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Journal Article**Author(s):**

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Publication date:

2004-09

Permanent link:

<https://doi.org/10.3929/ethz-b-000046080>

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Originally published in:

Geology 32(9), <https://doi.org/10.1130/G20629.1>



Native sulfur globules that had condensed, initially as a molten liquid, from an aqueous hydrothermal ore fluid in the Akeshi high-sulfidation gold mine (Kyushu, Japan). Prior to the deposition of sulfur, gold and some pyrite into vuggy quartz, the originally porphyritic host rock had been leached by acid volcanic vapor, leaving quartz-lined cavities at the site of former feldspar phenocrysts (32x45 mm; photo by L. Klemm taken during the 2004 Swiss – Japanese Field Workshop on Porphyry and Epithermal Ore Formation).

This is the Green Open Access version of: Heinrich C. A., Driesner, T., Stefánsson, A., and Seward, T. M., 2004. Magmatic vapor contraction and the transport of gold from the porphyry environment to epithermal ore deposits, *Geology*, v. 32, p. 761-764.

Original publication see: <https://doi.org/10.1130/G20629.1>

Magmatic vapor contraction and the transport of gold from the porphyry environment to epithermal ore deposits

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ABSTRACT

Fluid-phase stability relations combined with thermodynamic modeling using fluid-inclusion analyses and new gold-solubility experiments lead to an integrated geological interpretation linking epithermal gold mineralization and porphyry-style ore formation to the cooling of hydrous magma chambers. The essential chemical requirement for gold transport to low temperatures is an initial excess of sulfide over Fe in the magmatic fluid, which is best achieved by condensing out Fe-rich brine from a buoyant, low- to medium-salinity vapor enriched in volatile S. This vapor can contract directly to an aqueous liquid, by cooling at elevated pressure above the critical curve of the salt-water fluid system. Physical and chemical conditions are matched when magmatic fluid is released through a gradually downward-retracting interface of crystallizing magma beneath a porphyry stock, predicting the consistent zoning and overprinting relations of alteration and mineralization observed in magmatic-hydrothermal systems.

Keywords: gold solubility, magmatic deposits, vapor, brine, epithermal, porphyry, thermodynamic modeling.

INTRODUCTION

High-temperature porphyry Cu-(Mo-Au) deposits and epithermal high-sulfidation Au-Ag-(As-Cu) deposits are related globally to hydrous magmas, mostly at convergent plate margins (Giggenbach, 1992; Hedenquist and Lowenstern, 1994). The two ore types are geologically distinct, but have a similar element association of Cu, Au, and abundant S. Many porphyry-style deposits are major gold resources, but the highest-grade precious-metal enrichments are restricted to epithermal veins and breccias (Stoffregen, 1987; Jannas et al., 1990; Muntean et al., 1990). Both deposit types commonly occur in intimate spatial association and may be coeval within dating uncertainty (e.g., Arribas et al., 1995a), but epithermal ore formation invariably overprints porphyry-style mineralization at a given erosion level (Sillitoe and Hedenquist, 2003).

The association of the two deposit types implies a physical and chemical link between the ore-forming fluid processes (Gammons and Williams-Jones, 1997). Many high-sulfidation epithermal gold deposits show evidence of mixing between cool, salt-free meteoric water and hotter, low- to medium-salinity fluids of magmatic origin (e.g., Rye, 1993; Mancano and Campbell, 1995). Current debate centers on the origin and evolution of this magmatic fluid as the most likely gold contributor (Sillitoe and Hedenquist, 2003). It may be a single magmatic volatile phase that separates from a large magma chamber at depth and is then transferred, as a whole, to the epithermal environment (Hedenquist et al., 1998; Muntean and Einaudi, 2001). Alternatively, the magmatic fluid may separate into two phases at the source or during ascent. After physical separation from dense brine in a fractured porphyry stock, only the less viscous and more buoyant vapor phase may rise to the epithermal environment (Henley and McNabb, 1978; Sillitoe, 1983; Heinrich et al., 1999).

By combining recent thermodynamic and fluid-inclusion data, we explore the physical and chemical evolution of the two types of low- to medium-salinity magmatic fluids, the central question being how gold can be transported most effectively from the magmatic to the epithermal environment.

