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## An experimental study of the transport of Cu, Ag, and Au in the vapor phase

Par

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## SUMMARY

Existing models for the formation of porphyry Cu and epithermal Au-Ag deposits have been built on the assumption that the metals are transported to the site of deposition by an aqueous liquid. However, there is strong evidence that magmatic vapors may contain significant concentrations of Cu, Au, and Ag, and it is therefore possible that the vapor phase may play an important and even dominant role as an agent of metal transport in porphyry/epithermal ore-forming systems. The long term objective of the research described in this report is to contribute some of the key thermodynamic data needed to quantitatively test the vapor transport model of porphyry/epithermal ore genesis and to build on previous work in the system H<sub>2</sub>O-HCl. Noting that H<sub>2</sub>S partitions strongly into the vapor phase and that H<sub>2</sub>S has been shown to form strong complexes with Cu, Au and Ag, the current research is investigating the solubility of Cu, Au, and Ag in H<sub>2</sub>S vapor.

The behavior of the above metals was studied experimentally at temperatures between 200 and 400°C and established that metal solubility increases with increasing temperature and that H<sub>2</sub>S gas can dissolve up to 7.5 ppm Cu, up to 150 ppb Ag, and up to 37 ppb of Au at temperatures of 300, 350 and 400°C, respectively. The species responsible for the transport of Ag and Au were determined to be solvation complexes of the type  $Ag_2S \cdot (H_2S)^{gas}$  (T~350°C) and  $Au \cdot (H_2S)^{gas}$  (T~400°C) having statistical solvation numbers of approximately 1 at 350°C and 1.6 at 400°C respectively. The relatively high solubility of Cu and its apparent independence of  $fH_2S$  are tentatively attributed to an unusually high volatility of covellite, the copper reagent employed in the experiments. The results of this experimental study suggest that H<sub>2</sub>S may be very important in enhancing the solubility of Ag and Au metals in the vapor phase, and will add important data to the framework that will be needed to permit construction of quantitative models of the vapor transport of metals in natural systems.

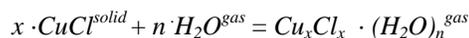
## INTRODUCTION

Successful metallic mineral exploration is increasingly dependent on the availability of comprehensive and reliable ore deposits models. In the case of porphyry Cu and epithermal Au-Ag systems, the currently accepted genetic model assumes that the metals are transported to the site of deposition in a brine. However, the fact that these systems are commonly dominated by vapor has long suggested that the vapor rather than the liquid phase is the principal agent of metal transport. Indeed, over fifty years ago, Brown (1948) and Walker and Walker (1956) suggested that sulfidic ore deposits could form from volatile sulfide or chloride species. The principal reason that the idea did not gain acceptance is that soon afterwards Krauskopf (1957, 1964), published thermodynamic calculations,

showing that the volatilities of metals only become significant at magmatic and higher temperatures (> 700°C).

With a few notable exceptions, e.g., the vapor plume model of Henley and McNabb (1978), the idea of the vapor transport of metals did not receive any serious attention until Heinrich et al. (1992) presented fluid inclusion evidence for magmatic vapors containing ore level concentrations of copper. Since then Heinrich and coworkers, e.g. Heinrich et al. (1999) and Ulrich et al. (1999) have shown, using LA-ICP MS analyses, that primary vapor-rich inclusions in porphyry systems commonly contain ore level concentrations of Fe, Cu, Pb, Zn, and Au (Table 1), and that the concentrations of Cu and Au frequently exceed those of Cu and Au in coexisting brine inclusions. They attributed this preferential partitioning of Cu and Au into the vapor to the formation of strong complexes with sulfur and the relatively high volatility of H<sub>2</sub>S.

These findings highlighted the essential flaw in trying to predict metal transport on the basis of component fugacities (volatility in the case of metals), namely that it ignores potentially important low-energy solute-solvent interactions, i.e., the formation of stable new gaseous compounds (chemical reaction) or the solvation of existing metal species by water vapor (solubility). This, in turn, prompted researchers at McGill University to start investigating the solubility of metals in simple analogues of natural systems. During the past eight years, these researchers have completed experimental studies on the solubility of Cu, Ag, Au, Sn, and Mo in H<sub>2</sub>O or H<sub>2</sub>O-HCl vapors (summarized in Williams-Jones et al., 2002; see also Rempel et al, 2006), and in each case have demonstrated that the solubility is substantially higher than that predicted from volatility data, due to the formation of hydrated species. For example, the solubility of AgCl in HCl-bearing water vapor at 300°C is up to six orders of magnitude higher than predicted theoretically and the enhancement is even greater for CuCl and Au (Migdisov et al., 1999; Archibald et al., 2001 and 2002). These studies indicate that the dominant species responsible for metal transport in H<sub>2</sub>O-HCl gas mixtures probably has the stoichiometry  $MeCl_m(H_2O)_n^{gas}$ , e.g.,



