Water-Rock Interactions, Ore Deposits, and Environmental Geochemistry: A Tribute to David A. Crerar
© The Geochemical Society, Special Publication No. 7, 2002
Editors: Roland Hellmann and Scott A. Wood

Vapor-transport of ore metals

ANTHONY E. WILLIAMS-JONES, ARTASHES A. MIGDISOV, SANDY M. ARCHIBALD, AND ZHIFENG XIAO

Dept. of Earth and Planetary Sciences, McGill University, 3450 University St., Montréal, Québec, Canada, H3A 2A7
e-mail: willyj@eps.mcgill.ca

Abstract—Recent analyses of the trace-element composition of fumarolic gases, sublimates, and vapor-rich fluid inclusions (rare) suggest that the vapor transport of metals may play a more important role in the formation of hydrothermal ore deposits than is currently recognized. Vapor transport has been modelled thermodynamically by a number of researchers who have generally concluded that it plays a relatively minor role in ore genesis. However, this modelling has been based on the assumption that the transport is controlled almost entirely by the volatility of the corresponding ore minerals, and ignores the potentially important contributions of solvation processes, e.g., interactions between water vapor and the volatilized species.

In this paper, we review the available analytical data for fumarolic gases, sublimates and vapor-rich fluid-inclusions, the experimental data on the volatility of some of the more important ore metals, and some recent experimental data produced mainly in our laboratory on the solubility of Ag, Au, Sn and Cu in chloride-bearing water vapor at temperatures up to 400 °C. Based on this review, and particularly the results of our own experiments, it appears that water vapor is capable of dissolving orders of magnitude higher concentrations of metals than is predicted from volatility calculations. In the case of several metals, notably Cu and Au, (and Hg from volatility alone) the concentrations may be comparable to or even higher than those considered necessary for an ore fluid. We conclude that vapor-transport may play an important role in the formation of a variety of ore deposit types, particularly those forming at higher temperature where vapor is a major or dominant phase in the hydrothermal system.

1. INTRODUCTION

Although there is overwhelming evidence that metallic minerals are concentrated by their precipitation from aqueous liquids in the vast majority of ore-forming hydrothermal systems, the widespread occurrence of boiling has lead some researchers to suggest that the vapor phase may also play an important role in metal transport. This is not a new idea. Indeed, as early as 1644, René Descartes, in his *Principia Philosophae*, proposed that silver-, gold- and lead-bearing veins were produced by the condensation of vapors emanating from the Earth's interior. Nicolas Steno came to the same conclusion in his *De solido intra solidum naturaliter contento* published in 1669. However, the idea was subsequently dismissed by hydrothermalists, notably Pryce (1778) and Charpentier (1778, 1799), who concluded that the main agent of metal transport is not vapor but water in its liquid state.

Pryce, from his observations of veins in the Cornish tin mining district, proposed that water, in its passage through the earth dissolves salts and metals from the surrounding rock and deposits them in fissures to form ores. Charpentier, from an extensive study of veins in the Freiberg silver-lead mines, concluded that the ores were the result of reactions between the country rocks (alteration) and the mineralizing waters. These ideas were expanded upon by Daubrée (1841) and Elie de Beaumont (1847) and by the mid 1800's the hydrothermalists' view of ore formation was firmly entrenched. Interestingly, however, Daubrée (1849) remained open to the possibility that the vapor phase might also deposit metallic minerals and conducted experiments that involved the transport of metals by vapors.

Twentieth century thinking on the genesis of hydrothermal mineral deposits has been very much dominated by the hydrothermalist perspective, i.e., that the medium of metal transport is an aqueous liquid (cf. textbooks by Lindgren, 1933; Bateman, 1950; Park and MacDiarmid, 1975; and Guilbert and Park, 1986; and review articles by Brimhall and Crerar, 1987; Barnes, 1997, Wood and Samson, 1998). In those environments where the vapor phase is volumetrically important, e.g., those of porphyry and epithermal deposits, the vapor is generally considered to be the product of boiling and to be instrumental in producing physicochemical changes favorable for mineralization (Drummond and Ohmoto, 1985).

The first modern papers to seriously attribute a role to vapor in metal transport were those of Brown (1948), who proposed that sulfidic ore deposits could be formed from volatile sulfide species, and Walker and Walker (1956), who proposed that the metals are transported predominantly as volatile chloride species. Krauskopf (1957, 1964) evaluated these proposals quantitatively using thermodynamic data, and concluded that it is feasible to transport most metals by vapor at concentrations sufficient to form economic mineral deposits. He also concluded that, while metals may occur in the vapor as both sulfide and chloride species, only chloride (as HCl) enhances metal solubility. More recently, Wood (1987) used volatility data to determine whether or not vapor transport might have been a significant factor in the formation of the Bushveld PGE deposits, and determined that the amounts of these metals that could be transported at the predicted conditions of ore deposition were insignificant. An important limitation of calculations of vapor-phase solubility based on volatility data, however, and one recognized by Wood (1987), is that they ignore the role of water vapor as a solvent.

One of the first studies to make a convincing geological case for ore formation from an aqueous vapor was by Henley and McNabb (1978). Based on data showing, 1) that intrusions associated with porphyry Cu-Mo deposits are typically emplaced at levels sufficiently shallow for the aqueous fluid to exsolve in the two-phase region, 2) that the mass of vapor exceeds that of liquid and 3) that the two fluids would be stratified by density, these authors developed a model in which the metals are transported to the site of deposition by a plume of vapor. Unfortunately, an important question that was left largely unanswered in their paper was whether the vapor phase was capable of transporting Cu and Mo in the concentrations required to form an ore deposit. The development of new micro-analytical techniques (synchrotron XRF, PIXE, LAM ICP-MS) for measuring concentrations of ore metals in fluid inclusions now offers an opportunity to address this question. Indeed, the first steps in this direction have already been made. Heinrich et al. (1992) showed, using PIXE analyses, that primary vapor-rich inclusions in a granite-hosted quartz-cassiterite vein in the Mole Granite, Australia contain ore level concentrations of Fe, Cu, Pb, and Zn (hundreds to thousands of ppm), and that the concentration of Cu exceeds that of Cu in coexisting brine inclusions. They attributed this preferential partitioning of Cu into the vapor to the formation of strong complexes with sulfur and the relatively high volatility of H_2S, and went on to suggest that, given the strong preference of Au for bisulfide over chloride ligands in hydrothermal liquids, gold might also concentrate in the vapor phase. However, instrumental limitations precluded their analyzing for gold; fortunately this is now possible using recent advances in LAM ICP-MS technology (cf. Heinrich et al., 1999).

In view of arguments by some ore deposit modelers that vapor may play an important role in metal transport, thermodynamic arguments that such transport is feasible, and recent evidence of high concentrations of metals in vapor-rich fluid inclusions, it is now timely to review what is known about the solubility of ore metals in hydrothermal vapors. Most of the data on the capacity of natural vapors to transport significant quantities of metal come from studies of active volcanoes, and particularly those reporting analyses of the condensates of fumarolic gases. Experimental data are limited largely to measurements of the volatility of metals but have been used to estimate metal solubilities in hydrothermal vapors. The few data that are available on the solubility of ore metals in water vapor are those on Au, Ag, Cu, and Sn, which are being collected from experiments performed on chloride-bearing systems at McGill University. In this chapter, we review the data that have been accumulated on the metal contents of volcanic gases and their sublimates, the experimental data that are available on vapor pressures of metals, and our own experimental data on the solubility and speciation of Au, Ag, Sn and Cu chloride-bearing aqueous vapors. Using this information, we make some tentative predictions of the possible concentrations of metals in the vapor phase of chloride-rich hydrothermal systems, and employ an idealized simulation for silver to illustrate the potential capacity of this vapor to transport metals in concentrations sufficient to play an important role in the ore-forming process.

