[94], can be explained by buffering between the melt and the exsolving fluid, with the escape of reduced volatile species (e.g. HS⁻) countering the effect of Fe^{3+} depletion by magnetite formation. Suffice to say that the effect of volatile exsolution on melt redox state remains a complex and unsolved problem.

   An alternative mechanism for melt reduction is the assimilation of reduced rocks (e.g. organic-rich shales or limestones) by the intruding magma[95]. Osmium isotope data from the Grasberg Cu-Au porphyry were interpreted in terms of sourcing of gold from the black shale country rocks by hydrothermal leaching[96]. However, it is more plausible that assimilation of these rocks both provided gold to the porphyry magma and resulted in melt reduction and enhanced gold partitioning into the MVP. Other gold-enriched porphyry deposits, such as Bingham Canyon in Utah, were also emplaced into relatively reduced sedimentary sequences. Although melt reduction is a viable mechanism for enhancing metal partitioning into hydrothermal fluids, in particular for gold, assimilation and reduction at depth could have the alternative effect of triggering sulfide saturation[87] (Box 2). At present, there appears to be no systematic correlation between more reduced porphyry melts and deposit metal endowment, although an association with gold enrichment does appear to exist for the allied family of reduced, pluton-related gold deposits[80].

Box 4 | Trigger 4 – Efficient precipitation at the deposit trap site. The precipitation trigger is commonly regarded as the key process in the formation of an economic concentration of ore minerals and so much study has been devoted to the investigation of ore deposits with the identification of such a control being a central aim. Host rocks may play a role in enhancing ore grade, with impermeable limestones (e.g. Grasberg) possibly preventing escape of fluids that may result of dispersion of metals in other systems and also providing a host for high grade skarns. Mafic host rocks can also host systems of unusually high hypogene grades (e.g. El Teniente, Resolution)[13,71] possibly due to the abundance of reactive mafic minerals hosting ferrous iron which can act as a reductant. Expansion and cooling of fluids through the steep temperature gradients that will be developed across the top of a porphyry intrusion has been proposed as an effective mechanism for the

deposition of ore minerals in a quasi-static position[65]. Chalcopyrite solubility decreases rapidly from 400-250°C[97], typical of the temperature range expected in this environment. Despite the feasibility of this mechanism, it is important to note that these conditions may be met in any cooling magmatic-hydrothermal system in which sufficient permeability is developed to allow significant fluxing of fluids from the magma into the overlying fractured rock column. The volatile content of the melt and tectonic activity may be important in this respect, as both play a role in driving rock failure. Nonetheless, the ubiquity of the depositional processes would seem to make precipitation efficiency an unlikely key trigger for the formation of rare, large deposits. Another way of considering this is that precipitation efficiency perhaps only varies by 1 order of magnitude in mineralizing hydrothermal systems and, in the few cases where it has been documented, is >85%[98,99]. By contrast, the metal content of fluids can vary by 4-5 orders of magnitude, e.g.[73,89-91]. Although part of this variability may reflect analysis of fluids part way through the precipitation process, data from apparently primary (pre-mineralization) fluids from economic porphyry deposits showed 1-3 orders higher copper concentrations than comparable fluids from barren intrusions[10]. Thus, although a trap mechanism is undoubtedly required, the processes that ultimately control the ore metal budget of fluids exsolving from the melt (Boxes 2 and 3) are arguably more important in governing the total mass of ore metal and the metal tenor of sulphides ultimately precipitated. This is supported by two key observations: (1) measurements of metal contents in fluid inclusions believed to represent the earliest fluids exsolved from a number of mineralized and barren porphyry intrusions show that mineralized intrusions are characterized by more metal-rich fluids[10]; and (2) metal ratios in porphyry orebodies match primary fluid compositions implying quantitative metal precipitation (even if metals are partly separated into different zones), suggesting that the dissolved metal budget directly controls the metal tenor of the sulfide mineralization formed[72,89]. Notwithstanding this argument, the importance of total fluid flux and degree of fluid focusing in the genesis of large porphyry deposits remain relatively poorly constrained.

