

The role of magmas in the formation of hydrothermal ore deposits

Jeffrey W. Hedenquist & Jacob B. Lowenstern

Magmatic fluids, both vapour and hypersaline liquid, are a primary source of many components in hydrothermal ore deposits formed in volcanic arcs. These components, including metals and their ligands, become concentrated in magmas in various ways from various sources, including subducted oceanic crust. Leaching of rocks also contributes components to the hydrothermal fluid—a process enhanced where acid magmatic vapours are absorbed by deeply circulating meteoric waters. Advances in understanding the hydrothermal systems that formed these ore deposits have come from the study of their active equivalents, represented at the surface by hot springs and volcanic fumaroles.

WHAT are the sources of metals concentrated in ore deposits? This question was first addressed in the sixteenth century by Agricola, who concluded that heated rainwater leaches metals from rocks and then transports the metals to the sites of ore deposition. A century later, Descartes proposed that vapours released during cooling and crystallization of the Earth's interior are responsible for filling fractures with ore. Thus, the stage was set for controversy between the Neptunists and the Plutonists, a debate that continues today.

Hydrothermal systems powered by magmatic intrusions dominate fluid movement in the upper crust¹, and are responsible for convecting a large proportion of Earth's heat to the surface. At the same time, the fluids transport metals, forming the single most important class of ore deposits, those of the hydrothermal category. For example, large, low-grade deposits of copper (plus molybdenum or gold) within shallow igneous intrusions, known as porphyries, provide more than half of the world supply of copper and molybdenum. Other types of hydrothermal ore deposit (Table 1), some of which form at a greater distance from the magmatic hearth, are also significant repositories of gold, silver, lead, zinc, tin, tungsten and other elements. Non-magmatic hydrothermal systems are also important in metallogenesis, such as the sedimentary-hosted deposits rich in copper, lead and zinc that form by compactive expulsion of fluids from large continental basins, and lode gold deposits associated with metamorphism. Nevertheless, the flux of hydrothermal fluids responsible for these deposits is minor compared to that caused by circulation due to intrusion of magma¹.

There is agreement that many hydrothermal ore systems derive their thermal energy from magmas^{2,3}, with multiple intrusions necessary to maintain activity for hundreds of thousands of years—the life of some hydrothermal systems⁴. But despite the close association of intrusions with many ore deposits, there is still considerable debate about the extent to which these magmas contribute water, metals, ligands (such as sulphur and chloride) and other components to hydrothermal systems. Many early studies of the stable-isotope composition of hydrothermal minerals indicated a dominance of meteoric water in a variety of types of hydrothermal system⁵, leading some workers to assume that the metals were largely scavenged from the rocks through which these fluids moved⁶. More recent studies, coupled with those of active hydrothermal systems, show that magmatic fluids are commonly present, but that their signatures may be masked or erased owing to later overprinting by large volumes of meteoric water, which represents >95% of the water ultimately convected during cooling of an intrusion in the shallow crust³.

For a hydrothermal ore deposit to form, the flow of metal-bearing fluid must be focused and coupled with a precipitation

mechanism operating in a restricted space, details of which may vary from deposit to deposit. Here we take a broader perspective and examine the evidence for the sources of water, metals and other components in magmas, their related hydrothermal systems and the ore deposits that they form. We focus on the magmatic intrusions and associated hydrothermal systems that occur along convergent plate margins, where oceanic crust is subducted under continental lithosphere, leading to the formation of volcanic arcs. This is the tectonic setting where most magma-related hydrothermal ore deposits are concentrated⁷.

We discuss two broad ore types: intrusion-associated porphyry copper deposits, and shallow-formed, epithermal precious and base-metal deposits. We choose these from the range of hydrothermal ore deposit types (Table 1) because they represent the proximal and distal extremes, respectively, relative to magmatic intrusions. Also, some of their active equivalents—such as volcanic systems with high-temperature fumaroles and acidic springs, and geothermal systems with neutral-pH hot springs and geysers—are known, and have thus been studied. This relationship between ore deposits and active hydrothermal systems has long been surmised⁸, though it is barely a decade since there has been general (though still not universal) acceptance that hydrothermal ore deposits form from systems similar to those now active⁹.

Evidence from active hydrothermal systems, coupled with results from a variety of field and experimental studies, clearly indicates that magmas contribute components such as water, metals and ligands to hydrothermal fluids. Not surprisingly, this evidence wanes as the distance from the intrusion increases, meteoric water becomes dominant, and the fluid salinity and acidity decrease. Even in such distal environments, though, there are indications that discrete, episodic addition of magmatic components in the form of high-pressure vapour may be critical to the ore-forming process.

Association between magmas and ore deposits

The genetic association between magmas and hydrothermal ore deposits is well documented in scores of geological studies of mineralization close to magmatic intrusions^{10,11}. Experimental and modelling studies have shown that the metals and ligands in such deposits could have been mobilized entirely from the associated magmas^{12,13}. Furthermore, the flux of metals measured from some erupting volcanoes indicates that, given sufficient time and a concentration mechanism, degassing magmas can exsolve sufficient metals to create an ore deposit (Table 2). For example, White Island, New Zealand (see cover) is an arc-related volcano with an associated hydrothermal system that has been active for at least the past 10,000 yr. The long-term

TABLE 1 Representative hydrothermal ore deposits associated with subduction-related magmatism

| Ore deposit type | Relation to magma | Temperature Depth | Fluid | Associated metals | Example of active analogue |
|--------------------------------|---|--------------------------------------|---|----------------------------------|--|
| Porphyry | Adjacent to or hosted by intrusion | >600 to 300 °C 2–5 km | Hypersaline and immiscible vapour | Cu ± Mo ± Au, Mo, W or Sn | Shallow magma bodies beneath stratovolcano |
| Skarn | Adjacent to intrusion in carbonate rock | 400–600 °C 1–5km | Saline to moderately saline | Fe, Cu, Sn, W, Mo, Au, Ag, Pb–Zn | Shallow magma bodies beneath stratovolcano |
| Pluton-related veins | Fractures in and near intrusion | 300–450 °C Variable | Moderate to low salinity | Sn, W, Mo ± Pb–Zn, Cu, Au | Shallow magma bodies beneath stratovolcano |
| Epithermal (high sulphidation) | Above parent intrusion | <300 °C Near-surface to >1.5 km | Moderate to low salinity, early acidic condensate | Au–Cu Ag–Pb | High-temp. fumaroles and acidic springs near volcanic vent |
| Epithermal (low-sulphidation) | Distant (?) from magmatic heat source | 150–300 °C Near-surface to 1–2 km | Very low salinity, gas-rich, neutral pH | Au(Ag, Pb–Zn) | Geothermal systems with neutral-pH hot springs, mud pools |
| | Distant (?) from magmatic heat source | 150–300 °C Near-surface to 1–2 km | Moderate salinity | Ag–Pb–Zn(Au) | Not observed, transient brine? |
| Massive sulphide | Near extrusive domes | <300 °C on or near sea floor | Near seawater salinity, gas-rich | Zn–Pb–Ag (Cu or Au) | Back-arc seafloor vents, black smokers |

The term 'fluid' is used to refer to non-silicate, aqueous liquid and/or vapour. The salinities (Na, K chloride) of fluids in these environments vary from hypersaline (>50 wt%) to moderate (10–20 wt%), low (<5 wt%) and very low (0.2–0.5 wt%) salinity.

