

Analogues of epithermal gold-silver deposition in geothermal well scales

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ACTIVE geothermal fields are generally recognized¹⁻⁵ as modern analogues of the systems responsible for the formation of epithermal gold-silver ore deposits. We have investigated this analogy by studying scales precipitated at various depths in a geothermal well containing boiling fluids. Our results, presented here, show that concentrations and distributions of gold, silver, copper, lead and zinc in well M-53 at Cerro Prieto, Mexico, are comparable to those found in economic epithermal vein deposits, and that the highest concentrations of metals occur at or near the fluid production horizon. The onset of vapour separation or flashing at these depths in the well indicates that boiling caused sequential base and precious metal saturation through the loss of CO₂ and H₂S, respectively, to the vapour phase. These phenomena provide direct evidence that boiling of chloride-rich hydrothermal solutions may be responsible for the deposition and zonation of gold, silver, copper, lead and zinc in epithermal vein deposits. Geothermal well scales can thus provide the opportunity to study epithermal ore genesis in a wide variety of natural environments.

Although well scaling is a problem in the exploitation of geothermal energy, scales are potentially of great value in studies of the geochemistry of mineralizing processes. Scales from surface installations have been reported to contain significant Ag, Cu and Fe at Salton Sea, California⁶, to host a variety of iron and base metal sulphides at Cheleken, Soviet Union^{7,8}, and Milos, Greece⁹, and to contain locally abundant Au, Ag and Cu at Ohaaki and Kawerau, New Zealand¹⁰. High concentrations of gold, silver and base metals have recently been found in well scales collected from various depths in the Cerro Prieto¹¹⁻¹³, Oku-Aizu (Japan)¹⁴ and Salton Sea¹⁵ geothermal fields. The distributions as a function of depth and depositional mechanisms of these metals, however, have not been evaluated. The discoveries of metalliferous scales are of particular importance as they provide a means of investigating mineralizing processes under known or controlled conditions in natural hydrothermal systems. Such processes are generally inferred from studies of mineralization^{5,16,17}, constrained by laboratory experiments¹⁸, or simulated by computer models¹⁹⁻²³. The chemical zonations reported here can be directly related to those of fossil ore deposits and some of the physico-chemical controls of their formation.

Well M-53 at Cerro Prieto is 1,997-m deep and intersects the producing aquifer between 1,845 and 1,996 m. Between 1974 and 1978, the well operated intermittently under variable but generally high-pressure conditions in a testing mode. From 1978 the well steadily produced liquid and vapour under relatively low well-head pressure until closure for maintenance in 1982. During this production phase, scales accumulated on the well liners. These scales occur mainly between 920 m and the bottom of the well and, to a lesser extent, near the top of the well; the former precipitated during the production period when pressure conditions were low, and the latter during the high-pressure pre-production phase. Table 1 provides data on typical fluid compositions and well conditions during the production period. These data indicate that the fluid temperature in the producing aquifer was 337 ± 10 °C (calculated using the Na-K-Ca geothermometer), and the pH was 5.9 (estimated from CO₂ and HCO₃⁻ discharge data). Extrapolation of data for the H₂O-NaCl system²⁴ indicates that the fluid boiled in the well at a depth similar

TABLE 1 Typical liquid compositions and well-head conditions (1978-82)

Species	Concentration (mg kg ⁻¹)	Species	Concentration (mg kg ⁻¹)	Conditions
Na ⁺	9,563	Mg ²⁺	<1	<i>P</i> _{well-head} 7.4 bar
K ⁺	3,004	SiO ₂	1,351	pH _{wellbox} 7.2
Ca ²⁺	403	Cl ⁻	18,306	<i>X</i> _{vapour} 0.37
Li ⁺	27	HCO ₃ ⁻	79	Production rate
Rb ⁺	26	CO ₂ *	16,255	66 t h ⁻¹
B ⁺	24	H ₂ S*	770	

* Vapour composition.

to that of the production horizon. Assuming isenthalpic boiling, the drop in temperature was 140 °C.