BOILING, CONDENSATION, AND VAPOR CONTRACTION

The phase evolution of magmatic-hydrothermal fluids is constrained by a large region of partial fluid immiscibility (Henley and McNabb, 1978), illustrated by the model system NaCl + H₂O (Anderko and Pitzer, 1993; Bodnar, 1995; Driesner and Heinrich, 2003). At any point of pressure (P), temperature (T), and total salinity (X) above the limiting miscibility surface, a single-phase fluid is stable (Fig. 1). At P - T - X points below this two-phase surface, two fluids coexist: a vapor phase of lower density and salinity, and a liquid phase of higher density and salinity. The crest of this surface, the critical curve, swings from high salinity at high P and T (e.g., ~25 wt% at 700 °C and 1250 bar) to the critical point and the boiling curve of pure water at much lower P and T .

Fluid of low to moderate salinity, ascending from an igneous source, may evolve to a low-temperature aqueous liquid without ever intersecting the two-phase surface. Alternatively, a single-phase fluid may breach the two-phase surface during ascent. If this occurs on the liquid side of the critical curve, the fluid boils by separating out lower-salinity vapor. More commonly in porphyry-style deposits (e.g., Redmond et al., 2004), a single-phase fluid with low to moderate salinity may breach the two-phase surface on the vapor side and condense out some brine with higher salinity. In either case, the more buoyant

vapor can depart from the two-phase surface again, by physical separation from the denser brine. If this vapor cools along any P-T path above the critical curve (as illustrated by the multiple paths that lie in the isochemical, single-phase plane in Fig. 1), it will increase its density and contract to an aqueous liquid. The term *vapor contraction*, which is driven by cooling at elevated pressure without any heterogeneous phase change, emphasizes the difference from the process of condensation, which describes phase separation of liquid from vapor. At $T < 350^\circ\text{C}$, a liquid derived by contraction of a magmatic vapor is completely miscible with any other aqueous liquid. It may also boil again by separation of a low-density steam phase, notably by decompression near the lithostatic to hydrostatic transition (Fournier et al. 1999).