SO₂ flux from White Island volcano, measured by correlation spectrometry, is about 0.13 × 10⁶ tons per year (t yr⁻¹), and is accompanied by 1.9 × 10⁶ t yr⁻¹ H₂O and 0.44 × 10⁶ t yr⁻¹ CO₂. Because the measured Cu/S ratio in the aerosols of the ~900 °C ash-laden plume is ~1.7 × 10⁻³ (ref. 14), the calculated Cu flux is 110 t yr⁻¹ (with >350 kg yr⁻¹ Au). High concentrations of Cu and other metals such as Au are also observed in the aerosols that accompany other erupting volcanoes, such as Augustine in Alaska, Mt Etna in Italy (Table 2) and elsewhere.

Other evidence bearing on the relationship between magmas and ore deposits comes from some correlations between the type of metal deposit and the composition of the associated magma. For example, peralkaline intrusions with high K₂O or Na₂O can host ores of lithophile elements such as Zr, Nb and lanthanides, whereas more aluminous F-rich systems are typically associated

with Sn, Mo and B ore bodies. Tin, and commonly W, tends to be found associated with reduced magmas (as indicated by the absence of magnetite), whereas Cu and Mo ore deposits tend to occur with more oxidized magmas (containing magnetite)^{7,15,16}. Even within volcanic arcs, correlations exist between the tectonic environment and the metallogeny of an ore district¹⁷. If ore formation were controlled solely by circulating meteoric water, these various correlations would be unexpected.

Sources of metals in magmas

Notwithstanding the evidence cited above for an association between magmas and ore deposits, we still want to know where magmas acquire their metals and how these metals are concentrated to form ore. Metals can enter magmas through a variety of pathways, including mantle melting, mass transfer from the subducting slab and melting of the crust. Most of Earth's siderophile (Fe-loving) elements such as Sn, Mo, Au and the Pt-group elements may be locked away in the Fe–Ni core, causing their crustal abundances to be much less than those of the global bulk. Nevertheless, many of these elements are also present in Fe–Ni sulphides in the upper mantle¹⁸. During partial melting of the mantle, these sulphides are partially consumed, and contribute metals to basaltic liquids that then ascend into the crust, both along mid-ocean ridges¹⁹ and at subduction zones (Fig. 1). In the former setting, these erupted basalts are commonly altered, and together with their associated oceanic sediments, are eventually subducted below the continental crust, inducing melting in the mantle wedge beneath the volcanic arc. Many arc magmas show clear evidence for the addition of components such as oxidized sulphur, alkali-group elements, water and Cl from the subducted slab^{20,22}, transferred as a fluid or a silicate melt. The lack of abundant Cl-bearing phases in the mantle, coupled with the high Cl contents of arc magmas (700–2,000 p.p.m.), further supports the idea that Cl is recycled during subduction of seawater-altered oceanic crust^{20,23}. Subduction may also contribute additional metals, such as Cu and Zn, to the resulting arc magmas, derived from hydrothermal mineralization of the subducted sea floor^{20,24,25}.

Ore components may also be acquired during magma transit through the crust. For example, the isotopic signature of porphyry Cu deposits in Arizona is strongly correlated with that

TABLE 2 Magmatic fluids discharged from volcanoes

| | White Island, NZ ¹⁴ | Satsuma Iwojima, Japan ⁶⁸ | Augustine, Alaska ^{69,77} | Mt Etna, Italy ^{78,79} | |
|--|--------------------------------|--------------------------------------|------------------------------------|---------------------------------|------------|
| Year | 1988 | 1990 | 1976 | 1987 | 1975, 1987 |
| Style of discharge | Eruption | Fumarole | Eruption | Fumarole | Eruption |
| Temp. (°C) | >850 | 877 | >900 | 870 | 900 |
| Flux (10 ⁶ t yr ⁻¹) | | | | | |
| H ₂ O | 1.9 | 5.2 | ND | 0.03 | 50 |
| CO ₂ | 0.5 | 0.04 | ND | 0.003 | 13 |
| Cl | 0.04 | 0.06 | >0.6 | 0.005 | 0.1–0.5 |
| S | 0.06 | 0.09 | >0.2 | 0.005 | 0.2–0.75 |
| Cu (t yr ⁻¹) | 110 | 0.16 | >1200 | 0.011 | 480–580 |
| Au (kg yr ⁻¹) | >36 | 0.02 | ND | ND | 80–1,200 |
| Abundance ratios* | | | | | |
| Na/S (×10 ³) | 55 | 0.08 | 50–800 | 0.4 | 40 |
| Cu/S (×10 ⁶) | 2,400 | 1.9 | 2,300–4,700 | 2.3 | 1,000 |

ND, not determined.

* For comparison with the erupted aerosols, the Na/S and Cu/S of fumaroles at White Island are 0.7 × 10⁻³ and 2.8 × 10⁻⁶, respectively.

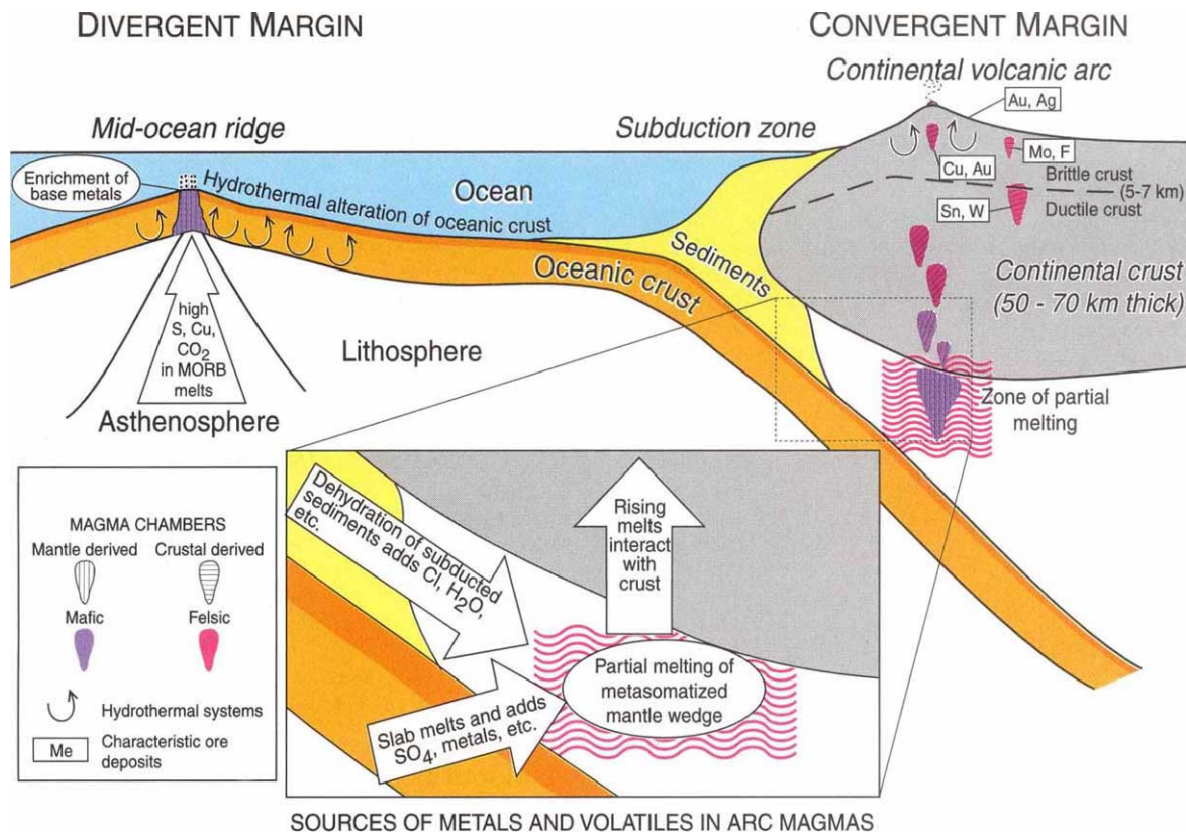


FIG. 1 Schematic section showing the principal components of magma genesis, fluid flow and metallogenesis in divergent- and convergent-margin settings.