2. METAL CONTENTS OF VOLCANIC GASES

The principal component of volcanic gases is H_2O (typically >90 mole%), which is therefore the dominant solvent for the metals. The next most important constituent is CO_2, which in some cases comprises up to 10 mole % of the total discharge (Table 2). Carbon dioxide is followed in turn by SO_2 and HCl, both of which have been reported to occur in proportions of up to 6 mole %. Other gases, the most important of which are H_2, HF, and H_2S, comprise <1 mole % of the bulk gas. Although water is the main constituent of volcanic gases, it does not necessarily follow that it entirely controls metal solubility. By analogy with liquid water, it is likely that metal solubility is greatly enhanced by complexation reactions involving CO_2, SO_2, HCl, H_2S and HF.

In contrast to the volatile species discussed above, ore metal concentrations in volcanic gases rarely exceed 10^{-5} moles (estimated from analyses of fumarole condensates). Although small by comparison with the major volatile species, these concentrations, as discussed below, are potentially significant in the context of metallic mineralization. In the section that follows we review the available literature on ore metal abundances in fumarolic gases.

Table 1. Proportions of major species in gases released by selected volcanoes. The data are taken from Symonds et al. (1994), and are reported in mole percent.

Volcano	**Momotombo**	**Poas**	**Mt. Etna**	**Merapi**	**St. Augustine**	**Showa-Shinzan**	**Mt. St. Helens**	**Usu**
Magma Type	**Thol. Basalt**		**Hawaiite**	**Andesite**			**Dacite**	
Temp (°C)	658-820	960-1045	1075	767-915	648-870	619-1015	663-802	656-678
log fO_2	-13.5 to -16.5	-9.35 to -10.82	-9.47	-12.49 to -14.86	-12.45 to-17.54	-9.93 to -18.09	-14.25 to -16.76	-16.45 to -17.20
H_2O	97.1 to 97.9	95.28 to 97.08	22.71 to 53.69	88.53 to 95.83	83.91 to 98.31	98.04 to 99.88	91.58 to 98.60	95.80 to 97.30
H_2	0.17 to 0.7	0.39 to 0.67	0.30 to 0.57	0.71 to 1.54	0.38 to 0.69	0.06 to 0.63	0.27 to 0.85	0.27 to 0.34
CO_2	1.44 to 1.47	0.53 to 1.00	17.08 to 33.93	3.26 to 7.56	0.74 to 2.40	0.01 to 0.47	0.89 to 6.94	1.70 to 3.02
CO	0.0015 to 0.0096	0.0031 to 0.01	0.36 to 0.71	0.02 to 0.16	0.002 to 0.016	0.000005 to 0.129	0.0013 to 0.06	0.0029 to 0.0050
SO_2	0.3 to 0.5	1.232 to 2.004	14.69 to 47.7	0.06 to 1.15	0.006-6.18	0.0046 to 0.043	0.067 to 0.208	0.142 to 0.258
H_2S	0.16 to 0.29	0.0055 to 0.4199	0.12 to 0.27	0.12 to 1.16	0.128 to 0.057	0.0004 to 0.109	0.099 to 0.355	0.350 to 0.714
HCl	2.68 to 2.89	0.011 to 0.121	—	0.59	0.157 to 6.04	0.021 to 0.092	0.076 to 0.089	0.0241 to 0.160
HF	0.240 to 0.259	0.011 to 0.121	—	0.4	<0.003 to 0.086	0.01 to 0.031	0.03	0.0116 to 0.0332

Table 2. Concentrations of metal species in fumarole gas condensates . All data are reported in ppm, except gold (ppb). NA: Not analyzed; -: Not detected.

Volcano	Cerro Negro [a]	Momo-tombo [a]	Momo-tombo [b]	Poas [a]	San Cristobal [a]	Tolbachik [c]	Etna [d]	Augustine [e]	Colima [f]	Kudryavy [g]	Merapi [h]	Merapi [i]	White Island [j]	Showa -Shinza [k, l]	Mt. St. Helens [m]	Usu [n, o]	Iwo Jima [p]
Magma Type	Basaltic						Alkali Basalt	Andesitic							Dacite		Rhyolite
Temp (°C)	300-315	456-770	875-886	344-852	562-588	1010	928	870	738-828	535-940	576-796	915	495	800	710	649	165-877
Hg	0.004-0.005	0.006-0.021	–	0.012-0.30	0.012-0.014	–	–	–	NA	0.015-0.340	–	–	–	–	0.020	0.0001	–
As	0.031-0.092	0.23-0.49	2.0-5.5	–	–	23.984	6.146	32.883	0.368-0.525	0.630-1.550	0.28-0.96	0.764	2.8	3.283	1.353	0.015	1.74-4.55
Sb	0.002-0.004	0.003-0.096	1.7	0.003-0.008	0.007-0.008	13.440	0.023	0.205	0.042-0.130	0.02-0.510	≤0.16	0.039	0.08	0.133	0.008	0.000	0.02-0.03
Au	1-2	1-24	5	–	–	4	24	–	1-5	NA	NA	–	NA	–	0.03	0.007	1.5-32
Ag	0.003-0.011	0.005-0.014	0.005	0.006-0.25	0.007-0.008	0.006	0.115	–	NA	NA	NA	–	NA	–	0.00001	0.0005	–
Cu	0.2-0.8	0.2-8.4	0.1-1.5	0.1-0.6	0.6	5.962	–	0.194	0.440-0.931	0.032-0.91	0.013-1.0	0.034	0.03	0.021	0.052	0.012	0.006-0.064
Pb	NA	1.9-7.0	0.05-0.6	0.8-5.4	0.4-0.5	0.572	11.999	2.205	0.078-0.480	0.110-9.7	0.32-1.6	1.207	0.18	0.068	0.533	0.006	0.24-1.77
Zn	0.3-0.6	0.4-7.6	0.4-6.0	0.5-8.6	0.9-1.1	9.743	12.620	1.855	4.970-8.140	0.25-13.5	3.6-82	7.935	1.2	0.347	0.019	0.040	0.027-0.24
Sn	0.78-0.98	1.1-2.4	1	1.4-3.9	1.4-1.6	0.092		–	NA	0.1-0.38		–	NA	–	–	7.213	0.2-0.78
W	–	–	–	–	–	–	–	–	NA	0.002-0.060	0.05-0.13	0.054	–	–	0.003	0.003	–
Mo	0.18-0.27	0.15-0.5	2	–	–	–	–	0.766	0.091-0.182	0.002-0.270	0.08-2.8	0.093	0.003	0.049	0.094	0.058	0.005-1.07

a) Gemmell, 1987; b) Quisefit et al., 1989; c) Menyailov and Nikitina, 1980; d) Le Guern, 1988; e) Symonds et al., 1991; f) Taran et al., 2000; g) Taran et al., 1995; h) Symonds et al., 1987; i) Le Guern et al., 1982; j) Tedesco and Totain, 1991; k) Nemeto et al., 1957; l) Symonds, 1992; m) Bernard, 1985; n) Giggenbach and Matsuo,1991; o) Le Guern (unpub.); p) Hedenquist et al., 1994

2.1. Fumarolic Gas Condensates

Analyses of the condensates of volcanic gases indicate that they commonly contain appreciable concentrations of a variety of base and precious metals (Table 1). The distribution of these metals in a given volcano depends on the composition of the associated magma. For example, volcanic gases produced by basaltic magmas will tend to have higher concentrations of copper than those produced by dacitic magmas. By contrast, volcanic gases derived from dacitic magmas will have relatively high concentrations of tin and tungsten. As discussed below, temperature is also an important factor in determining the metal composition of volcanic vapors.