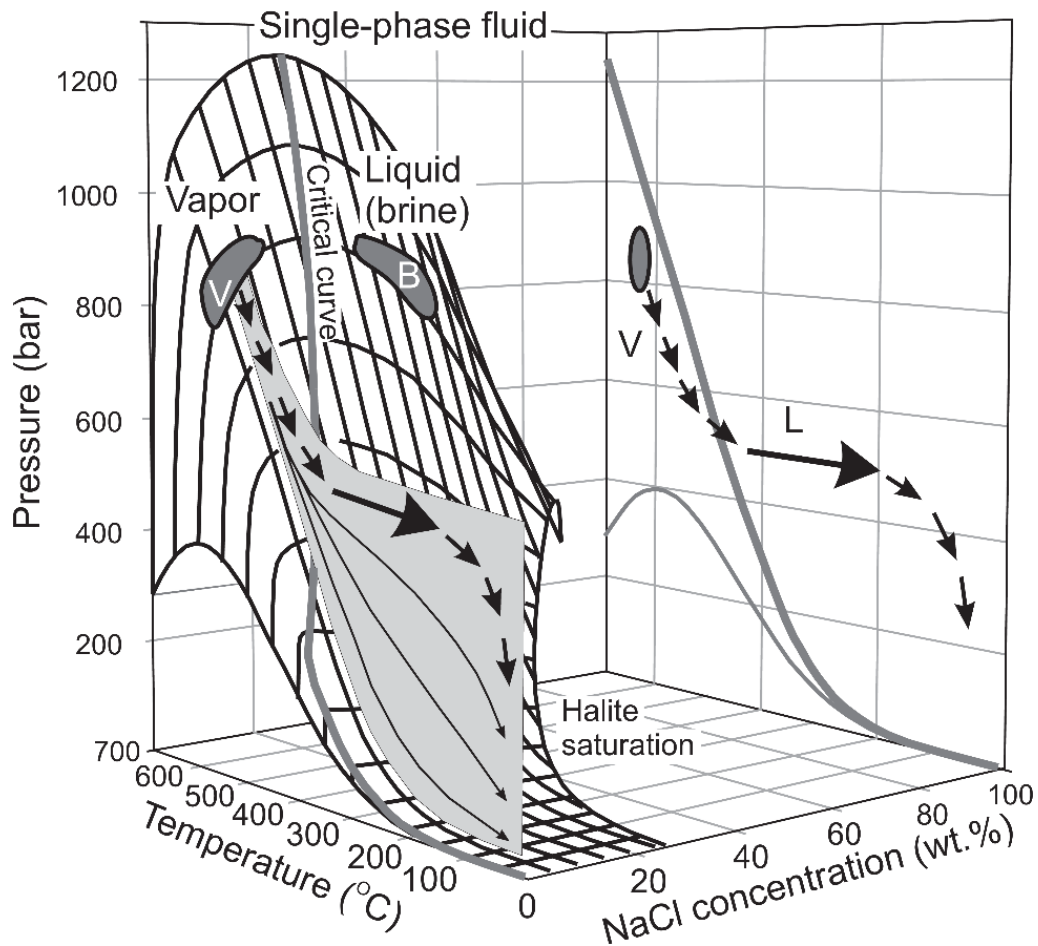


Fig. 1. Phase stabilities in NaCl + H₂O fluid system, emphasizing two-phase coexistence surface (vapor + brine; gridded by isopleths and isotherms; Driesner and Heinrich, 2003). Critical curve (heavy gray line at crest of two-phase surface) swings from high salinities at high P and T across to lower salinities at low P and T . Hot vapor-like fluid (V) of low to medium salinity—originating from slightly above two-phase surface or coexisting with brine (B) along that surface—can be cooled and contracted to an aqueous liquid (L) without heterogeneous phase change provided that, during this stage of cooling, P remains above two-phase surface (arrows in 7% NaCl plane). Backface shows projection of critical curve (thick gray), halite saturation envelope (thin line), and one P-T-path including the isobaric cooling interval (long arrow segment) modelled in Figure 2.

A wide range of cooling paths can generate low- to medium-salinity aqueous liquid either from a high- T vapor (Heinrich et al., 1999; Fig. 1) or from a single-phase magmatic fluid (Hedenquist et al., 1998). The two alternative processes require similar physical conditions, but the chemical consequences with regard to gold transport are likely to be decisively different.

THERMODYNAMIC REACTION MODELING OF GOLD TRANSPORT

Reinvestigation of gold solubility with a flow-through technique has yielded high-precision equilibrium concentrations under controlled thermodynamic conditions (Stefánsson and Seward, 2003, 2004). Our multicomponent reaction modeling combined these thermodynamic data with vapor-inclusion compositions from the Grasberg porphyry Cu-Au deposit. This vapor has a salinity of ~ 7 wt% NaCl equivalent, and LA-ICP-MS (laser-ablation-inductively coupled plasma-mass spectrometry) analysis indicated an average composition of $1.2m$ (mol / kg H₂O) NaCl, $0.33m$ KCl, $0.18m$ FeCl₂, $0.19m$ CuCl, $0.003m$ H₃AsO₃, and $5 \times 10^{-5}m$ AuCl (~ 10 ppm Au; Ulrich et al., 1999). The medium-salinity vapor inclusions occur together with brine inclusions containing almost tenfold higher concentrations of Na, K and Fe, trapped near 650°C and ~ 800 bar. Volatile sulfur species could not be analyzed but are likely to be major components, particularly in the vapor phase. The concentrations of H₂S and SO₂ thus become the critical unknown parameters explored by chemical reaction modeling. Figure 2 shows the predicted chemical evolution of the vapor-derived fluid for three sets of assumptions regarding initial total S/Fe ratio and degree of wall-rock buffering during cooling to 450–200 °C at 500 bar. Wall-rock interactions are reduced to feldspars and sheet silicates within the Na-K-H-Al-Si-O system (Table DR1¹; study with additional components in preparation).

Figure 2A is based on the assumption that the fluid initially contains less S than Fe and cools in chemical contact with feldspathic wall rocks. Alteration of feldspars to muscovite and quartz will neutralize the acidity generated by the disproportionation of magmatic sulfur dioxide upon cooling ($4\text{SO}_2 + 4\text{H}_2\text{O} = \text{H}_2\text{S} + 3\text{HSO}_4^- + 3\text{H}^+$; Giggenbach, 1992; also $\text{HCl} = \text{H}^+ + \text{Cl}^-$). Due to the initial Fe excess, pyrite precipitation causes rapid depletion of reduced S upon cooling. As a result, gold bisulfide complexes [AuHS⁰, Au(HS)₂⁻] are destabilised, while AuOH⁰ and AuCl₂⁻ are inadequate to support high gold concentrations in near-neutral fluids at low temperatures. Precipitation of pyrite (and other sulfides) from a S-deficient fluid thus forces most of the gold to precipitate above 400°, preventing effective gold transport to epithermal temperatures.