of the local basement, implying that the intrusions contain a significant amount of assimilated crust²⁶, whereas in the case of Sn and W deposits such as those of southwest England and southwest Japan, the ore-bearing magmas may be produced entirely by melting of the crust¹⁵. Crustal melts produced in the presence of either elemental C or Fe sulphide may be reduced in nature, and are thus ideal for accumulation of Sn¹⁶. Fusion of previously melted crustal rocks can result in high magmatic concentrations of F, due to the breakdown of refractory, F-rich hydrous silicates. These minerals may also contain significant amounts of Sn and Mo, which are concentrated with F in some ore deposits. But exceptions to these relationships are common, and the source of the metals may be less important, in terms of metal concentration, than the magmatic processes that operate during final ascent and differentiation of the magma.

The effects of crystal fractionation. Crystallization is one of the main controls on the concentration of ore components in magmas. The dominant minerals that crystallize in most igneous systems are silicates and oxides; elements that partition into these minerals can have their concentrations lowered, whereas incompatible elements (those that remain in the melt) may become more concentrated. The degree of compatibility is a function of crystal structure, melt composition, magma oxidation state, and the temperature and pressure of crystallization. For example, Mo and Zn concentrations are commonly high in magmas that contain low abundances of Fe-Ti oxides and titanite, minerals that tend to be rich in these elements²⁷. The enrichment of Sn and W in granites formed from melting of crustal rocks, noted above, may also be due to the composition and low abundance of oxide minerals^{28,29} in these reduced rocks. The lack of Cu mineralization associated with high-silica granites may be attributed to the early crystallization of pyrrhotite (Fe_{1-x}S), which acts as a sink for Cu (and Au?) and lowers its concentration in the melt²⁸. Conversely, because Mo starts at a lower concentration and is more incompatible than Cu, crystal fractionation is necessary to produce the higher Mo/Cu of high-

silica granites²⁸. But even after extensive crystallization, metal concentrations in the magma are still at least two or three orders of magnitude less than grades of economic ore in associated porphyry-style mineralization (Table 3). Other processes are therefore necessary to concentrate metals from the magma into an ore deposit.

Fluids in magma. Given the appropriate fluid composition, most ore metals can be partitioned strongly into a magmatic-hydrothermal fluid as chloride, bisulphide and hydroxyacid complexes³⁰⁻³³ (Table 3). At magmatic temperatures and

TABLE 3 Typical metal concentrations in granites and porphyry ores

| Metal | Average concentration in granite (p.p.m.) ⁸⁰ | Common phenocryst host | Typical concentration (p.p.m.) in porphyry ore ⁸¹ | Likely ligand component in magmatic fluid | Maximum vapour/melt partition coefficient ^{28,31,35} |
|-------|---|------------------------|--|---|---|
| Cu | 12 | po | >5,000 | Cl | 100-200 |
| Pb | 20 | Kf, bi | 40-100+ | Cl | 10-20 |
| Zn | 50 | FeOx and FeMg | 60-100 | Cl | 15-25 |
| Mo | 1.5 | FeOx and FeMg | >1,000* | OH | 2-10 |
| Sn | 3 | FeOx and FeMg | 3,000* | Cl | >1 |
| W | 1.5 | FeOx and FeMg | 5,000* | OH | 4 |
| Ag | 0.04 | ? | 1-3 [†] | Cl? | ? |
| Au | 0.002 | po | <0.1- >0.5 [†] | Cl?(HS) | ? |

Phenocrysts: the common phenocryst host for the metal in crystallizing granitic plutons. Abbreviations: po, pyrrhotite; FeOx, Fe-Ti oxides; FeMg, ferromagnesian minerals such as fayalite, pyroxene, amphibole and biotite; Kf, K-feldspar; bi, biotite. Likely ligand and common phenocryst host are from various sources, though little is known about either; OH refers to hydroxyacid complexes.

*For Mo-, Sn- or W-rich porphyry, not typical of Cu porphyry ore.

[†]Concentrations listed are for disseminations in porphyry systems. In epithermal vein deposits, Au commonly ranges from 3 to 10 p.p.m., and can exceed 100 p.p.m. as an average in a few deposits.

pressures, insufficient data exist to define the ideal conditions for partitioning of any given metal from a magma into an exsolved hydrothermal fluid. Even so, the limited data available indicate that metals such as Cu^{28,34} can be scavenged by exsolving magmatic fluids, especially at low magmatic pressures³⁵, raising the question: when do these fluids separate from magmas and what controls the fluid composition?

Many magmas contain exsolved fluids during their ascent through the middle to upper crust. There is evidence that basalts from a variety of tectonic settings are saturated with a CO₂-rich fluid phase at depths >30 km (refs 36–38). Because of its high solubility in silicate melt, H₂O will represent only a small fraction of this fluid in the deep crust, although H₂O increasingly exsolves at low pressures until it dominates the fluid, as observed in volcanic emanations (Table 2). Unless felsic magmas originate as isolated systems, and receive no input of volatiles from mafic forerunners and subjacent heat sources, they too are likely to be saturated with a fluid phase throughout their history³⁹. The addition of SO₂ and other gases to magmatic systems decreases the solubility of H₂O and CO₂ in the melt by decreasing their activity in the fluid phase(s), resulting in fluid saturation with even lower concentrations of gases dissolved in the melt. Thus, if magmas in the upper crust are normally fluid-saturated, the key questions related to metal transport are not if or when fluid saturation occurs in the associated magma, but what controls fluid composition, which fluids are most likely to scavenge metals

from the silicate melt, and how much fluid can be channelled to a site of metal deposition.

At shallow crustal depths, metal partitioning becomes more complicated because magma may contain more than one non-silicate fluid phase. For example, at 1 kbar and 800 °C, the NaCl–H₂O system will consist of two phases (a low-density vapour and a hypersaline liquid; Fig. 2) if the bulk composition of the fluid(s) exsolved from the melt is between ~2 and ~70 wt% NaCl. Indeed, the Cl contents of many silicic magmas are consistent with the concentrations necessary to result in saturation with both vapour and a hypersaline liquid^{4,40}. Addition of CO₂ (and most probably SO₂) will increase the field of immiscibility so that the two aqueous phases may coexist over a wide range of crustal conditions (up to pressures ≥5 kbar, ref. 41).