Despite the success of these experiments, the concentrations of metals in the vapor phase are

Table 1. Average concentrations of metals in vapor-rich fluid inclusions (Ulrich et al., 1999)

	Alumbrera	Grasberg
Au, ppm	<0.53	10.17
Ag, ppm	<40	100
Mo, ppm	<300	60
Cu, wt%	3.3	1.2
Zn, wt%	0.12	0.15
Pb, wt%	0.02	0.04

substantially lower than those measured in the fluid inclusion studies of Heinrich and co-workers, particularly for Au and Cu, suggesting that ligands other than Cl must be involved in enhancing metal solubility in natural vapors. Inasmuch as H<sub>2</sub>S is an important component of natural fluids, partitions very strongly into the vapor phase and has the highest dipole moment of any common natural solvent other than H<sub>2</sub>O, it is an obvious candidate to help explain the higher solubility of Au and Cu in natural vapors.

The objective of the current experimental study is to investigate the solubility of Cu (*CuS*), Ag (*Ag<sub>2</sub>S*), and Au (*Au metal*) in pure H<sub>2</sub>S at temperatures of 200 to 400°C and pressures of up to 200 bar. The choice of silver and gold phases was quite obvious because they are stable at the proposed experimental conditions. In order to determine which copper phase is stable at the conditions of experiments, preliminary sets of experiments were conducted with different copper (I) and copper (II) sulfides, namely chalcocite (Cu<sub>2</sub>S) and covellite (CuS). These experiments indicated clearly that, in an atmosphere of hydrogen sulfide, copper (II) sulfide (covellite, CuS) is the only stable phase; based on the results of X-Ray diffraction analysis, all Cu (I)-bearing phases were converted into CuS. Subsequent experiments involving copper were therefore conducted with covellite.

## METHOD

The method used in this study was similar to that described in our previous studies devoted to the vapor transport of metals (e.g., Migdisov et al, 1999, Archibald et al., 2001 and 2002, Migdisov and Williams-Jones, 2004, Rempel et al., 2006). The experiments were carried out in titanium-alloy autoclaves (with volume of ~40-50 cm<sup>3</sup>), which were preconditioned with nitric acid to produce a protective layer of TiO<sub>2</sub> on the internal surfaces (Figure 1). Autoclave volumes were determined by filling the autoclaves with 25°C distilled water from a

Teflon flask, and weighing this flask before and after filling. The weighing was performed to an accuracy of 0.1 g. A solid phase (CuS, Ag<sub>2</sub>S, or Au-metal) was placed in each autoclave in a quartz ampoule. After purging with nitrogen gas (~40 minutes) to expel the atmospheric gases the autoclaves were filled with liquid H<sub>2</sub>S (1-6 g), which was condensed out of a purified gas flow by cooling to a temperature below -70°C. The ampoules were open at the top, and stand well above the liquid solution, thereby isolating the solid from the liquid. Experiments were performed at temperatures between 200 and 400°C in an electric furnace equipped with the box with thick aluminum walls to reduce temperature gradients. A thermal regulator allowed the temperature to be controlled to an accuracy of approximately 1°C. The vertical temperature gradient measured with two chromel-alumel thermocouples, located in the top and bottom of the furnace was typically less than 1.0 °C · m<sup>-1</sup>. At the conditions of the experiments, liquid H<sub>2</sub>S was converted entirely to gas, which filled the autoclaves and reacted with the solid in the holders. The redox potential was buffered by the presence of the redox pair of *MeS/S* or *H<sub>2</sub>S/S*. At the end of a set of experiments, the autoclaves were quenched to room temperature, and metals condensed on the inner walls of the autoclaves (sublimates) were dissolved by acidic solutions. Acanthite (Ag<sub>2</sub>S) and covellite (CuS) condensed on the walls of the autoclaves were dissolved using 3 to 7 ml of diluted (~10%) nitric acid at temperature of 200°C. Gold was dissolved by 7 ml of aqua regia. The concentrations of silver and copper in the washing solutions were determined using graphite-furnace atomic absorption spectroscopy while those of gold were determined using the neutron activation technique at Ecole Polytechnique (Montreal). In order to ensure that no precipitates remained in the autoclaves, a blank experiment without a sample was conducted after each run.