Examples of basaltic volcanoes include Etna (Italy), Momotombo and Cerro Negro (Nicaragua), Poas (Costa Rica), Tolbachik (Russia), and Kilauea (USA). Concentrations of copper analyzed in fumarolic condensates range up to 8.4 ppm, the highest value being from Momotombo (Gemmell, 1987). Significantly, this sample was taken from a fumarole discharging gases at a temperature of 770 °C, the highest temperature recorded by Gemmell (1987) for the fumaroles sampled by him at Momotombo; the other fumaroles had temperatures ranging down to 456 °C and concentrations ranging between 0.2 and 0.4 ppm. Other metals having high concentrations in volcanic gases emanating from basaltic magmas include, Zn, Pb, Sb, As, Ag, and Au. With the exception of As, Sb, and Ag, the highest concentrations reported for these metals are all from Etna (Zn, 13 ppm; Pb, 12 ppm; and Au 24 ppb; Le Guern, 1988). It should be noted, however, that Momotombo is tied with Etna in having the highest reported gold concentration (Gemmell, 1987). The highest concentrations for As (24 ppm) and Sb (13 ppm) are from Tolbachik (Menyailov and Nikitina, 1980) and for Ag (250 ppb) are from Poas (Gemmell, 1987). It is probably significant that the data for Etna and Tolbachik were from fumaroles discharging gases at temperatures of 928 °C and 1010 °C, respectively, two of the highest fumarole temperatures ever recorded.

Studies of andesitic volcanoes, e.g., Merapi in Indonesia (Symonds et al., 1987), Kudryavy in Russia (Taran et al., 1995), White Island in New Zealand (Tedesco and Totain, 1991), Colima in Mexico (Taran et al., 2000) and Augustine in Alaska (Symonds et al., 1992), indicate that the gases are characterized by high concentrations of Zn, Pb, Mo, W, As, Au, and Hg (there are no data for Ag). The highest concentrations of Zn, Pb, and As, are comparable with those of gases from basaltic volcanoes. However, the concentrations of Mo and Hg are substantially higher, up to 3 ppm (Merapi; Symonds et al., 1987) and 340 ppb (Kudryavy; Taran et al., 1995), respectively.

In contrast to those of basaltic and andesitic volcanoes, the gases of felsic volcanoes (rhyolitic and dacitic), e.g., Mount St. Helens in the USA (Bernard and Le Guern, 1986), Usu (Giggenbach and Matsuo, 1991; Le Guern, unpublished data) and Satsuma Iwo-jima, both in Japan (Hedenquist et al., 1994), only have high concentrations of Sn, Mo and Au. Volcanic gases from Usu have the highest concentration of tin (7 ppm; Giggenbach and Matsuo, 1991; Le Guern, unpublished data) and those from Satsuma Iwo-jima have the highest concentrations of Mo (up to 1 ppm) and Au (32 ppb) reported from any volcano (Hedenquist et al., 1994).

2.2. Volcanic Gas Sublimates

Further insights into the role of the vapor phase in transporting metals can be gleaned from fumarole sublimates. The first studies of this type were carried out by Bunsen (1853) who described sublimates from Icelandic volcanoes, and drew attention to the potential importance of HCl and ammonia as possible agents of metal transport. Deville (1862) subsequently provided detailed observations of sublimates from Italian volcanoes and noted that the fumaroles and associated sublimates changed with distance from the volcanic center. The first study that attempted to relate sublimate mineralogy to temperature was that of Lacroix (1907), who reported that fumaroles with temperatures in excess of 650 °C deposited mainly halite, sylvite and aphthitalite ($K_3Na(SO_4)_2$), whereas lower temperature fumaroles (below 650 °C) also deposited sulfides and oxides. At temperatures ≤ 300 °C the variety of minerals decreased, and the sublimates consisted mainly of salammoniac (NH_4Cl), and below 100 °C only gypsum, native sulfur and opal. Somewhat different observations were made by Zeis (1929) in the Valley of 10,000 Smokes. He noted that the principal phases in the high-temperature sublimates were magnetite, ilsemannite ($Mo_3O_8 \cdot nH_2O$), sphalerite, chalcocite, covellite and galena, and that the low-temperature fumaroles consisted primarily of native sulfur and a substance, which he described as "orange arsenic sulphide". The most comprehensive modern studies of volcanic sublimates are those Naboko (1964), on several Kamchatka volcanoes and Stoiber and Rose (1974) on Central American volcanoes. The latter paper also provided an extensive review of sublimate mineralogy for numerous volcanoes in other parts of the world, and noted the occurrence of the following ore minerals in addition to those mentioned above; cassiterite, barite, pyrite, pyrrhotite, orpriment, realgar, and galena-bismuthinite. An important mineral not reported by either Naboko (1964) or Stoiber and Rose (1974) is native gold. However, Fulignati and Sbrana (1998) have since reported the presence of prismatic crystals of this mineral in sublimates of the high-temperature silica zone of a fumarole near the rim of the La Fossa volcano, Vulcano, Italy. These researchers also documented the presence of native tellurium containing minor quantities of selenium. Finally, Korzhinsky et al. (1994) reported the occurrence of rhenium sulfide as 1- to 2-mm thick coatings containing flakes with plate-like morphology on rocks around some high temperature fumaroles at Kudryavy volcano.

Some important limitations of the above studies are that: 1) the fumarole temperatures did not necessarily represent the temperatures at which the sublimates formed; 2) the condensates were rapidly oxidized by the atmosphere, which changed the resulting mineralogy of the sublimates; and 3) interaction of the gases and their condensates with the wall-rock may have produced sublimates substantially different in composition to those initially in equilibrium with the fumarolic gases. In order to overcome these limitations, Le Guern and Bernard (1982) introduced the silica-tube method, which involved inserting a long (≥ 1 m) quartz-glass tube deep into the fumarole and leaving it there for periods ranging from days to months. During this time, sublimates precipitate along the length of the tube, and are zonally distributed in respect to mineralogy due mainly to gradients in temperature. These gradients can be measured accurately, and may correspond to temperatures as great as 1000 °C at the bottom of the tube, and as low as 100 °C at the top. At temperatures <100 °C, condensation of water vapor precludes further sublimate formation. These silica-tube experiments make it possible to reliably relate sublimate minerals to temperature, and thereby avoid the contamination problems mentioned above. In the paragraphs below we document the data available from silica tube experiments conducted on volcanoes of a variety of magma types.

The main high-temperature ore minerals are magnetite, molybdenite, greenockite (CdS) and wolframite, which precipitate only at temperatures >450 °C (Fig. 1). Several other ore minerals, e.g., chalcopyrite, sphalerite, and pyrite, occasionally precipitate at temperature >450 °C but generally form at lower temperature. By contrast, galena, native arsenic, tellurium and selenium, and several Pb-bearing sulfosalts, with rare exception, precipitate at temperatures <450 °C. Some important ore metals, notably gold and silver, are in such low concentrations that, although detected chemically, they are rarely observed as minerals in silica-tube experiments. Important exceptions are the observations of crystals of native gold in silica-tube experiments at Colima (550 and 600 °C; Taran et al., 2000) and Kudryavy (Shmulovich and Churakov, 1998). The Kudryavy volcano is also important as the location of the first discovery of rhenium sulfide (see above). In an experiment of two months duration, rhenium sulfide (ReS_n) was also observed to form in silica tubes together with molybdenite and a solid solution intermediate in composition between the Re sulfide mineral and molybdenite (Korzhinsky et al., 1994).

Among non-ore minerals, the most important at high temperature, and the dominant constituent of many sublimates, is cristobalite. The next most important non-ore minerals precipitated at high temperature are halite and sylvite. However, in contrast to the other minerals discussed above they commonly precipitate along the complete length of a silica tube, i.e., over a very wide interval of temperature. For example, at Momotombo, the range over which these phases precipitated was 860 °C to 200 °C (Quisefit et al., 1989). Other important non-ore minerals precipitating at high temperature are thenardite (Na_2SO_4), aphthitalite ($K_3Na(SO_4)_2$) and salammoniac (NH_4Cl), which like halite and sylvite also persist to low temperature. An observation of possible significance with respect to salammoniac is that the variety of ore minerals is much higher in sublimates containing this mineral than in sublimates from which it is absent (Figure 1). The only non-ore mineral restricted to low temperature is native sulfur, which deposits as a liquid at temperatures <200 °C and as a crystalline solid at temperatures <120 °C.