The large density contrast between the vapour and hypersaline liquid commonly results in these two phases separating within the magma chamber or its adjacent hydrothermal system^{4,42}. The aqueous vapour contains CO₂, SO₂, H₂S, HCl and so on, and tends to ascend on formation, either discharging to the surface as volcanic fumaroles (Table 2), or becoming absorbed at depth, forming an acidic water that can leach the host rock⁴². The dense hypersaline liquid remaining at depth will be richer in Cu and other chlorophile elements than the low-salinity vapour³³. Evidence for these immiscible fluids is abundant in intrusive rocks and some volcanic products⁴³. However, it is in porphyry ore deposits that the remnants of these fluids, trapped as inclusions in minerals, have been studied most intensively.

Mineralization associated with intrusions

Porphyry Cu mineralization is dominated by magmatic fluid in the early stage, although late meteoric water is not only common but is perhaps critical in enhancing porphyry metal concentrations to ore grade^{10,33}. These deposits typically consist of sulphides that are both disseminated and located in veinlets; these occurrences are found within and adjacent to porphyritic, silicic to intermediate-composition intrusions, and commonly form at depths of 2–5 km under lithostatic pressures. Detailed studies of hydrothermal alteration, mineralization and fluid inclusions, integrated with stable-isotope data, indicate that the hydrothermal systems that form these deposits are initially hot (>500–600 °C) and dominated by a magmatic, hypersaline liquid coexisting with a low-density vapour. Because of the depth and high temperature, active examples have yet to be studied. Zoned alteration assemblages form as the reactive, metal-bearing magmatic fluid moves away from the intrusion, cools and reacts with the country rock^{10,33}. The intrusions themselves are altered, with a central zone of biotite ± K-feldspar (K-silicate zone), that typically gives way outward to an intermediate zone of quartz plus chlorite, commonly overprinted by sericite and pyrite (sericite zone). The wall rocks farther from the intrusion may be altered to epidote, chlorite and albite (propylitic zone). High-temperature Cu-sulphide mineralization, accompanied by magnetite, may be present as a shell at the boundary of the K-silicate and sericite zones. Where preserved, these alteration zones are always capped by rock that has been leached by an acidic water formed by the absorption of magmatic vapour into meteoric water. The resultant advanced argillic alteration usually extends to the palaeosurface¹⁰.

The strong spatial association between plutons and porphyry-related ore deposits emphasizes the genetic role of magmas in the mineralization process. Another line of evidence comes from the fluids trapped as inclusions in minerals⁴; many of these inclusions formed at near-magmatic temperatures of 700–800 °C. At room temperature, the hypersaline fluid inclusions contain a brine, a vapour bubble and daughter crystals of halite, sylvite and minor ore minerals such as chalcocite (Fig. 2a). The hypersaline liquid at its trapping temperature contains 40 to >60 wt% NaCl equivalent (eq.) and 250–5,000 p.p.m. Cu³⁷, the latter based on the amount of Cu-bearing daughter minerals and recently confirmed by direct analysis⁴⁴. Inclusions that trapped

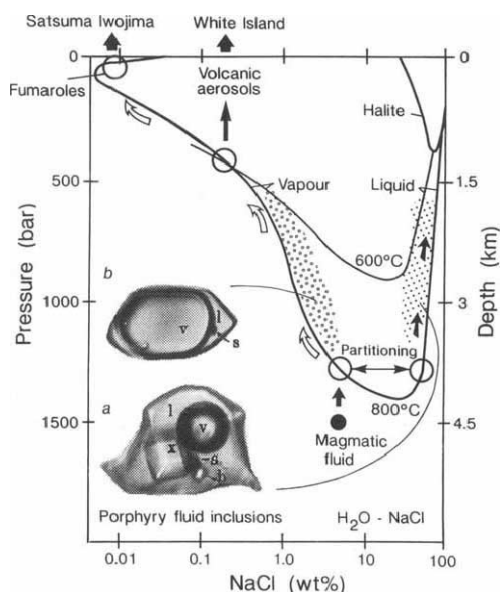


FIG. 2 The composition of immiscible fluids in the system H₂O–NaCl⁸², as a function of pressure at 800 °C (and 600 °C, light line); the approximate depth is for a lithostatic pressure gradient. If a 5 wt% NaCl solution (filled circle) exsolves from a magma at 800 °C and 1,500 bar and then isothermally decompresses, it will unmix to give a low-density vapour and a high-density, hypersaline liquid at ~1,300 bar; chloride-complexed metals will partition to the liquid, whereas gaseous components will be largely contained by the vapour. Upon further isothermal decompression (curved arrows), the liquid and vapour will progressively become more and less saline, respectively, by condensation of NaCl-rich liquid from the vapour. The vapour of high-temperature volcanic fumaroles contains <100 p.p.m. NaCl, and is metal poor, whereas high-pressure vapour accompanying volcanic eruption is relatively NaCl- and metal-rich (for example, White Island⁸³, Table 2). The stippled fields indicate the compositions of fluid inclusions at temperatures and pressures typical of porphyry Cu formation. The photographs show representative quartz-hosted fluid inclusions (at room temperature) from a porphyry Cu deposit (a, hypersaline inclusion containing NaCl-saturated liquid, l; vapour bubble, v; daughter minerals of halite, x; possibly anhydrite, b, and hematite, s; b, vapour-rich inclusion containing low-salinity condensate, l; bubble of compressed gas, v; and small opaque mineral, s). Inclusions are each ~50 µm long.