Examination of polished thin sections indicates that scales at the top of the well consist of 0.1-0.5-mm-thick layers of clear to black botryoidal amorphous silica with ~10% of sulphide layers containing pyrrhotite and traces of sphalerite. The colour of the darker silica results from finely disseminated inclusions of a probable iron silicate phase²⁵. The proportion of dark silica gradually increases with depth. The percentage of sulphide decreases to <1% below 200 m and then increases sharply, composing >60% of samples below 1,100 m. These sulphides consist mainly of isocubanite with irregular layers of sphalerite and galena, and are locally accompanied by up to 0.5% silver-rich electrum (Fig. 1). Below 1,600 m, scales consist mainly of sulphide. Traces of calcite occur at irregular depths in the well.

As might be expected from the observed sulphide abundances, analyses of Cu, Pb and Zn show slightly elevated values near the top of the well which decrease with depth down to 890 m, and then sharply increase between 1,063 and 1,189 m (Fig. 2a). All three metals display similar distributions. The highest values occur near the bottom of the well (Cu, 12.87 wt%; Zn, 8.88 wt%; Pb, 8.28 wt%). Silver grades are high throughout the well (>280 g tonne⁻¹), but increase abruptly below 890 m to reach a peak of 22,900 g tonne⁻¹ at 1,349 m; silver contents are markedly lower towards the bottom of the well (Fig. 2b). The profile of gold values is similar. Gold concentrations are low at the top of the well (0.11 g tonne⁻¹) and rise gradually to a depth of 1,063 m (Fig. 2c). Below 1,063 m, gold increases sharply to a maximum value of 270 g tonne⁻¹ at 1,487 m, and then decreases rapidly further down the well.

The most striking feature of the metal distributions in Fig. 2 is that the gold and silver concentrations peak 365 m and 495 m above the top of the production horizon, respectively, whereas the Cu, Pb and Zn concentrations are highest near the bottom of the well. In solutions with physico-chemical characteristics similar to those of well M-53 fluids, gold is transported dominantly as a bisulphide complex^{26,27}, and silver mainly as a chloride complex above 300 °C and as a bisulphide complex

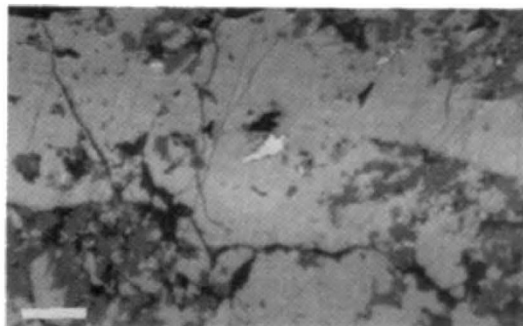


FIG. 1 Photomicrograph of silver-rich electrum (white), isocubanite (light grey), sphalerite (dark grey) and amorphous silica (black) in scales from 1,349-m depth in well M-53, Cerro Prieto. Scale bar, 25 µm.

at lower temperatures^{28,29}. Copper is transported as a chloride complex at aquifer conditions, but bisulphide complexing may be important at lower temperatures³⁰. Lead and zinc solubilities are dominated by chloride complexing for all relevant temperatures^{31,32}.

As noted above, boiling in the well starts at a depth similar to that of the production horizon. The principal effects of such phase separation on the liquid are to decrease temperature, increase pH and decrease H₂S activity. Most of the increase in pH occurs within the first few per cent of boiling, whereas significant loss of H₂S requires a more advanced degree of boiling²⁰. Chloride complexes are destabilized by decreasing temperature and hydrogen ion activity. By contrast, the stability of bisulphide complexes is enhanced by the increased pH of the liquid (gold solubility increases by ~1 log unit per pH unit for the well conditions^{26,27}), and is relatively insensitive to temperature. Precipitation of sulphide minerals and resultant decrease of reduced sulphur species in the fluid may also affect bisulphide stability. Thus the principal cause of bisulphide complex instability is the loss of H₂S and resulting decrease in ligand concentration (HS⁻).