Important conclusions that can be drawn from the sublimate mineralogy are: 1) the deposition of minerals like molybdenite, chalcopyrite, sphalerite, greenockite, and pyrite at high temperature suggests that only condensates collected from high-temperature fumaroles provide reliable estimates of the concentrations of the corresponding metals in volcanic gases; 2) the predominance of halite and sylvite suggest that chloride complexation may play an important role in metal transport in volcanic gases; 3) the common occurrence of thenardite and salammoniac suggest that sulfate and ammonium may also be important ligands for metal complexation; 4) the variation in mineralogy with magma type and tectonic setting is evidence for corresponding changes in the chemistry of the volcanic gases; and 5) the variety of ore minerals precipitated with salammoniac and the limited variety with halite and sylvite may indicate that ammonium is able to complex a significantly larger number of metals than chloride.

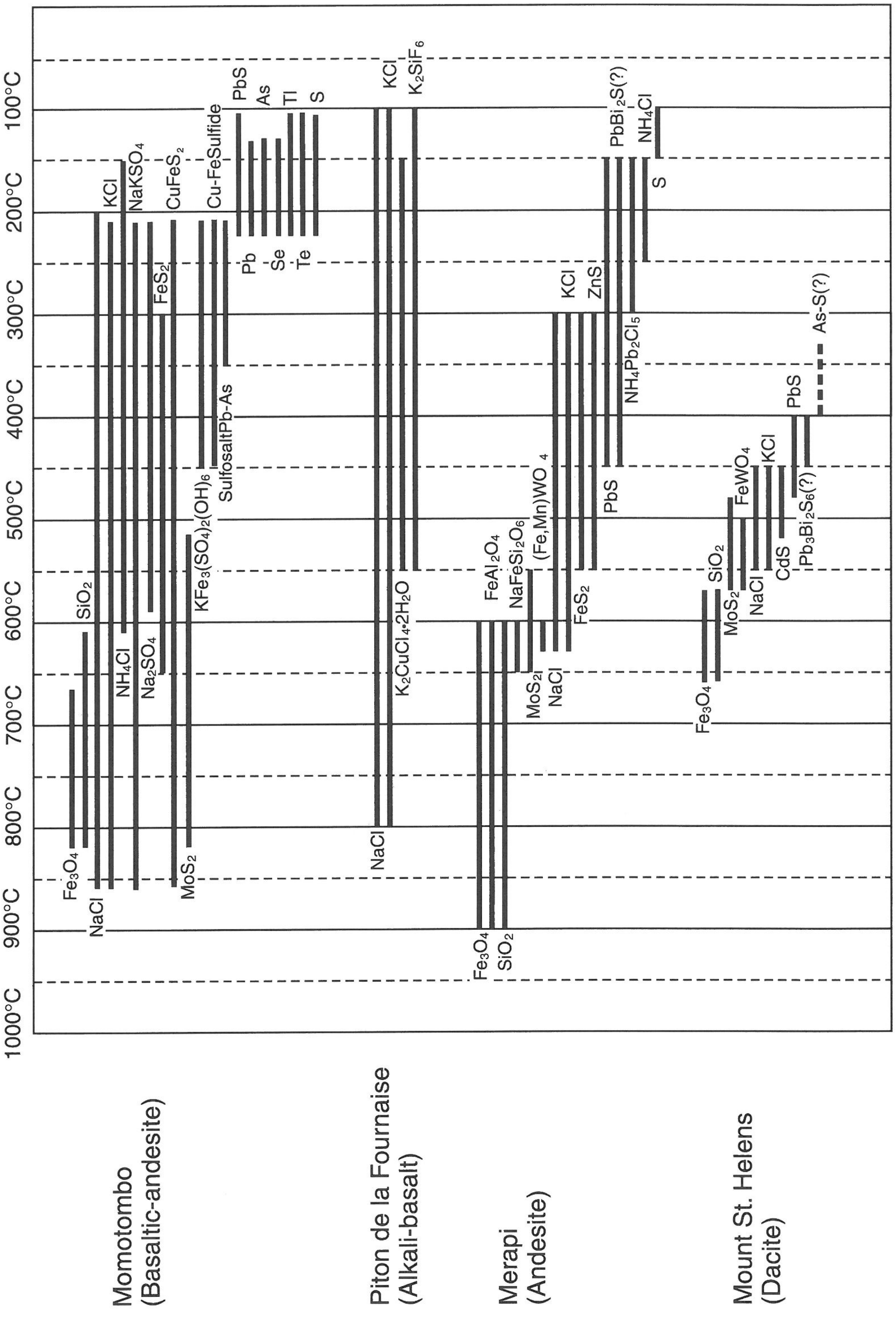

Figure 1. The sublimate mineralogy for silica-tube experiments on fumaroles of four compositionally different volcanoes. Data taken from Quisefit et al., 1989 (Momotombo); Toutain et al., 1990 (Piton de la Fournaise); Le Guern and Bernard, 1982, Bernard, 1985, and Kavalieris, 1994 (Merapi); Bernard and Le Guern, 1986 (Mount St. Helens).

3. THERMODYNAMIC MODELING OF NATURAL GASEOUS SYSTEMS

As discussed in the previous section, measured concentrations of metals in natural volcanic gases vary widely, and depend in large part on the metal considered. Some of this variation is undoubtedly due to differences in natural abundances of the elements. However, a large part of the variation relates to the capacity of a metal to form stable gaseous compounds.

A number of researchers have attempted to estimate metal concentrations in volcanic gases thermodynamically using data on metal volatility and the initial composition of the fluid (e.g., Symonds et al., 1987; Wood, 1987; Spycher and Reed, 1989; Symonds and Reed, 1993; Getahun et al., 1996). These estimates are based on the assumption that for any given temperature the concentration of a metal in the gaseous phase is equal to or less than that required to saturate the vapor with the least volatile mineral containing the metal. They also take into account chemical reactions in the gaseous phase and incongruent evaporation of the minerals. The latter notwithstanding, it follows that metals of highly volatile minerals will saturate at relatively low temperature and those of weakly volatile minerals will saturate at high temperature, leading to a zonation of metals. The concentration of an element in the gas phase of a natural system is thus, to a first approximation, a simple function of the volatility of the corresponding mineral. This volatility can be determined from experimental studies of the partial pressure and composition of the vapor over solid or liquid phases. Data of this type are compiled for many ore and related elements in handbooks of thermochemical data such as the *Gmelin handbook of inorganic chemistry* (periodical), the *Thermodynamic properties tables* of Pankratz (1982, 1984, 1987), *The NBS tables of chemical thermodynamic properties* (Wagman et al., 1982), and *Thermodynamic properties of gases* by Rivkin (1988). In the paragraphs below we review briefly the volatility of a small selection of the more important elements in hydrothermal systems.

3.1. Highly Volatile Elements

Mercury is the most volatile metal in natural systems, and its saturated vapor pressure has been experimentally and theoretically determined over a wide range of temperature using a variety of techniques (e.g., Shpil'rain and Nikanorov, 1971; Cordes et al., 1971; Ambrose and Sprake, 1972; Hubbard and Ross, 1982). Several equations of state have also been developed for mercury vapor (e.g., Alcock et al., 1984). The partial pressure measured over liquid mercury varies from 4×10^{-3} bar at 150 °C to 0.3 bar at 300 °C, which is 3-4 orders of magnitude greater than its vapor pressure over cinnabar (Kulakov, 1975; Ferro et al., 1989).