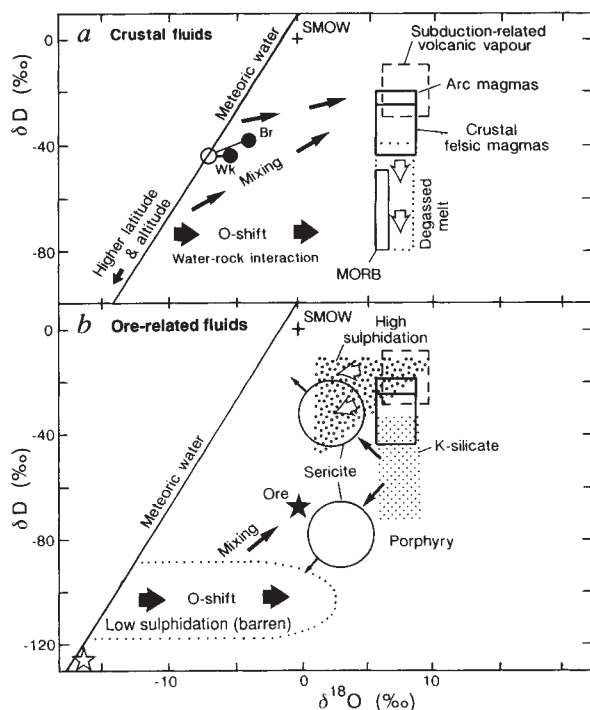


FIG. 3 a, Variation in the O- and H-isotope composition of crustal magmas and waters ($\delta^{18}\text{O}$ and δD , respectively, relative to Standard Mean Ocean Water—SMOW⁵). Felsic magmas underlain by continental crust have slightly heavier H-isotope ratios than island arc magmas, presumably due to incorporation of crustal material⁴⁷. These magmatic waters are both isotopically distinct from that associated with mantle-derived mid-ocean-ridge basalts (MORB)⁴⁶. The isotopic composition of 'subduction-related magmatic vapours' outgassing from arc volcanoes has a narrow range²¹, enriched from their parent arc magmas due to fractionation during degassing⁴⁶, with the degassed melt (open arrows pointing down) becoming lighter in H-isotope composition. There are two trends for neutral-pH geothermal waters, one caused by meteoric water-rock interaction ('O-shift' from the meteoric water line⁸⁴; for example, that of Wairakei, Wk), and the other from mixing between meteoric water of variable (local) isotopic composition and low-salinity magmatic vapour²¹ (small solid arrows with trends pointing towards volcanic vapour; for example, that of Broadlands, Br). Connate waters trapped in sediments and waters related to metamorphism have wide ranges of isotopic composition⁸⁵ (not shown here). b, The isotopic composition of hydrothermal fluids associated with porphyry ore deposits is deduced from the composition of high-temperature K-silicate alteration minerals (stippled field)^{5,45}. Lower-temperature sericitic alteration indicates various mixtures (typically plotting in the two large circles) between late-stage magmatic water (derived from a degassed melt⁴⁸) and meteoric water with a range of isotopic composition depending on the palaeolatitude and altitude; this meteoric water is sometimes O-shifted⁴⁹. 'High-sulphidation' waters⁵⁴ (see text) are similar in isotopic composition to volcanic vapour, with trends projecting towards meteoric water of variable isotopic composition (open arrows) depending on location of the deposit. The waters that precipitate barren quartz in 'low-sulphidation' deposits commonly show an O-shift from local meteoric water values^{5,61}, whereas high-grade ore samples (Comstock lode; solid star) have both an O- and H-isotopic shift from local meteoric water (open star) caused by a component of magmatic water⁶¹; such a huge shift cannot be caused by boiling of meteoric water²¹.

the immiscible vapour (Fig. 2b) are low in salinity (<1–2 wt% NaCl eq.) and relatively high in CO_2 (≤ 10 wt%; ref. 37).

Constraints from O and H isotopes. The isotopic composition of water in a magma was initially approximated by analysing minerals in eroded intrusions and then using mineral-water fractionation factors³ to calculate the values of the coexisting water. These data were used to define the isotopic composition of "primary magmatic water"⁴⁵ (Fig. 3a; dotted-line box). But because there is a strong fractionation of H isotopes during early

degassing⁴⁶, the late-formed hydroxyl-bearing igneous minerals represent the isotopic composition of a degassed melt rather than that of the initial magmatic water (Fig. 3a; open arrows). The best current estimate of the initial isotopic composition of H_2O in arc and crustal felsic magmas⁴⁷ (Fig. 3a; solid-line boxes) is intermediate between that of the degassed magma (dotted-line box) and the isotopically heavy outgassed H_2O , the latter sampled as volcanic vapour²¹ (dashed-line box).

The O- and H-isotope compositions of hydrothermal minerals in ore deposits also help to trace the origin(s) of the hydrothermal water. In porphyry deposits, hydroxyl-bearing minerals include biotite, which forms close to the intrusion at near-magmatic temperatures (>500–600 °C), chlorite and sericite (which form at ~300 °C) and kaolinite (~200 °C). Early-formed, high-temperature biotite and K-feldspar^{5,45} provide evidence that the $\delta^{18}\text{O}$ of the fluids altering the intrusions have a narrow range of +6 to +9‰ (Fig. 3b; stippled box), consistent with the water being in equilibrium with the large O reservoir in the associated magmas. But the δD value of this early magmatic fluid (based on biotite compositions) has a wide range, from –35 to –75‰ (Fig. 3b), and is shifted to lower values than the primary water of most felsic and arc magmas (–20 to –45‰). This may be explained by open-system degassing of the magma⁴⁶, as noted above, which can thus account for the large δD variations (>40‰) at constant O-isotope composition observed for biotite from a single deposit⁴⁸.

Lower-temperature alteration commonly has an isotopic signature indicating a large component of meteoric water^{45,49}, although in some deposits there is also evidence that sea water or an evolved formation water was present, and this saline liquid may have had a role in mineralization⁴⁸. The isotopic variations of lower-temperature, sericitic alteration among several North American deposits are systematic with latitude and hence palaeo-meteoric water composition⁴⁵ (Fig. 3b; hydrothermal waters typically plotting in the circled areas). This meteoric water has commonly been shifted in O-isotope composition through water-rock interaction before its flow past the intrusion⁴⁹ (for example, lower circled area). But in some South American deposits⁵⁰, there is clear evidence that the fluid related to late-stage sericite samples had a magmatic vapour component, as their compositions indicate a fluid with +5 to +8‰ $\delta^{18}\text{O}$ and –20 to –40‰ δD (Fig. 3b; dashed-line box).

Other isotopes. The Pb- and S-isotope compositions of porphyry Cu ores from South and North American porphyry deposits^{51,52} are equivocal regarding their origin. In some cases there are Pb-isotope trends consistent with subducted pelagic sediments as the major source of Pb, indicating that Pb was recycled during subduction and then contributed to the porphyry hydrothermal system. Crustal sources appear only locally important to the Pb budget of most of these systems; in contrast, Sr sometimes shows high isotopic ratios, consistent with a large crustal component⁵¹. In Arizona, however, there is a strong correlation between mineralizing intrusions and the Pb-isotope composition of the lower-crustal basement²⁶. The range of $\delta^{34}\text{S}$ of most porphyry Cu deposits lies between –3 and +9‰, (ref. 53), suggesting the bulk of the S was derived from local intrusions, though the wide range of S-isotope composition in some cases may be caused by contribution from the wall rock^{50,53}. The fresh-rock $\delta^{34}\text{S}$ value has a geographical variation, which in island arcs probably reflects a contribution from subducted marine sediments⁵³. Thus isotopic evidence from porphyry deposits indicates a variety of sources for components such as H_2O , Pb and S, although it seems that a magmatic source dominates the early history of the systems. As the distance from the magma to ore increases, such evidence weakens.

Mineralization distant from magmatic intrusions

The term 'epithermal' refers to a class of hydrothermal ore deposits formed at relatively low temperatures (<300 °C) and shallow depths (surface to 1–2 km; Table 1). Despite the shallow

depth, there is still evidence for a magmatic component to the fluids.

Epithermal ore deposits can be divided into two main types (Table 1), according to their alteration mineralogy. One type is formed by acidic and oxidized fluid (high sulphidation), typical of acidic springs near volcanoes; the other type is formed by a near-neutral pH, reduced fluid (low sulphidation), as found in geothermal systems⁹.

High-sulphidation epithermal ore deposits. Although formed at shallow depths, high-sulphidation ore deposits have characteristics that indicate involvement of magmatic components in their formation⁵⁴. The early stage of these deposits is characterized by extensive leaching of the host rocks by fluids with a pH <2 (ref. 55) and an O- and H-isotope composition (Fig. 3b; triangular area)⁵⁴ similar to that of magmatic vapour²¹ mixed with meteoric water (Fig. 3b; open arrows). The leaching creates a porous silica residue (>95 wt% SiO₂) that may subsequently host ore minerals such as Au-bearing Cu- and Fe-sulphides. The high-sulphidation style of mineralization shares many mineralogical and stable-isotope characteristics with the advanced argillic zone of alteration that caps porphyry Cu deposits^{33,54}, and indeed there is commonly a close spatial relationship between these deposits¹¹. The hydrothermal fluid is oxidized, based on S-isotope compositions of the sulphide and sulphate minerals⁵⁴; a majority of the sulphur species originate from the disproportionation of magmatic SO₂ to form H₂SO₄.