The distribution of gold and silver in the well scales demonstrates that these metals generally became saturated several hundred metres above the production horizon. For gold, this can be explained by the fact that significant depletion of H₂S in the liquid required considerable boiling. Silver deposition,

on the other hand, may have been controlled by the destabilization of both chloride and bisulphide complexes. If this were the case, precipitation of silver would have occurred in response to decreasing temperature and increasing pH, and to loss of H₂S respectively. But the remarkable similarity in the silver and gold concentration profiles (Fig. 2b, c) indicates that the transport of silver, like gold, was dominated by HS⁻ complexing in the well. Precipitation of the precious metals is thus primarily dependent on the partitioning of H₂S to the vapour phase during boiling.

Deposition of base metals is strongly controlled by temperature and pH. The estimated large drop in temperature and the decrease in hydrogen ion activity owing to boiling reduced the solubilities of Cu, Pb and Zn by several orders of magnitude. We therefore conclude that the Cu, Pb and Zn concentrations in scales near the bottom of the well were caused by boiling when high-pressure aquifer fluids entered the lower-pressure well environment. Localized base-metal-bearing scales near the top of the well are as yet poorly understood. These may reflect boiling near the top of the well in response to the high well-head pressures that prevailed during the pre-production phase.

The extreme concentrations and distinctive zonations of gold, silver, copper, lead and zinc in the geothermal well scales mimic those commonly described^{33,34} for epithermal Au-Ag and polymetallic vein deposits. Mineralization in many of these deposits is hosted by quartz veins precipitated from boiling hydrothermal fluids. Well M-53 seems to model an open-vein system in which ascending silica-saturated fluids boil and sequentially deposit base and precious metals. Although this analogy and type of zonation has been reported for mineralized geothermal fields¹⁷, it has not been previously recognized in well scales. As geothermal fields around the world tap compositionally diverse hydrothermal fluids under widely variable physico-chemical conditions, well scales should provide the opportunity to investigate the genesis of a broad spectrum of ore deposits. □

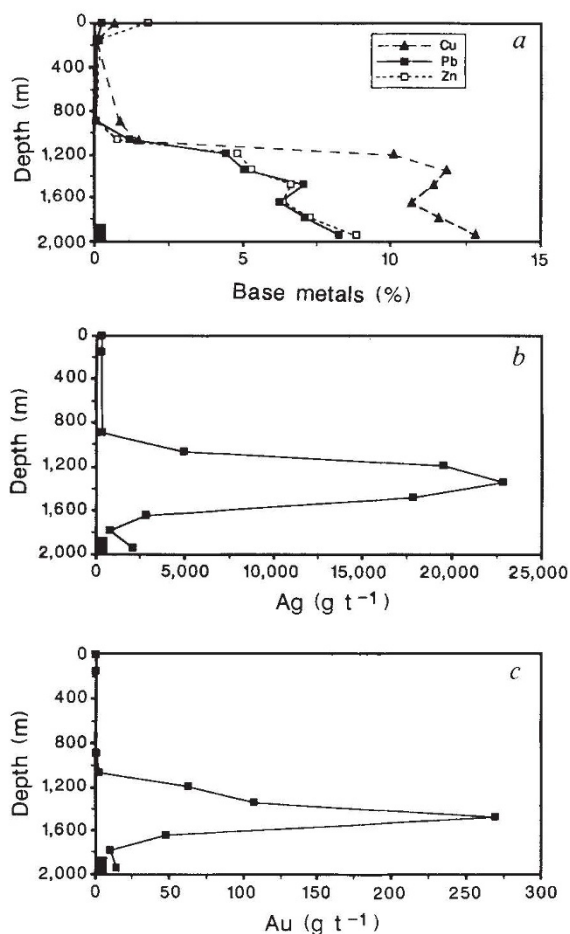


FIG. 2 Concentration profiles for copper, lead and zinc (a), silver (b) and gold (c) in well M-53, Cerro Prieto. Black bars between 1,845 and 1,996 m on the depth ordinates indicate the fluid production horizon, and level of initial boiling. Samples were analysed by inductively coupled plasma spectroscopy for Cu, Pb, Zn and Ag. Gold was analysed by a combination of fire assay and graphite-furnace atomic absorption techniques.

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