The next most volatile metal among those commonly occurring in nature is arsenic. Minerals such as orpiment (As_2S_3) and realgar (As_4S_4) are characteristic of low-temperature hydrothermal processes and are commonly found in the sublimates of volcanic gases or post-volcanic fumaroles. The vaporization of realgar has been investigated by mass spectrometry and mass-loss torsion-effusion (Brittain et al., 1983; Munir et al., 1971) as well as by the Knudsen method (Pashinkin et al., 1982; Steblevskii et al., 1986) and Raman spectroscopy (Ozin, 1969; Rogstad, 1972). These studies showed that the primary constituent of the vapor of crystalline As_4S_4 is $As_4S_4^{gas}$, but that minor proportions of $As_4S_5^{gas}$, $As_4S_3^{gas}$, $As_2S_3^{gas}$, $As_2S_2^{gas}$, and S_2^{gas} are also present. The vaporization of orpiment has been investigated using high-temperature mass spectrometry (Lau et al., 1982; Pashinkin et al., 1974), mass spectrometric Knudsen effusion, and thermogravimetric Knudsen effusion (Faure et al., 1973), and measured using a quartz-membrane manometer (Ustyugov et al., 1968). As in the case of realgar, $As_4S_4^{gas}$ was found to be the dominant component of the vapor There were also appreciable proportions of $As_2S_3^{gas}$, and S_2^{gas}, and minor $As_4S_5^{gas}$. The partial pressure of the vapor over realgar varies from 5×10^{-5} to 1 bar at temperatures from 150 to 600 °C, respectively, and over orpiment varies from 1×10^{-5} to 0.5 bar for the same temperature range (Mills, 1974)

Antimony, like As, is also relatively volatile, and this volatility has been investigated extensively through studies of the vaporization of stibnite (Sb_2S_3) (e.g., Hsiao and Schlechten, 1952; Sullivan et al., 1970, Gospodinov et al., 1970). The vapor phase over crystalline and molten stibnite is composed mainly of SbS^{gas}, $Sb_2S_3^{gas}$, and S_2^{gas}. Other components that are present in the vapor include: $Sb_2S_2^{gas}$, $Sb_3S_2^{gas}$, $Sb_3S_3^{gas}$, $Sb_3S_4^{gas}$, $Sb_4S_4^{gas}$, $Sb_4S_5^{gas}$ (Sullivan et al., 1970; Faure et al., 1972; Novoselova and Paschinkin, 1978). The measured vapor pressure over stibnite varies from 10^{-10} to 10^{-3} bar at temperatures from 150 to 600 °C, respectively.

Among the important non-metallic elements occurring in hydrothermal mineral deposits, sulfur is without question the most volatile. The low temperature of melting of sulfur at standard pressure (115 °C) and the low critical temperature of sulfur (444 °C) ensure its high stability in the gas phase. An important characteristic of sulfur vapor is that it displays a high level of polymerization. Sulfur polymers up to S_8 have been reported from experimental studies (Steudel, 1984; 1987), with those of higher order ($S_6 - S_8$) predominating at lower temperature (Rau et al., 1973;

Steudel, 1984; 1987; Lenian et al., 1988). At higher temperatures, S_2^{gas} is the dominant form of sulfur, although there is some disagreement over the temperature at which it becomes dominant. Thus, while Rau et al. (1973) report that the S_2^{gas} polymer predominates at temperatures above 800 K (526.85 °C), Lenian et al. (1988) concluded that the lower temperature limit of S_2^{gas} predominance is 600 K (326 °C). The partial pressure of sulfur vapor over liquid sulfur varies from 10^{-4} bars at 150 °C to 10^{-2} bars at 300 °C.

3.2. Weakly Volatile Elements

In comparison with the metals discussed above, minerals containing copper, gold, and silver have extremely low volatility at temperatures commonly encountered in ore-forming hydrothermal systems (<600 °C). Early studies of Cu(I) chloride volatility were conducted by Brewer and Lofgren (1950) at very high temperature (715 °C - 1067 °C) and yielded partial pressures between 0.5×10^{-4} to 6.6×10^{-4} bar. However, the data do not vary systematically with temperature, and total pressure varied significantly. We have estimated the partial vapor pressures of copper (I) chloride ($P_{CuCl^{gas}}$) over the corresponding solid based on data presented in Pankratz (1984) as 2×10^{-15} and 2×10^{-7} bar at 300 °C and 600 °C, respectively. The vaporization of copper (II) has been studied by Dienstbach et al. (1977) using UV/visible and Raman spectroscopy. These authors showed that at elevated temperatures the vapor contains $CuCl^{gas}$, $CuCl_2^{gas}$, and $Cu_2Cl_4^{gas}$.

Owing to the extremely low partial pressure of vapor over native gold, experimental investigations of gold volatility have been performed in a chlorine atmosphere (James and Hager, 1978; Tagirov et al., 1993) and the partial pressures obtained can not be related directly to conditions in natural hydrothermal systems. Based on the results of these studies, gold generally evaporates in the form $Au_2Cl_6^{gas}$ and $AuCl^{gas}$, and at 300 °C and P_{HCl} of 0.4 bars, yields vapor pressures on the order of 10^{-36} bars. Several groups of researchers have reported experimental data on the partial pressures of silver chloride compounds over crystalline and liquid AgCl (e.g., Hildenbrand and Lau, 1996; Tagirov *et al.*, 1993; Gräber and Weil, 1972). Silver chloride evaporation proceeds mainly with the formation of $AgCl^{gas}$ and lesser proportions of $Ag_3Cl_3^{gas}$ (Gräber and Weil, 1972; Visnapuu and Jensen, 1970; Chang and Toguri, 1974). The estimated partial pressures of $AgCl^{gas}$ over liquid (molten) AgCl are 10^{-7} bar at 500 °C and 5×10^{-6} bar at 650 °C.

Owing to the importance of NaCl in natural systems, we decided to also review briefly the volatility of halite, which has been investigated extensively over a wide range of temperatures. These studies have shown that the vapor over halite contains polymers of $Na_nCl_n^{gas}$ dominated by the monomer $NaCl^{gas}$ and the dimer $Na_2Cl_2^{gas}$. (e.g., Kvande, 1979; Ewing and Stern, 1974; Lukashenko et al., 1970; Pitzer, 1996). The measured partial pressures of the vapor over sodium chloride range from 1.9×10^{-15} bar at 300 °C, and 2×10^{-7} bar at 600 °C.

3.3. Application of Volatility Data

Volatility data provide an important starting point from which to model vapor-phase transport of elements in nature, and have been used by numerous authors to estimate the trace-element composition of volcanic gases and that of the vapor phase in several active geothermal systems. These models have had some success in predicting the sequences of mineral zonation in the sublimates of volcanic gases and in the case of geothermal systems predicted metals that could potentially have been deposited predominantly from the vapor phase instead of from the liquid. Thus, for example, Quisefit et al. (1989), in simulating the formation of silica-tube sublimates from Momotombo, were able to correctly predict the high-temperature (>650 °C) deposition of native gold, chalcocite and molybdenite, if the corresponding metals were transported as Au-S, Cu-Cl, Cu-Br and Mo-F species. However, they had difficulty in simulating the sequence of mineral deposition at lower temperature. Similarly, although Symonds et al. (1987) were able to correctly predict the high-temperature formation of molybdenite, they overestimated the temperature of sphalerite deposition and failed to predict the deposition of galena despite the fact that this was the principal mineral in sublimates formed at intermediate temperature.

The principal conclusion that can be drawn from the application of volatility data to the behavior of metals in geothermal systems is that, with the exception of mercury, none of the common ore metals fractionate sufficiently into the vapor phase for the latter to constitute an important agent of ore metal transport. Although elements with high volatility like arsenic and antimony are predicted to achieve high concentrations in dry systems, and might therefore be good candidates for vapor-transport in geothermal systems (liquid-vapor), their much higher solubility in the liquid phase (Smith et al., 1987; Spycher and Reed, 1989) precludes their significant fractionation into the vapor phase. Indeed, Spycher and Reed (1989) note that at temperatures ≤300 °C a Broadlands-type geothermal fluid must undergo at least 97% boiling for there to be appreciable concentration of these elements in the vapor phase.

3.4. Vapor-Phase Hydration/Solvation

An important limitation of the modeling discussed in the previous section is that reliance on component fugacities to describe the behavior of gas species ignores potentially important low-energy interactions between the components dissolved in the gas and the gas-solvent. As discussed below, these interactions can significantly enhance the capacity of the vapor to transport metals, and, in some cases, ignoring these interactions may lead to underestimation of the solubility of the metal in the vapor phase by many orders of magnitude.