Fluid inclusions in ore-related minerals, including Cu-sulphosalts (transparent only to infrared wavelengths) and quartz, indicate that the mineralizing fluid may have a salinity of 2–5 wt% NaCl eq., though there can be a marked increase in salinity with depth, to 20–30 wt% NaCl eq. below the ore zone⁵⁶. This spatial separation of low-salinity liquid associated with high-sulphidation ore above higher-salinity liquid at depth is distinct from that noted for deeper porphyry Cu deposits, where hypersaline brine coexists with low-salinity vapour; this separation may be caused by the high density of the brine, which cannot ascend easily to shallow depths. The close association of Cu and Au in the relatively oxidized high-sulphidation and porphyry environments suggests that both metals may be transported under similar conditions, though in the high-sulphidation epithermal environment mineralization is related to a lower temperature and less saline liquid.

Low-sulphidation epithermal ore deposits. In contrast to porphyry and high-sulphidation deposits, magmatic signatures in low-sulphidation epithermal Au deposits are more elusive. Ore concentrations of Cu do not occur, presumably because the low-salinity, near-neutral pH and reducing (sulphide-dominant) fluids preclude efficient transport of Cu. In general, low-sulphidation deposits form distant from the inferred magmatic heat source¹¹ at temperatures of 200–300 °C (ref. 57). Pressures are controlled by hydrostatic conditions, meaning that the maximum temperature at a given depth is constrained by boiling, a common process in these systems⁵⁸. Although a variety of classifications of this deposit type exist⁵⁹, a division based on metal assemblage appears to reflect intrinsic geochemical differences. One style is Au-rich (with Ag/Au of 1/10 to 10/1 and only trace base metals), whereas the other is Ag-rich (with Ag/Au of >100/1) with economic quantities of Zn and Pb present. The Au-rich deposits are associated with low-salinity but gas-rich fluids (<1–2 wt% NaCl but up to 4 wt% gases, mainly CO₂ with H₂S)⁵⁸. By contrast, deposits rich in Ag and base metals are associated with more saline fluids (10–15 wt% NaCl)⁶⁰. This difference in salinity is important for the metal-transporting capacity of the fluids, as Au is transported as a bisulphide complex whereas Ag, Zn and perhaps Pb are dependent on transport by Cl complexes in this reduced environment³². The low-salinity fluids of Au-rich epithermal deposits are largely similar to the fluids of most active geothermal systems^{9,58}, whereas there are no saline geothermal systems in a tectonic environment similar to that hosting Ag- and base metal-rich epithermal deposits.

This lack may be due to transient, tectonically-induced pulses of saline, mineralizing fluid into an otherwise low-salinity, metal-barren hydrothermal system⁶⁰, a process we have not yet seen.

Stable-isotope studies of low-sulphidation deposits commonly demonstrate the predominance of meteoric water⁶¹, with O-isotope compositions of both water (Fig. 3b; 'O-shift') and rock modified to varied degrees by their mutual interaction⁵. However, most samples studied to date have been late-stage, barren quartz veins, formed after the period of ore deposition⁶¹. Where samples are associated directly with bonanza (high-grade) ore, such as from the famous Comstock lode, Nevada (Fig. 3b; solid star), a large shift in both $\delta^{18}\text{O}$ and δD values from the composition of local meteoric water (open star) is taken as evidence for a significant magmatic-water component⁶¹. Paradoxically, the evidence for meteoric-water dominance in epithermal systems is most obvious where magmatism was most voluminous, because the large magmatic heat source creates large and long-lived cells of convecting meteoric water, convection that will erase most of the evidence for any early component of magmatic water. For example, in the Pacific Northwest of North America, a region of many eroded plutons, the rocks exposed over >5% of the region bear an O-isotope signature indicating alteration by meteoric water⁶². Furthermore, the S- and C-isotope evidence indicates that many epithermal deposits can have a magmatic source for both elements⁵³, although there is commonly also a sedimentary component to the S, as well as occasionally an influx of organic C. The results of Pb-isotope studies on a variety of epithermal deposits indicate several sources for the Pb, including leaching of basement rocks and the overlying volcanic rocks or their intrusive equivalents⁶³, not surprising given that meteoric-water convection can extend to depths of 5–7 km (ref. 62).

The multiple sources of components in low-sulphidation epithermal fluids is caused largely by the extensive amount of interaction between thermal waters and crustal rocks that occurs in this environment. Any reactive magmatic components are neutralized and reduced, in turn deriving components from the host rocks. This process leads to an integrated isotopic signature that may mask a variety of discrete fluids present in the early stages of activity; that is, pulses of fluid recorded by cycles of mineral deposition. Despite the overprinting that may occur in epithermal deposits, advances in microanalytical techniques now allow the isotopic composition of preserved domains in minerals to be analysed, domains that show evidence for a variety of discrete water and gas sources⁶⁴, including magmatic and crustal components⁶⁵.

Geothermal systems. In some volcanic arc-hosted geothermal systems, the evidence for a magmatic component is common and unequivocal. These systems are characterized at depth by neutral-pH fluids of low salinity (<1 wt% NaCl) but variable gas content (up to 4 wt%, including CO₂ and H₂S)⁵⁸. Coupled with their alteration mineralogy, these characteristics indicate they are analogous to the epithermal systems responsible for forming low-sulphidation ore deposits; indeed, in two of the world's largest and youngest epithermal Au deposits (Hishikari, Japan and Ladolam, Papua New Guinea) late-stage waters (70 to >150 °C) still flow through the veins.

The advantage in studying active systems is that discrete fluids can be sampled, allowing an examination of 'time-slices' through the history of hydrothermal activity. For example, the isotopic compositions of the highest-temperature waters in a variety of these geothermal systems have two different trends (Fig. 3a); one trend suggests a mixture of up to 50% magmatic water with local meteoric water²¹, whereas the other indicates only meteoric water-rock interaction⁵ (horizontal arrows). In the case of the Broadlands geothermal system, New Zealand, the deep thermal water (Fig. 3a; filled circle, Br) has a H-shift that indicates about a 20% component of low-salinity magmatic vapour mixed with local meteoric water (open circle). The deep liquid is also gas-rich (~2 wt%, mainly CO₂), and has a N₂/Ar ratio characteristic of arc magmatism (caused by subduction of N₂-rich

sediments)⁶⁵. By contrast, the deep liquid from the nearby Wairakei geothermal system (filled circle, Wk) has an isotopic composition similar to meteoric water that is slightly O-shifted. This fluid is low in total gas content (<0.1 wt%), and has a N₂/Ar ratio typical of air-saturated ground water, indicating no significant magmatic contribution to the system⁶⁵. This distinction in fluid composition may help explain the observed differences in mineralization between these two systems. The Broadlands system is mineralized locally with Au-rich precipitates in hot springs (to 80 p.p.m.) and wellhead pipes (to 6 wt%, ref. 66), and Pb–Zn sulphides are common at depth, whereas precious metals and Pb–Zn sulphides are absent at Wairakei. The difference in mineralization also correlates with Pb-isotope signatures. Broadlands' sulphide minerals have a homogenous signature, identical to that of local calc-alkaline intrusions, suggesting these are the source rocks, either through contribution from a magmatic fluid or by leaching, whereas the Pb-isotope compositions of altered rocks from Wairakei indicate that most of the Pb was leached from sedimentary rocks.