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Acknowledgements

Additional Information

Figure Legends

Figure 1 | Supra-subduction zone setting for the formation of porphyry ore deposits (modified after Winter[18]). The four environments where key trigger processes operate that may lead to the formation of large porphyry ore deposits are numbered 1-4 (see Boxes 1-4).
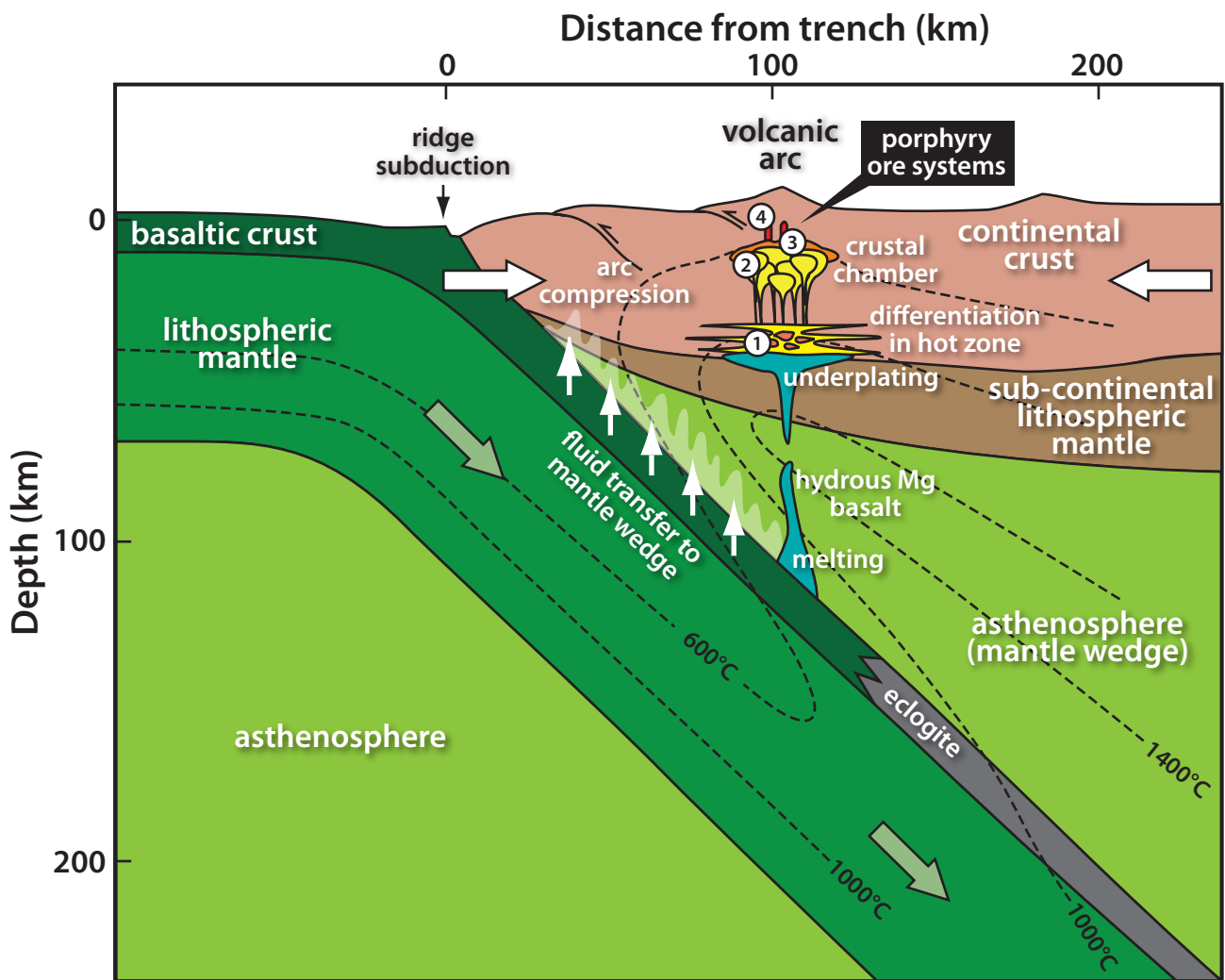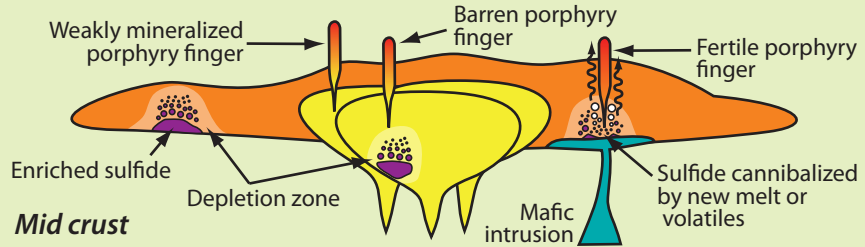
TRIGGER 1: HOT ZONE DIFFERENTIATION