One of these interactions is predicted to involve the formation of ion-water clusters and has been studied experimentally by several authors (Kebarle, 1975; Davidson and Kebarle, 1976; Kebarle et al., 1977; Sunner et al., 1981; Blades et al., 1990; 1995). The results of these studies suggest that the presence of such clusters may change the properties of dissolved components and solvents sufficiently to allow components with very low volatility to be relatively soluble in water vapor. This explains why the solubility of halite in water vapor, which has been measured by numerous researchers, is several orders of magnitude higher than predicted from volatility data (Styrikovich, 1969; Martynova, 1964; Sourirajan and Kennedy, 1962; Galobardes et al., 1981; Bischoff and Rosenbauer, 1986; Alekhin and Vakulenko, 1987; and Armellini and Tester, 1993). The solubility of NaCl can therefore be described by the following solvation-type reaction:

$$\text{Halite} + n\cdot H_2O^{gas} \leftrightarrow NaCl\cdot(H_2O)_n{}^{gas} \qquad (1)$$

which involves formation of $NaCl$-H_2O clusters; n, the hydration number, varies between 1 and 4. A more complex and potentially more accurate cluster-based statistical mechanical model for NaCl-solvation has been presented by Pitzer and Pabalan (1986).

4. EXPERIMENTAL INVESTIGATIONS OF METAL SOLUBILITY IN WATER VAPOR

In view of the need for experimental data on the solvation of metals by water vapor, we have initiated investigations of a number of systems involving economically important ore-forming metals and elements. As a result of this work, preliminary data are now available for the systems $AgCl$-HCl-H_2O, Au-HCl-H_2O, SnO_2-HCl-H_2O, and $CuCl$-HCl-$NaCl$-H_2O.

Experimental studies of the speciation of metals in water vapor can be performed either in dry-vapor systems, i.e., systems undersaturated in respect to liquid water, or in liquid-vapor systems. The former systems involve only solid-vapor interactions, whereas in the latter systems the metals are partitioned among solid, liquid, and vapor. Owing to the overwhelming predominance of molecular species (uncharged) in dry water vapor, investigation of metallic mineral solubility in "dry" systems is associated with fewer technical problems and the number of controlling parameters is smaller. However, it should be noted that the speciation in "dry" systems may differ significantly from that in "liquid-vapor" systems unsaturated with respect to a solid. This results from the fact that in systems unsaturated with respect to solid, the activity of the vapor species is correspondingly lower. We have conducted experimental studies in both kinds of systems. The systems $AgCl$-HCl-H_2O, Au-HCl-H_2O, and SnO_2-HCl-H_2O were investigated in the "dry" state, while the system $CuCl$-HCl-$NaCl$-H_2O was investigated along the liquid-vapor saturation curve. The latter system was also saturated with respect to a solid. Future experiments are planned to investigate metal partitioning between liquid and vapor in systems unsaturated with respect to a solid.

4.1. Methods

4.1.1. Dry systems

The experimental method is similar to that employed by Migdisov et al. (1998, 1999). Experiments were carried out at temperatures between 300 and 360 °C in an electric furnace (internal diameter 15 cm, height 50 cm) equipped with thick aluminum or copper walls to reduce temperature gradients. A thermal regulator allowed the temperature to be controlled to an accuracy of approximately 0.5 °C. Before runs, the temperature gradient in the experimental system was measured with 3 thermocouples, located at the top, bottom and center of the furnace. The vertical temperature gradient was typically in the range 1.0 to 2.5 °C m^{-1}, but during the first 2 to 3 hours it was between 8 and 20 °C m^{-1} due to the initially cold state of the autoclave. Temperature was measured with two chromel-alumel thermocouples, located in the top and bottom of the furnace.

The experiments were performed in titanium autoclaves, and involved measuring the solubility of synthetic chlorargyrite (AgCl), or cassiterite (SnO_2) or native gold in HCl-bearing water vapor. The autoclaves were constructed from titanium alloy (grade 2 ASTM B348) obtained from Titanium Industries, Inc. (Figure 2). Each autoclave was conditioned initially with nitric acid to produce a protective layer of TiO_2 on the internal surface. Autoclave volumes (100 cm^3) 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 ±0.1 g. Autoclaves were

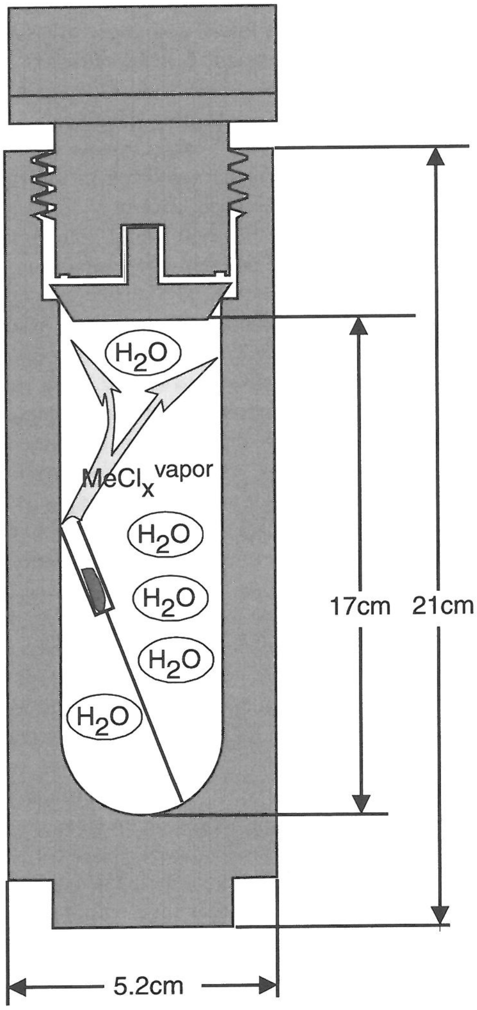

Figure 2. A section through a titanium autoclave of the type used in this study. The autoclaves were constructed from titanium alloy (grade 2 ASTM B348).

loaded with pre-weighed quartz ampoules containing several milligrams of one of the above solids (AgCl, SnO_2, or Au).

The ampoule was suspended near the top of the autoclave using a quartz holder (Fig. 2). A known mass of HCl solution, prepared using distilled nanopure (18-MΩ-cm) water and Optima-grade HCl from Fisher Scientific, was placed in the bottom of the autoclave. The HCl was added in quantities that yielded solutions with pH values of 1.5 to 4.0. Care was taken to ensure that the quantity of HCl solution was insufficient to saturate the system with liquid at the experimental conditions, and that dissolution of the metal was restricted to the vapor. Owing to the extremely low vapor pressures of silver, gold and tin chlorides, compared to that of water vapor, the total pressure in a run was assumed to be equal to the pure water vapor pressure, and was calculated using the measured autoclave volume and the equation of state for water of Kestin et al. (1984).

The redox potentials of the gold and tin systems were buffered by a MoO_2/MoO_3 oxide mixture. One to two grams of this mixture (MoO_2:MoO_3 = 1:1) were placed in a quartz glass tube open at one end, which was suspended in the autoclave. The fO_2 values at the experimental conditions were calculated from data given in Pankratz (1982). This buffer was chosen because of its higher stability in an HCl atmosphere compared to more commonly used Ni/NiO or Fe-containing buffers. Buffer stability calculations were performed using data summarized in Pankratz (1982, 1984). These calculations showed that solid Mo-chlorides are orders of magnitude less likely to form than Fe and Ni chlorides at the conditions investigated. However, the HCl concentration may have varied as a result of interaction between the buffer mixture and gaseous HCl, and consequent removal of HCl from the system. The pH of the condensate was therefore measured after each run. The partial pressure of HCl at the experimental conditions was calculated using the measured pH of the condensate and an assumption that HCl^{gas} behaves ideally.

Before a run, a stream of nitrogen was passed through the autoclave for 20 to 40 minutes to remove atmospheric gases. After the run, the autoclave was air-cooled to room temperature (20 to 30 minutes), and the condensates were collected for analysis. The ampoule was dried at 120°C for 1 to 2 hours to remove water condensed on its walls and on the solid, and was then re-weighed. Chlorargyrite (AgCl) condensed on the walls of the autoclave was dissolved using 3 to 7 ml of nitric acid (pH = 0.5). Gold was dissolved by 5 ml of aqua regia, and tin by a 0.5 HCl solution. The concentrations of dissolved silver and tin in the condensates and washing solutions were determined by graphite furnace-atomic absorption spectroscopy and inductively coupled plasma-mass spectrometry (Activation Laboratories Ltd.), while those of gold were determined by neutron activation at Ecole Polytechnique (Montreal).