Owing to the extremely low vapor pressures of silver and copper sulfides and of gold, compared to that of H<sub>2</sub>S, the total pressure of the system was assumed to be equal to that of pure hydrogen sulfide, and fugacities were calculated using the measured autoclave volume (minus ampoule with sample and buffer), the mass of H<sub>2</sub>S introduced and an appropriate equation of state for hydrogen sulfide gas (Rau and Mathia, 1982). Attainment of equilibrium was tested with a set of kinetic experiments of varying durations at the lowest temperature investigated. Subsequent experiments were run for durations exceeding those of the kinetic experiments, thereby ensuring that the measured metal concentrations represented equilibrium concentrations.

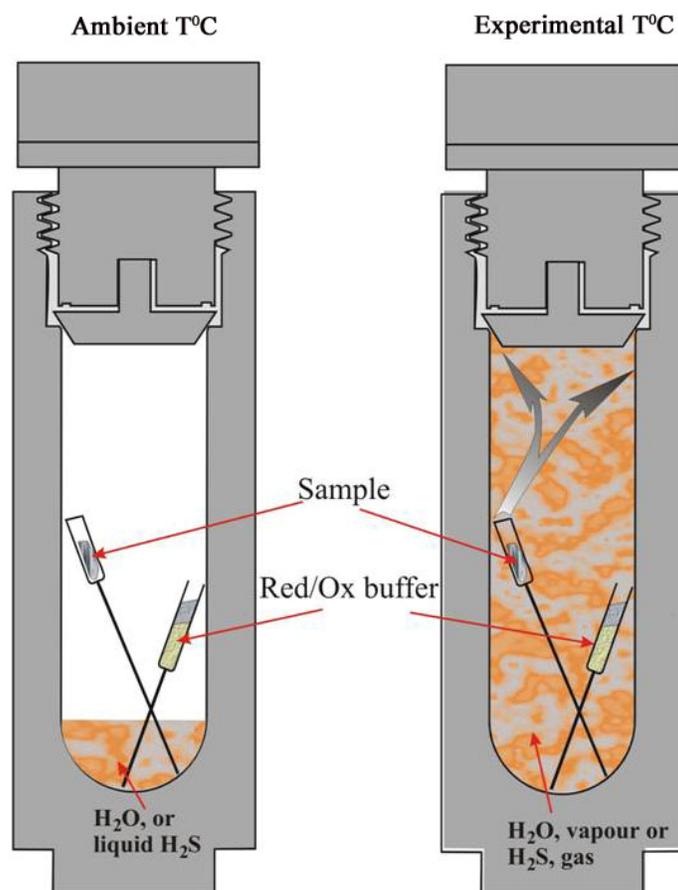


Figure 1. Schematic sketch of the experimental set-up.

A potential source of error in the method is the transport of metals across a thermal gradient as a result of the possible precipitation of the metal-bearing phases on the relatively colder walls of the autoclave during heating or quenching. In order to investigate this possible source of error, a series of blank experiments was undertaken in an atmosphere free of hydrogen sulfide (e.g., nitrogen). The mass of solid precipitated in each of these experiments was less than the detection limit of the analytical technique, thereby eliminating precipitation of metallic phases on the walls of the autoclaves as a possible source of error. Another possible source of error is partitioning of metal from the vapor phase into elemental sulfur liquid during heating or quenching. However, even though the solubility of  $\text{Ag}_2\text{S}$ ,  $\text{CuS}$  and  $\text{Au}$  in the liquid phase is much higher (by several orders of magnitude) than in the vapor the actual amounts of elemental sulfur observed in the autoclave after quenching were negligible and therefore could not have affected estimates of the

equilibrium solubility. Finally, additional minor uncertainties may be related to the estimates of pressures of hydrogen sulfide gas due to the solubility of  $\text{H}_2\text{S}$  in liquid sulfur.