Similar geothermal systems with variable magmatic inputs (based on chemical and isotopic signatures) are common also in other circum-Pacific volcanic arcs^{65,67}. Drilling in some systems in Japan and the Philippines has encountered deep fractures containing hot, acidic fluids within otherwise neutral-pH waters; the acidity is caused by an absorbed magmatic vapour that is not neutralized by water–rock interaction⁶⁷. Perhaps such a magmatic fluid, although neutralized at depth, directly contributes metals to the Broadlands system. Alternatively, the acidic vapour may contribute only ligands such as Cl⁻ and HS⁻, causing the resulting fluid to leach metals from the wall rock. This variability in magmatic signatures between geothermal systems may be caused by intermittent contributions (or lack thereof) of magmatic fluid. Thus, gas and isotopic analysis of fluid inclusions in ore-related versus barren minerals will help to determine the role of magmatic contributions to hydrothermal fluid composition and ore formation.

Magmatic fluids and hydrothermal environments

We have mentioned the relationship between magma type and style of intrusion-related mineralization, stressing the need for metal scavenging from the magma by an exsolving aqueous fluid. Here we examine how this magmatic fluid may be involved in mineralization away from the intrusion.

The acidic environment. Studies of high-sulphidation epithermal ore deposits have confirmed the involvement of fluids with isotopic composition similar to high-temperature volcanic vapours^{21,54,68} (Fig. 3b). When such vapours are absorbed by meteoric water, they form acidic springs, which commonly have a pH of 0.5–1.5 (ref. 68). The composition of these acidic springs reflects isothermal dissolution of the rocks through which they flowed, a process that forms leached zones similar to those that host ore in high-sulphidation deposits. However, studies of the metal concentrations of high-temperature fumaroles^{68,69} associated with quiescent degassing of volcanoes indicate that these vapours cannot form ore deposits⁶⁸. For reasonable lifespans of magma degassing and hydrothermal activity related to a single intrusion (~10⁴ yr; ref. 2), the metal fluxes related to fumaroles (Table 2) and their associated acidic springs⁶⁸ are insufficient to account for the amount of Au (10–100 t) and Cu (>10³ t) found in high-sulphidation ore deposits¹¹.

There are several possible explanations for this seeming paradox. First, these deposits may form over much longer time spans, in association with multiple intrusions (as suggested for some porphyry deposits⁴). Second, the acidic water may leach metals as it reacts with the wall rock at depth⁷⁰. Third, the greater depths of these deposits (in contrast to the surficial fumaroles) means that pressures are high, thus increasing the concentration of metal chlorides in the vapour⁷¹. For example, aerosols associated with magmatic eruption are responsible for much higher metal fluxes than quiescently degassing volcanoes, even though

the discharge temperatures and flux of species such as H₂O, S and Cl are similar (compare White Island and Satsuma Iwojima; Table 2). This observation can be explained if a relatively NaCl- and metal-rich vapour, equilibrated with a magma at a pressure of several hundreds of bar (Fig. 2), accompanies eruption, thus accounting for the high Na/S and Cu/S in aerosols, in marked contrast to the low Na/S and Cu/S in the metal-poor fumarolic vapour associated with quiescent degassing. Absorption of a similar high-pressure and metal-rich vapour by a hydrothermal system may therefore form the low-salinity fluid (<5 wt% NaCl) responsible for mineralization in high-sulphidation systems⁶⁸. The deeper, high-salinity (≤30 wt% NaCl) fluid beneath these deposits, referred to earlier, may be related to the immiscible hypersaline counterpart of the vapour.

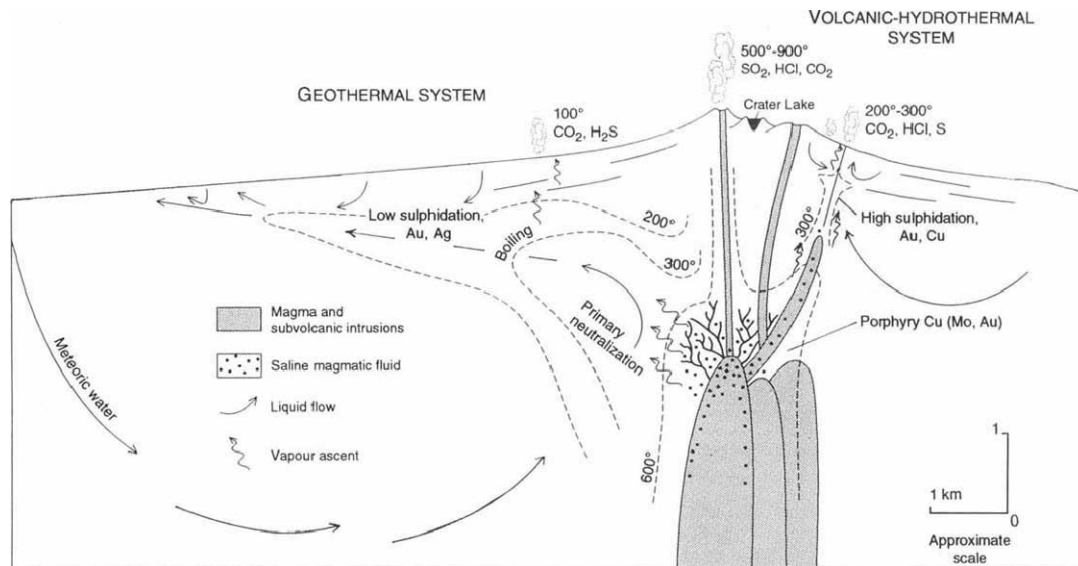
The neutral-pH environment. The source(s) of Au and other metals in low-salinity, neutral-pH fluids of low-sulphidation deposits is open to more speculation compared with porphyry and high-sulphidation systems, where there is evidence for a large magmatic component to the system. If the isotopic signature of water in a low-sulphidation system indicates that the fluid has a component of magmatic water mixed with meteoric water (for example, Comstock, Fig. 3b), then the magmatic component must have a low salinity to account for the dilute waters associated with epithermal Au deposition. Therefore, the magmatic fluid phase must be the low-density vapour noted earlier from volcanic aerosol studies (rather than the hypersaline liquid), which may have an appreciable metal content at the pressures of several kilometres depth⁷¹. Any acidic gases contributed by magmatic vapour to the meteoric-water system will undergo neutralization by reaction with the host rock (Fig. 4), causing an exchange of H⁺ for cations, including metals⁷⁰, thus adding this component to the metals contributed by the vapour. At present, there is no geological evidence that low-sulphidation deposits are underlain by pervasive acidic alteration, suggesting that when magmatic vapours are absorbed at the base of the low-sulphidation epithermal environment, the resulting neutralization may occur over a broad scale⁶⁴ (Fig. 4). This is consistent with the huge expanses (hundreds to thousands of square kilometres) of propylitic alteration (weak hydrogen metasomatism) characteristic of eroded, volcanic-hosted epithermal districts.