A potential source of error in the method is prequench condensation of the solid phase on the cold parts of the autoclave during runs. The latter may occur if the sample is at a higher temperature than other internal parts of the autoclave, notably the walls, and could lead to considerable overestimation of metal solubility in the vapor phase. However, since the autoclave was externally heated, it follows that temperatures were highest at the walls and lowest in the center, i.e., the solid reagent was located in the coldest part of the autoclave. Thus, it is very unlikely that any significant condensation occurred during heating and at the experimental temperature. On the other hand, additional quantities of metal could have been released from the solid during quenching, and condensed on the cooler walls of the autoclave together with metal, which had been dissolved in the vapor at the end of the experiment. Another possible source of error is the partitioning of metal from the vapor phase into the liquid (water) during heating or quenching. Owing to the much higher solubility of AgCl, SnO_2 and Au in the liquid phase (by several orders of magnitude higher), this could result in gross overestimation of the solubility of these metals in the vapor phase.

In order to investigate the possibility of significant experimental error due to condensation of metallic species on the walls of the autoclave, we undertook a series of blank experiments in an atmosphere free of water vapor (nitrogen atmosphere, P = 1-80 bar). The mass of solid sublimed in each of these experiments was less than the detection limit of the analytical technique, thereby eliminating the possibility of error due to metallic species condensation.

The issue of experimental error, particularly due to partitioning of components into the liquid water, was further investigated through a series of "kinetic runs". Experiments were carried out under constant water pressure for periods ranging from 1 to 15 days. For all metal species investigated, equilibrium was attained in less than 14 days. Once equilibrium was attained, solubilities were reproducible to approximately ±15-20 %. If there had been significant condensation of metallic species onto the autoclave walls or this species had been partitioned into the liquid water during the experiments, none of the experimental results would have been reproducible, and consequently equilibrium would never have been attained.

4.1.2. *Wet system*

Experiments measuring the solubility of Cu in water vapor were conducted in a subcritical liquid-saturated CuCl-HCl-NaCl-H_2O (NaCl:HCl = 9:1) system at temperatures of 380 and 400 °C, and total chloride concentrations from 0.01 to 5 *M*. In order to study the partitioning of copper between aqueous vapor and liquid, it is desirable to sample simultaneously the vapor and liquid phases at equilibrium. However, for a variety of reasons, this was not practical in the present study. Owing to the low density of the vapor, a large volume of this phase was needed to obtain enough condensate for analysis. The withdrawal of large volumes of vapor from an autoclave of fixed volume causes the liquid to boil, changing the concentration of both liquid and vapor drastically during the time that a sample is being retrieved. Furthermore, boiling can induce precipitation of $CuCl^{solid}$ in the autoclave or sampling apparatus.

To avoid these problems, experiments were designed to determine copper solubility in the vapor phase by measuring the copper content of condensate collected in isolation of the bulk liquid. Experiments were conducted in the titanium-alloy autoclaves described above. A pressed $CuCl^{solid}$ pellet and copper foil (this buffered the redox potential of the system: $CuCl + H_2 \leftrightarrow Cu + HCl$) were placed in a quartz-glass tube sealed at one end to isolate these solids from the HCl/NaCl solution. The tube and a measured amount of solution were then placed in the autoclave, the tube being oriented vertically with its open end up. The amount of solution, which corresponded to that required to maximize the amount of vapor coexisting with liquid at the conditions of the experiment, was determined from the density data of Bischoff (1991). Three additional quartz-glass tubes (Vycor, 9 mm O.D, 7 mm I.D., volume pre-determined), also sealed at one end, were placed vertically inside the vessels, with their open ends up to collect the vapor condensed at the end of the experiments. At the end of each series of experiments, the autoclaves were quenched rapidly by immersing them vertically in water. This caused vapor occupying the open quartz-glass tubes to be condensed to liquid, and to collect at the bottom of the quartz-glass tubes. The latter were weighed and the solution was then withdrawn and transferred into pre-weighed high-density polyethylene (HDPE) bottles. Any precipitates in the quartz-glass tubes were dissolved with aqua regia, which was then transferred to the HDPE bottles containing the quenched solution. The masses of quenched products were determined by weighing the HDPE bottles and the dried quartz-glass tubes. Other aspects of the experimental procedure were as discussed above for the dry runs.

Theoretically, the mass of solution condensed from vapor in a quartz-glass tube should be the product of the density of the vapor and the internal volume of the tube. However, as quenching is never 100% efficient, some of the high-temperature vapor was lost from the tubes, and the measured masses of condensate were typically lower than the theoretical values. It was therefore necessary to correct for this mass loss to determine the original concentration of copper in the vapor. The correction factor was determined using the following equation:

$$\{Cu\}_{eq} = \{Cu\}_{meas} \times (\text{mass of water vapor})_{calc}/(\text{mass of condensed water})_{meas} \qquad (2)$$

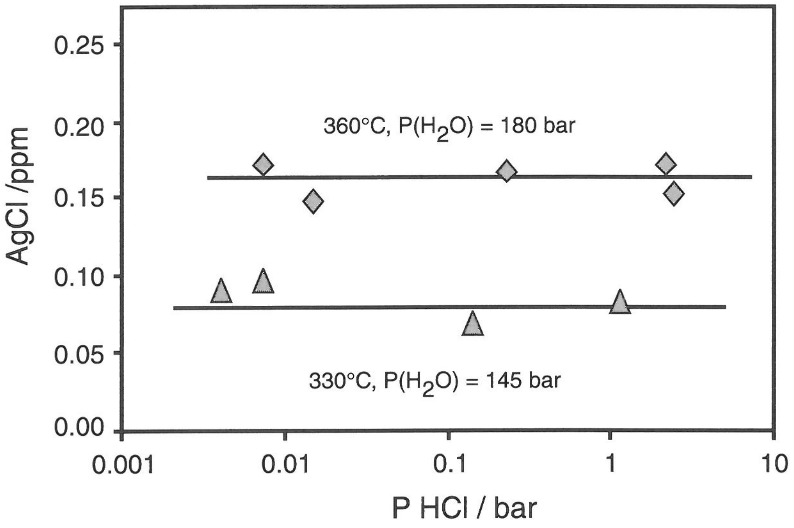

Figure 3. Concentration of silver chloride in water vapor versus the partial pressure of HCl ^{gas}. The zero slope of the data distribution indicates that AgCl solubility was independent of P_{HCl}.

where (mass of water vapor)$_{calc}$ is the mass of water vapor calculated from the internal volume of the quartz glass tube and the density of water vapor at the temperature of the experiment.

The total Cu concentration of each sample was determined either by flame atomic absorption spectrometry (FAAS) or graphite-furnace atomic absorption spectrometry, the latter method being required for samples containing <0.05 mg/kg, Cu, the detection limit for FAAS.

4.2. Results

4.2.1. Dry systems

4.2.1.1. AgCl - HCl - H_2O system. A series of 31 experiments at temperatures of 300, 310, 330, 340, 350 and 360 °C were conducted to evaluate the solubility of AgCl in the vapor phase of the AgCl-H_2O system, and 9 experiments at 330 and 360 °C to evaluate its solubility in the AgCl-HCl-H_2O system. Vapor pressure in the AgCl-H_2O system varied from 20 to 160 bars, and was close to that of the liquid-vapor phase boundary in the system AgCl-HCl-H_2O.

The mole fraction of AgCl in the vapor was calculated from the silver concentration in the quenched condensate. Owing to the low partial pressure of AgCl^{gas}, the total pressure in the autoclave was effectively that of H_2O vapor. Consequently the mole fraction of AgCl;

$$X_{AgCl} = \frac{M_{AgCl}}{M_{H_2O} + M_{AgCl}}$$

in the vapor could be approximated as:

$$X_{AgCl} \cong \frac{M_{AgCl}}{M_{H_2O}},$$

where M is number of moles of the corresponding compound.