Alternatively, if the initial fluid contains an excess of H₂S over FeCl₂ (Figs. 2B, 2C), pyrite precipitation cannot consume all the reduced S, which therefore remains available for gold complexation and effective precious-metal transport to epithermal conditions. If the fluid becomes strongly channelized by structural focusing into narrow veins, it may cool in effective isolation from reactive feldspars and become increasingly acid by the H⁺-producing SO₂ disproportionation (Fig. 2B). The resulting low pH reduces

¹GSA Data Repository item 2004###, Table DR1, Species and sources of thermodynamic data for parts of the chemical system Na-K-Al-Si-Fe-Au-Cl-S-O-H at 500 bar and 25–400 °C with comments about modelling approach is available online at www.geosociety.org/pubs/ft2004.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

the $\text{HS}^-/\text{H}_2\text{S}$ ratio and thus the HS^- ligand concentration available for gold complexation. Such fluid-dominated cooling will produce a very acid aqueous liquid ($4 > \text{pH} > 1$) with high S content suitable for advanced argillic alteration and sulfate precipitation (alunite, anhydrite). Under these conditions, significant gold concentrations as AuHS^0 and minor AuCl_2^- are possible, nevertheless most of the gold at will precipitate before reaching the epithermal regime.

The most effective transport of gold to epithermal deposits occurs by combination of an initial sulfide excess over Fe with partial acid neutralization due to wall-rock reactions during cooling (Fig. 2C; total sulfur only limited by liquid sulfur condensation; Gammons and Williams-Jones, 1997). This model path maximizes the free HS^- ligand concentration, allowing the vapor-derived fluid to transport as much as 10 ppm gold down to any temperature as low as 150 °C, without ever reaching gold saturation.