## RESULTS

In order to test for solvation and the possible formation of inner-sphere Metal- $\text{H}_2\text{S}$  complexes, experiments were conducted for a range of pressures of  $\text{H}_2\text{S}$ . The results of the experiments show clearly that appreciable concentrations of *Au*, *Ag* and *Cu* can be transported in  $\text{H}_2\text{S}$ -bearing vapours, i.e., up to 7.5 ppm of *Cu* (at  $300^\circ\text{C}$ ), up to 150 ppb of *Ag* (at  $350^\circ\text{C}$ ), and up to 37 ppb of *Au* (at  $400^\circ\text{C}$ ). These values, in the case of *Au* and *CuS*, are orders of magnitude greater than predicted by volatility data (data for  $\text{Ag}_2\text{S}$  are unavailable). However, whereas  $\log f \text{Me}^{\text{gas}}$  increases linearly with  $\log P(\text{H}_2\text{S})$  in the case of *Ag* and *Au*, it is apparently independent of  $\log P(\text{H}_2\text{S})$  in the case of *Cu* (Figures 2a, 3a, and 4a).

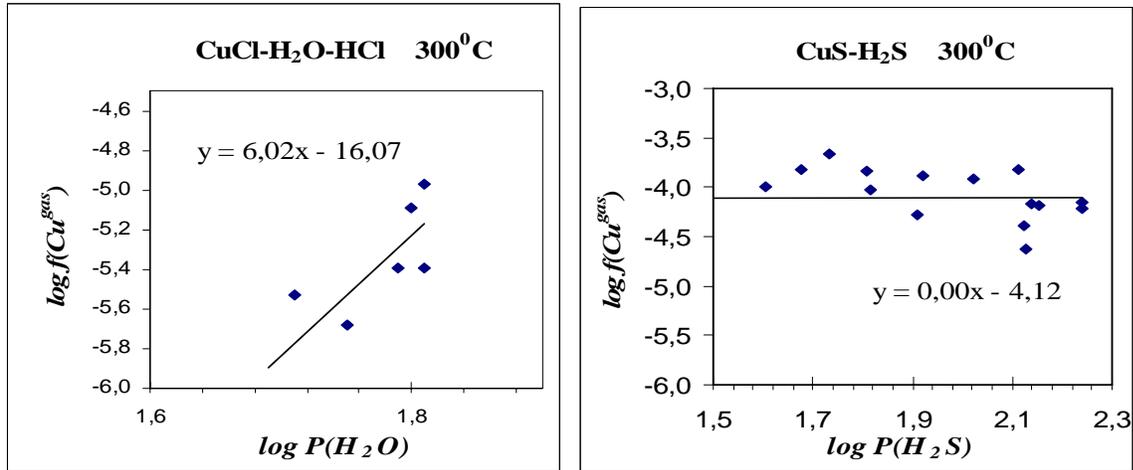


Figure 2. Experimental results for copper illustrated as plots of  $\log f(\text{Cu}^{\text{gas}})$  versus solvent pressure in the CuS-H<sub>2</sub>S (a-left) and CuS-S-H<sub>2</sub>O-HCl (b-right) systems at 300°C.

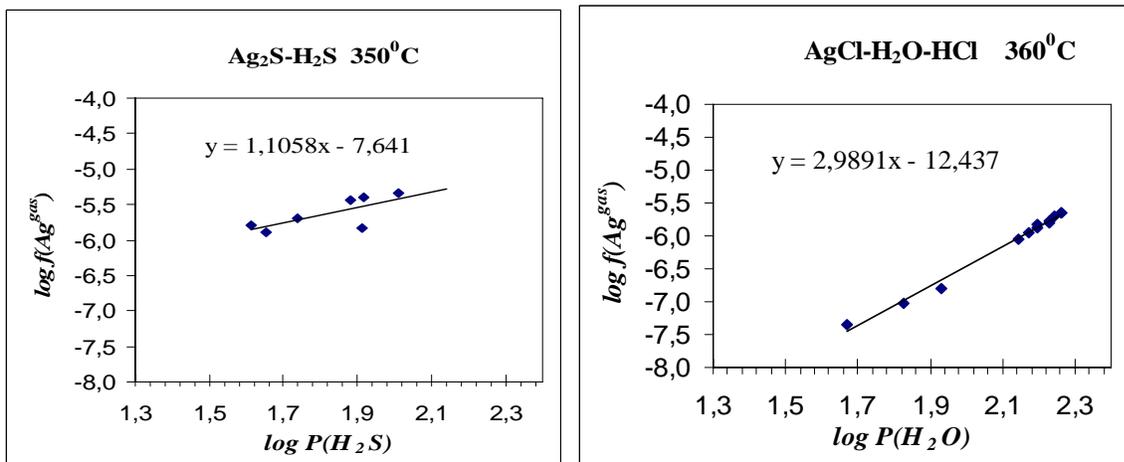


Figure 3. Experimental results for silver illustrated as plots of  $\log f(\text{Ag}^{\text{gas}})$  versus solvent pressure in the Ag<sub>2</sub>S-H<sub>2</sub>S (a-left) and Ag<sub>2</sub>S-H<sub>2</sub>O-HCl (b-right) systems at temperatures of 350°C and 360°C respectively.