We infer the geochemical evolution of a hydrothermal fluid and its resultant alteration and mineralization as the distance from a magma body increases, because of the progressive reaction of fluid with rock. But there is no requirement that a porphyry Cu deposit is overlain by a high-sulphidation deposit, or vice versa, or that a low-sulphidation deposit will be rooted by porphyry mineralization adjacent to the intrusive heat source (Fig. 4). Nevertheless, these are possibilities, and some deposits may reflect this proposed geochemical transition, both in space¹¹ and/or in time. At Porgera, Papua New Guinea, early hypersaline magmatic fluids gave way to later meteoric waters of lower temperature and salinity, with Au probably remobilized from the initial porphyry mineralization⁷². The nearby Ladolam deposit, containing >400 t of Au, had a similar evolution, though the transition from porphyry to epithermal was probably caused by the catastrophic collapse of the host stratovolcano about 300,000 yr ago¹¹. The Kelian low-sulphidation Au deposit in Borneo⁷³ appears to span the epithermal to near-magmatic environment in terms of fluid salinity, temperature and isotopic characteristics. These few examples indicate that it is at present unwise to place sharp boundaries around the types of hydrothermal ore deposits discussed here.

Future directions

The occurrence of ore deposits is uncommon compared to the widespread evidence for extinct hydrothermal activity, indicating that only a small proportion of hydrothermal systems form ore, now or in the past. An outstanding problem in the study of hydrothermal ore deposits is to identify the factors that distinguish systems with ore-forming potential—factors so uncommon

FIG. 4 Schematic cross-section showing shallow, sub-volcanic intrusions, an associated stratovolcano, and the environments deduced for the formation of porphyry Cu, and high- and low-sulphidation epithermal ore deposits^{9,86}. Active volcanic-hydrothermal systems extend from the degassing magma to fumaroles and acidic springs, and incorporate the porphyry and/or high-sulphidation ore environments, whereas low-sulphidation ore deposits form from geothermal systems characterized by neutral-pH waters that may discharge as hot springs and geysers, such as those in Yellowstone National Park, USA.



that perhaps we have yet to observe them in active systems. This perceived lack of active ore-forming systems might also be accounted for by the common evidence indicating the episodic nature of formation of hydrothermal deposits. The fluids responsible for mineralization may be present only for short periods during the lifetime of the hydrothermal system, possibly at times of individual tectonic or hydraulic fracturing events^{4,54,60,74}.

Meteoric waters continue their deep circulation long after an intrusion has solidified. This leads to the masking of signatures of early events in the lives of hydrothermal systems. Nevertheless, advances in stable-isotope microanalysis now allow discrimination among the many events that occur during the histories of hydrothermal systems. Each event may have a different signature for O, H, S and C that can be determined only through study of preserved domains of individual populations of crystals, or even growth zones within crystals, now possible with laser microprobe techniques⁷⁵. Recognition of gas signatures in active systems⁶⁵ can also be applied to the extinct environment because of continuing advances in the analysis of inclusion fluids^{37,64}. Moreover, techniques such as proton-induced X-ray emission (PIXE)⁷⁶ or the X-ray microprobe³⁴ now permit investigations of p.p.m.-level metal concentrations in fluid inclusions as small as several micrometres. By determining the metal contents of a wide range of crustal fluids trapped in minerals, we can better understand why some hydrothermal fluids form ore deposits whereas others do not. As an example, the inclusion fluids associated with granite-hosted Sn mineralization in Australia have been analysed by PIXE⁷⁶. Vapour-rich inclusions appear to have an order of magnitude higher Cu concentrations than coexisting hypersaline inclusions, opposite to the findings in the more oxidized porphyry Cu deposits^{37,44}. Such results provide more questions than answers, and indicate the exciting work ahead on hydrothermal fluids, not only regarding mineralization and the diverse sources of metals, but also the effect these fluids have on crustal processes⁷⁴. □

Jeffrey W. Hedenquist is at the Mineral Resources Department, Geological Survey of Japan, Tsukuba 305, Japan. Jacob B. Lowenstern is at the US Geological Survey, MS 910, 345 Middlefield Road, Menlo Park, California 94025, USA.

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Phosphatidylinositol-3-OH kinase as a direct target of Ras

Pablo Rodriguez-Viciana^{*}, Patricia H. Warne^{*}, Ritu Dhand[†],
Bart Vanhaesebroeck[†], Ivan Gout[†], Michael J. Fry[†],
Michael D. Waterfield^{†‡} & Julian Downward^{*§}

^{*} Imperial Cancer Research Fund, 44 Lincoln's Inn Fields, London WC2A 3PX, UK

[†] Ludwig Institute for Cancer Research, 91 Riding House Street, London W1P 8BT, UK

[‡] Department of Biochemistry and Molecular Biology, University College, Gower Street, London WC1E 6BT, UK

Ras (p21^{ras}) interacts directly with the catalytic subunit of phosphatidylinositol-3-OH kinase in a GTP-dependent manner through the Ras effector site. *In vivo*, dominant negative Ras mutant N17 inhibits growth factor induced production of 3' phosphorylated phosphoinositides in PC12 cells, and transfection of Ras, but not Raf, into COS cells results in a large elevation in the level of these lipids. Therefore Ras can probably regulate phosphatidylinositol-3-OH kinase, providing a point of divergence in signalling pathways downstream of Ras.

THE Ras proteins are key regulators of cell growth and other functions¹; the elucidation of the identities of their critical cellular targets, or 'effectors' through which they exert their biological effects has long been a major goal of research into the regulation of eukaryotic cellular proliferation. The interaction of Ras proteins with their effectors occurs through a stretch of amino acids (32–40), generally known as the effector region, which assumes a different conformation in GTP-bound (active) Ras compared to GDP-bound (inactive) Ras. An effector of Ras would be expected to possess, or control, some sort of enzymatic activity that is regulated by its interaction with Ras.GTP, and which is responsible for at least some of the effects of Ras on the cell. It is possible, indeed likely, that Ras has multiple effectors.

The first protein for which evidence for a possible Ras effector role was found was p120^{GAP} (ref. 2). This protein interacts only with GTP-bound Ras and fails to interact with most effector region mutants. This is also true for the GAP-related protein neurofibromin, the product of the *NF1* gene³. Because both these

proteins strongly stimulate the GTPase activity of Ras they are both negative regulators of Ras: this activity could be incorporated in an effector as a negative feedback mechanism. Some reports indicate that p120^{GAP} can have an influence downstream of Ras in various signalling pathways^{4,7}, but it seems unlikely that it can account for all the signals emerging from Ras. The effectors discovered so far that are most likely to mediate the growth stimulatory signals from Ras are the cytoplasmic serine/threonine Raf kinases. These function downstream of Ras and activate the MAP kinase, and possibly other, pathways⁸. It is not clear whether Raf can activate all the signalling pathways that Ras can, but it can act as a very potent oncogene, unlike GAP. Recently several groups have reported that Ras directly interacts in a GTP-dependent manner with the amino-terminal domain of Raf through its effector region^{9,13}. It remains to be determined whether interaction of Raf with Ras.GTP can result in an increase of its kinase activity.

Raf kinases may not be the sole mediators of the effects of Ras on cellular behaviour. Phosphatidylinositol-3-OH kinase (PI(3)K) coimmunoprecipitates with Ras^{35,36}. This suggests that

§ To whom correspondence should be addressed.