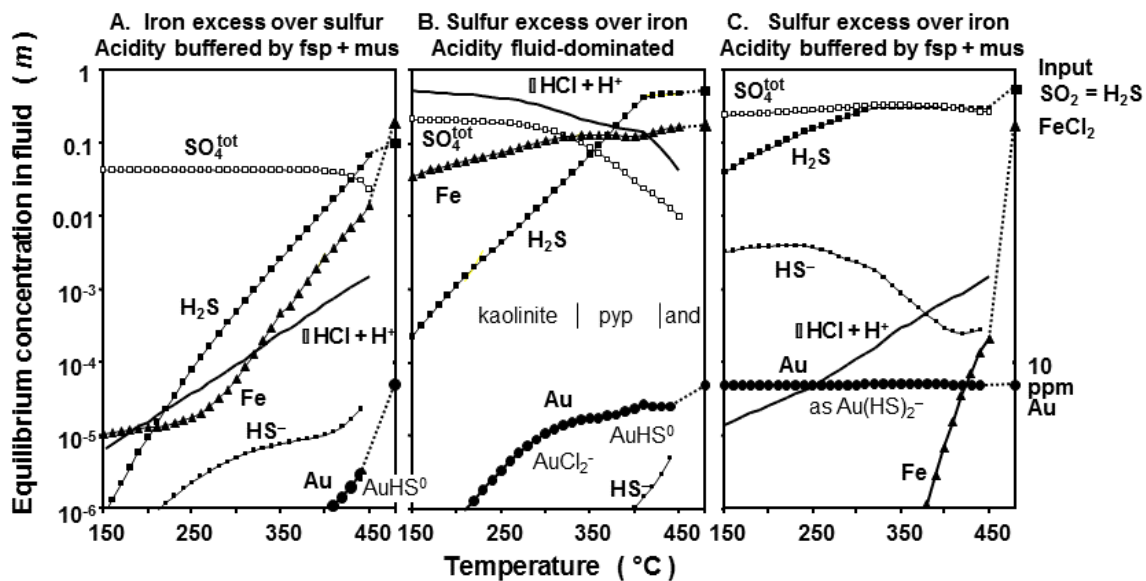


Fig. 2. Results of multicomponent reaction modeling for feldspar-muscovite-buffered or fluid-dominated cooling of an intermediate-salinity fluid with high initial Au content, as measured by LA-ICP-MS microanalyses of vapor inclusions from Grasberg porphyry-Cu-Au deposit (Ulrich et al., 1999). Analyzed total Au (circles), FeCl_2 (triangles) and variable assumed SO_2 and H_2S concentrations (squares) marked on right axis of each diagram. Three series of heterogeneous equilibrium states (A, B, C; computed for closed systems at 500 bar and variable T between 450 and 150 °C) approximate three extreme chemical evolution paths, illustrating the decisive influence of S/Fe ratio in starting fluid and of pH buffering by wall-rock alteration reactions. Initial Fe excess (A; most likely for single-phase magmatic fluids) prevents effective Au transport to low temperatures. Initial S excess (aided by earlier separation and removal of Fe-rich brine) and acid neutralization by wall-rock reaction (C) maximize efficiency of gold transport from magmatic to epithermal conditions. Abbreviations: fsp—albite + K-feldspar; mus—muscovite; pyp—pyrophyllite; and—andalusite.

THE ROLE OF BRINE AND VAPOR SEPARATION

Figure 2C predicts that gold concentrations in cool, low- to medium-salinity magmatic fluids can be orders of magnitude higher than those found in active geothermal waters of dominantly meteoric origin (Brown, 1986). The key condition for gold transport from the magmatic source to the epithermal environment is the cooling of a low-salinity,

S-rich but Fe-poor magmatic fluid at sufficient confining pressure to allow its isochemical contraction to an aqueous liquid. Supra-hydrostatic P - T conditions in the compressive or low-differential-stress regime surrounding porphyry-related magma chambers (Tosdal and Richards, 2001) are probably important to sustain the elevated pressure required for vapour cooling and contraction above the critical curve (Fig. 1; Fournier et al., 1999).

Single-phase magmatic fluids can have similar Na, K, Fe, Cu (and possibly Au) contents as the Grasberg vapor, as shown by deep fluids in the Butte porphyry (Rusk et al., 2004). Experimental and analytical data for magmatic conditions are limited, but single-phase magmatic fluids are likely to initially contain a slight excess of chalcophile metals, notably Fe, relative to sulfur available as sulfide upon cooling (Burnham and Ohmoto, 1980). Single-phase fluids are thus more likely to follow the evolution of Figure 2A. Therefore, physical separation of Fe-rich brine from sulfide-rich vapor in the porphyry domain may be the *pivotal* step in the generation of an ore fluid supporting high gold solubility at lower temperature (Fig. 2C).

VAPOR CONTRACTION AND ISOTHERM RETRACTION

The “isotherm retraction – vapor contraction” model illustrated in Figure 3 links porphyry-style and epithermal ore deposits to the gradual cooling of a common igneous fluid source. Although the physical processes are not yet quantified, the model explains the fluid-inclusion characteristics observed in both deposit types and integrates the characteristic zoning and overprinting relations in the field (“telescoping”; Sillitoe and Hedenquist, 2003) with the chemical modelling presented above.

At an early stage after the emplacement of a porphyry stock above a larger magma chamber (Fig. 3A), exsolution of a low-density volatile phase rich in SO_2 , H_2S , and HCl will take place in the uppermost part of the crystallizing magma column. This acidic vapor will escape across initially steep gradients in P and T at relatively low lithostatic to hydrostatic P , leaving behind some highly saline brine or even halite. These conditions are most favorable for argillic alteration and the formation of barren vuggy quartz, by mixing of groundwater with acidic vapor that has too low a density for significant gold transport (Williams-Jones et al., 2002).

Later in the cooling history (Fig. 3B), the magma-crystallization front retracts to progressively greater depths, leading to fluid exsolution at higher P , first in the two-phase fluid stability field and later perhaps also in the single-phase field. The region of brine + vapor coexistence above the magma interface also retracts downward, leading to porphyry-style Cu-Au mineralization and potassic alteration by cooling of the ascending two-phase fluid through the 400–350 °C temperature interval (Ulrich et al., 2001; Redmond et al., 2004). As this zone expands downward, separation of the buoyant and less-viscous but S-enriched vapor phase from the condensing Fe-rich brine occurs at progressively greater depth and higher pressure, probably in the lithostatic regime. The ascending vapor is forced to pass through an increasing thickness of K-feldspar-enriched rock. The result—cooling of H_2S -enriched vapor at elevated pressure and in chemical contact with feldspathic wall rocks—matches exactly the predicted requirement for optimal gold transport from the porphyry domain to the epithermal environment (Figs. 1, 2C). Downward-tapering fracture zones with sericite + pyrite alteration overprinting potassic alteration observed in most porphyry-style ore deposits are interpreted as the linking channelways for gold-transporting, vapor-derived fluids to epithermal ore deposits.