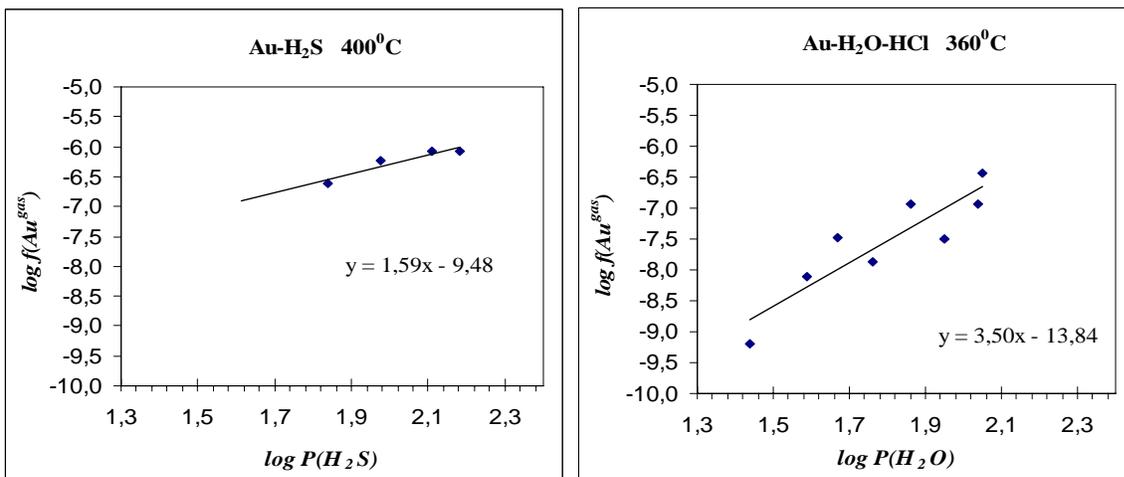
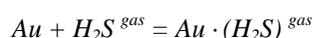
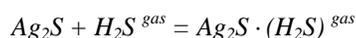


Figure 4. Experimental results for gold illustrated as plots of  $\log f(\text{Au}^{\text{gas}})$  versus solvent pressure in the Au-H<sub>2</sub>S (a-left) and Au-H<sub>2</sub>O-HCl (b-right) systems at temperatures of 400°C and 360°C respectively.

The positive correlation of  $\log f Ag^{gas}$  and  $\log f Ag^{gas}$  with  $\log P(H_2S)$  was entirely expected in light of the high solubilities of these metals, and provides clear evidence of solvation, which as discussed above, would enhance metal solubility. By contrast, the apparent independence of  $\log f Me^{gas}$  with  $\log P(H_2S)$  was totally unexpected as it suggests that the concentration of Cu in the vapor phase is controlled entirely by volatility; i.e.,  $CuS^{solid} \Rightarrow CuS^{gas}$ . This is inconsistent with the very much lower solubility predicted by the volatility data for CuS and for solids in general. However, it should be cautioned that the data for the volatility of CuS at low temperatures were extrapolated from high-temperature ( $>1000^\circ C$ ) experiments by Mills (1974), and it is therefore possible that the actual volatility may be much higher.

By analogy with our studies of the solubility of Ag and Au in the system HCl-H<sub>2</sub>O (Migdisov et al., 1999; Archibald et al., 2001, 2002), we interpret the linear relations of  $\log f Me^{gas}$  with  $\log P(H_2S)$  for Ag and Au to reflect the formation of solvated complexes of the type  $Ag_2S \cdot (H_2S)^{gas}$  and  $Au \cdot (H_2S)^{gas}$ . Furthermore, we propose that, as for the H<sub>2</sub>O-HCl system, these species have statistical solvation numbers of approximately 1 and 1.6 (determined from the slopes on Figures 3a and 4a), respectively at the corresponding experimental temperatures (350 and 400°C). The respective solvation reactions are:



Although direct comparison of these results with those obtained previously for H<sub>2</sub>O-HCl mixtures is difficult, it is worth noting that the solubility of Cu as CuS is about an order of magnitude greater than that obtained for Cu in the system H<sub>2</sub>O-HCl, and that

the solubility of Au and Ag is consistently higher than for those metals in the H<sub>2</sub>O-HCl system for  $P(H_2S) > 70$  bars (Figures 2b, 3b, and 4b).