Mafic magma underplates the continental crust, triggering melting and crustal assimilation. Magmas trapped in deep crustal sills in compressional tectonic regime evolve to intermediate-felsic compositions. Cycles of addition of fresh mafic magma and fractionation increase content of volatiles and metals to generate fertile magmas. Amphibole fractionation generates fertile signature of high Sr/Y, Zr/Y.

Deep crust
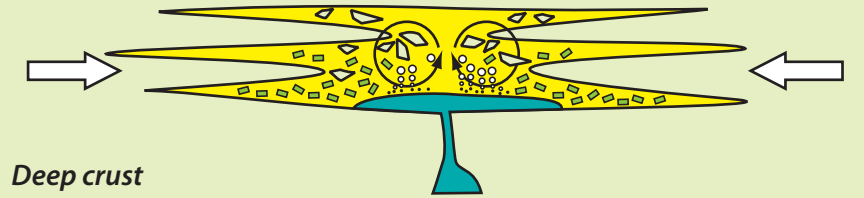
TRIGGER 2: SULFIDE MELT SATURATION

Sulfide saturation of intermediate to felsic magmas leads to stripping of siderophile and chalcophile metals into a sulfide melt phase. This produces a highly enriched anomaly and a depleted silicate melt. If the sulfide is later remelted or dissolved by exsolving volatiles then a highly enriched melt or volatile phase will be generated.

Weakly mineralized porphyry finger

Barren porphyry finger

Fertile porphyry finger

Enriched sulfide

Depletion zone

Sulfide cannibalized by new melt or volatiles

Mafic intrusion

Mid crust

TRIGGER 3: ENHANCED PARTITIONING

Melt reduction could be triggered by magnetite crystallization or assimilation of reducing crustal rocks. This could favor partitioning of reduced sulfur species into volatiles exsolving from the melt, efficiently extracting copper, gold and other sulfur-complexed metals to produce highly enriched ore fluids.
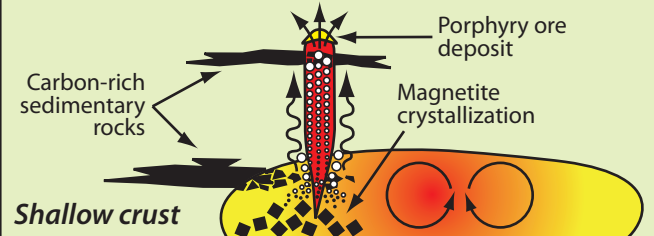
TRIGGER 4: EFFICIENT PRECIPITATION

Efficient focusing of flow through a narrow window and cooling across a steep thermal gradient, combined with expansion of an ascending single phase fluid, could force sulfide mineral precipitation in a limited rock volume, creating rich mineralization.