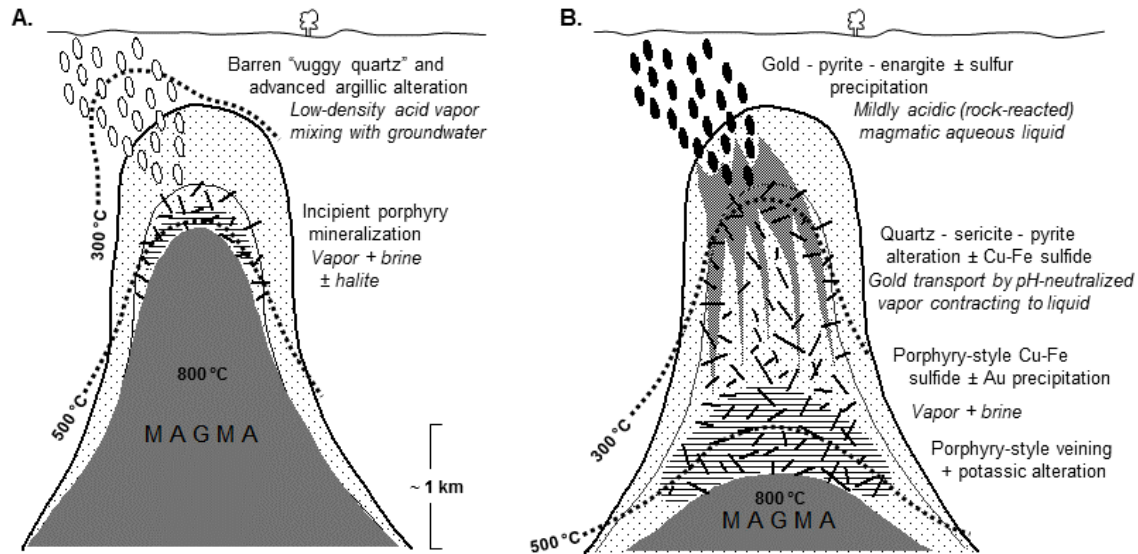


Fig. 3. Cartoon illustrating two stages in evolution of porphyry and epithermal ore deposits, linked by a process of downward retraction of magma interface and surrounding isotherms during continued fluid exsolution from a large subjacent magma reservoir: the *isotherm retraction – vapor contraction model* explains the sequence of alteration and mineral precipitation observed in magmatic-hydrothermal systems. Downward retraction of vapor + brine separation front, and contraction of magmatic vapor by cooling at increasingly higher pressures, are a common consequence of large-scale cooling of the entire magmatic system.

Local differences in the mass ratio between brine and vapor, which mainly depend on the initial Cl/OH ratio of the magma and the evolving P - T distribution in the hydrothermal system, will affect the proportion of gold trapped in a porphyry-Cu-Au deposit relative to the proportion of gold carried into the epithermal domain. The total metal endowment of the entire magmatic-hydrothermal system is ultimately limited by the size of the fluid-producing magma chamber, so that not all economic epithermal deposits are associated with economic porphyry deposits, even though the fluid processes are intimately linked.

The formation of a rich gold deposit further depends on an efficient precipitation mechanism. Steep gradients in gold solubility occur near the interface between the magmatic fluid domain and the near-surface environment dominated by meteoric water. Precipitation can occur by mixing of magmatic with meteoric fluid, sudden desulfidation of the magmatic fluid due to reaction with Fe-bearing host rocks, or low-pressure boiling at the transition to the shallow hydrostatic regime (Fournier et al., 1999). Differences in the local geology of the precipitation setting probably cause the great variability and complexity of epithermal gold deposits, despite a common source process contributing exceptionally gold-rich ore fluid: the contraction of an Fe-depleted but sulfide-enriched magmatic vapor phase from a gradually retracting magmatic interface.

Acknowledgements: Research supported by Swiss National Science Foundation. We thank Timothy Baker, Paul Barton, Lluís Fontboté, Jeff Hedenquist, Stephen Kesler and John Muntean for discussion and constructive comments.

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