Once additional experiments have been conducted, these data will be used to determine equilibrium constants for the formation of the above species using a methodology similar to that described by Migdisov et al. (1999), thereby permitting extrapolation of the measured solubilities to temperatures and pressures higher than those employed in our experiments. Moreover, as metal solubility in complex gases can be modeled, to a first approximation, using the Lewis-Randall rules for ideal mixtures of non-ideal gases, it should be possible to use the data in conjunction with our previous data for the solubility of Cu, Ag, and Au in chloride-bearing water vapor to predict the solubility of metals in more complex chloride- and H<sub>2</sub>S-bearing systems, such as those potentially responsible for the formation of porphyry and epithermal deposits.

The solubilities experimentally determined in this study agree well with those measured in natural vapors, i.e., the condensates of low-temperature ( $<400^\circ C$ ) volcanic gases and fumaroles, although it should be cautioned that the fugacities of H<sub>2</sub>S are significantly higher than those of natural vapors (Table 2). Nevertheless, it is interesting to note that the silver concentrations of volcanic gases at temperatures  $<400^\circ C$  are in the range 3 to 10 ppb and can reach 250 ppb in high-temperature fumaroles (Gemmell, 1987), whereas in our experiments, we obtained concentrations of up to 150 ppb Ag at a temperature of 350°C. The highest concentration of gold reported in the literature for the condensate of a volcanic gas is 32 ppb, which was collected from a fumarole on Usu volcano (Giggenbach and Matsuo, 1991), but typically these concentrations range between 1 and 3 ppb (Gemmell, 1987). The concentrations obtained in our experiments were up

Table 2. Concentrations of metal species in fumarolic gas condensates (data from Gemmell, 1987; Taran et al., 1995; Symonds et al., 1987; Bernard, 1985; Hedenquist et al., 1994)

Magma Type	Basaltic		Andesitic		Dacite	Rhyolite
	Cerro Negro	Momotombo	Kudryavy	Merapi	Mt. St. Helens	Iwo Jima
Temp(°C)	300-315	456-770	535-940	576-796	710	165-877
Au, ppb	1-2	1-24	Not analyzed	Not analyzed	0.03	1.5-3.2
Ag, ppm	0.011	0.014	Not analyzed	Not analyzed	0.00001	0.0005
Cu, ppm	0.2-0.8	0.2-8.4	0.032-0.91	0.013-1.0	0.052	0.006-0.064

to 37 ppb at 400°C. Concentrations of copper in volcanic gases are considerably higher than those of gold or silver, the highest reported value being 8.4 ppm from a high-temperature (770°C) fumarole on Momotombo (Gemmell, 1987). In our experiments, the copper concentrations were up to 7.5 ppm at 300°C.

## CONCLUSIONS

The results of this study demonstrate that gaseous hydrogen sulfide can dissolve appreciable concentrations of Cu, Ag and Au; the maximum concentrations of these metals obtained were 7.5 ppm of Cu (at 300°C), 150 ppb of Ag (at 350°C) and 37 ppb of Au (at 400°C). The solubility of metals in gaseous hydrogen sulfide is thus orders of magnitude greater than that predicted by volatility data. The complexes responsible for the transport of Ag and Au in pure H<sub>2</sub>S are likely to be  $Ag_2S(H_2S)^{gas}$  ( $T \sim 350^\circ C$ ) and  $Au(H_2S)^{gas}$  ( $T \sim 400^\circ C$ ), i.e. the solubility of acanthite (Ag<sub>2</sub>S) and native gold in gaseous H<sub>2</sub>S is governed by formation of a solvated complexes having statistical solvation numbers of approximately 1 at 350°C and 1.6 at 400°C respectively. The nature of Cu speciation is still unknown in view of the apparent independence of CuS solubility from P(H<sub>2</sub>S), but may reflect unusually high volatility of CuS. Finally, we note that our experimentally determined solubilities are in good agreement with those of natural vapors as shown by the measured concentrations of metals in the condensates of low-temperature volcanic gases and fumaroles.

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