The dependence of the concentration of silver chloride in water vapor on the partial pressure of HCl is illustrated in Figure 3. From this diagram, it is evident that AgCl solubility is independent of P_{HCl}, within experimental error, at constant temperature and partial pressure of H_2O. This indicates that there was one dominant gaseous silver species with a stoichiometry Ag:Cl = 1:1.

The concentrations of AgCl in the vapor phase determined from our experiments are shown as a function of P_{H_2O} in Figure 4. From this figure, it can be seen that the isothermal concentration of AgCl in the vapor increases sharply with increasing H_2O pressure.

4.2.1.2. Au-HCl-H_2O system. The solubility of Au in the vapor phase of the system Au-HCl-H_2O was investigated via 23 experiments carried out at temperatures of 300, 340 and 360°C. Water vapor pressures were held constant at each isotherm, from 86 bars (at 300°C) to 144 bars (at 340 and 360°C), and were calculated to be within the vapor-only field at the temperatures of interest.

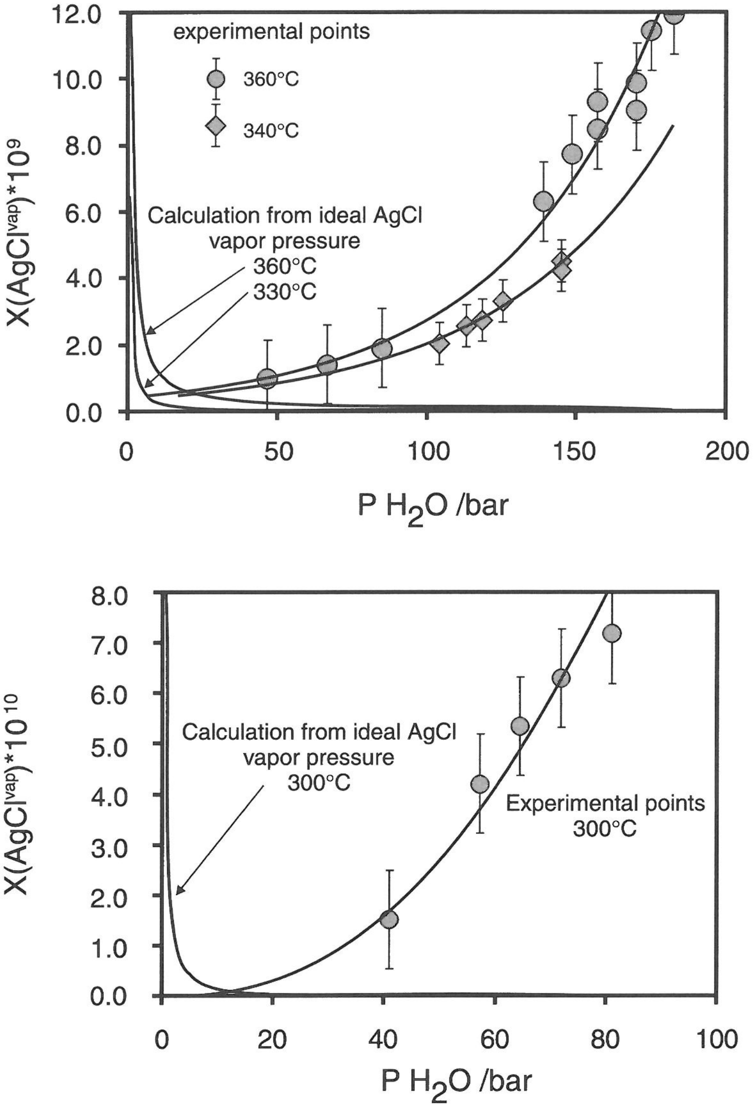

Figure 4. AgCl concentrations in water vapor versus the pressure in the system. Owing to the low partial pressure of $AgCl^{gas}$, the total pressure in the autoclave was effectively that of the water. The heavy solid lines show the silver chloride concentration calculated assuming no hydration of AgCl. The calculations were performed using the data on $AgCl^{gas}$ vapor pressure over crystalline chlorargyrite reported by Tagirov et al. (1993).

The mole fraction of Au in the vapor was calculated from its concentration in quenched condensates using an equation analogous to that employed for Ag:

$$X_{AuCl_m} = \frac{M_{AuCl_m}}{M_{H_2O} + M_{AuCl_m}}$$

and is shown as a function of P_{HCl} in Figure 5. From this figure, it is apparent that the solubility of Au increases with increasing P_{HCl}, but decreases with increasing temperature.

4.2.1.3. SnO_2-HCl-H_2O system. Forty experiments were conducted in the system SnO_2-HCl-H_2O to determine the solubility of SnO_2 in the vapor phase at temperatures of 300 and 320 °C.

The mole fraction of Sn in the vapor was calculated in essentially the same way as that of Ag and Au. Its

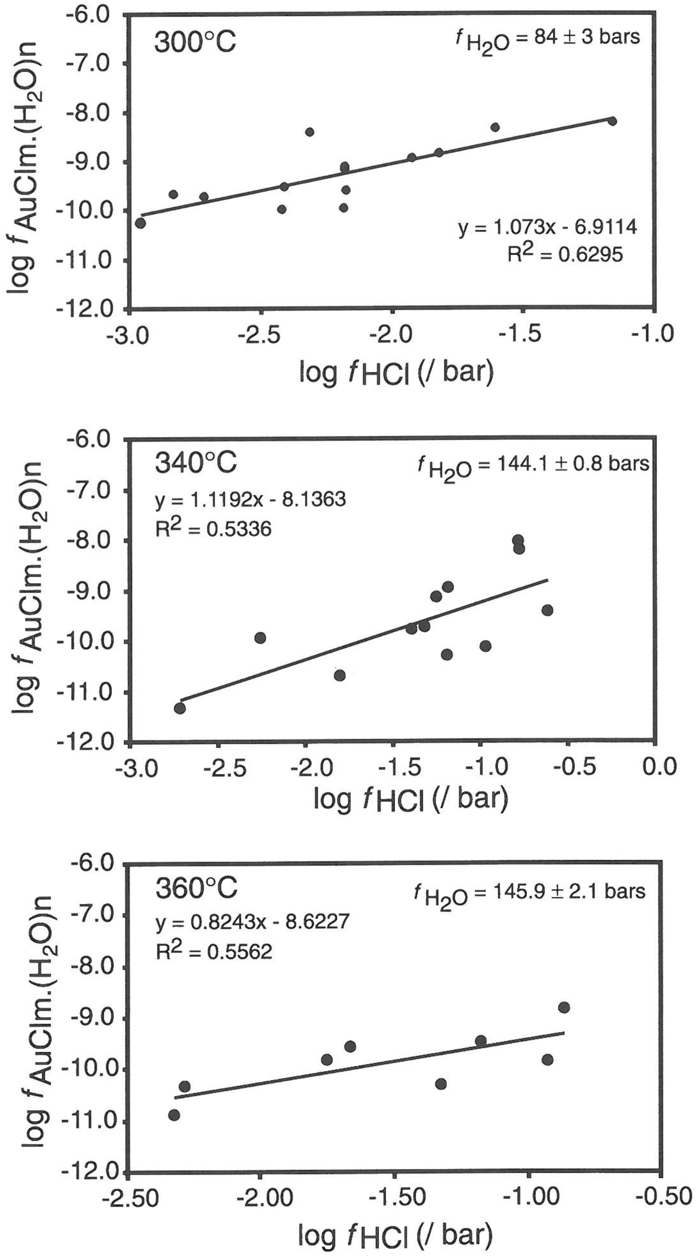

Figure 5. Mole fractions of $AuCl_m{\cdot}H_2O_n$ in water vapor as a function of P_{HCl} in the Au-H_2O-HCl system at 300, 340 and 360 °C. The slope of ~1 for the these temperatures suggests the stoichiometry $AuCl(H_2O)_n$.

dependence on HCl pressure is illustrated in Figure 6. As was the case for the Au-HCl-H_2O system, the solubility of SnO_2 increased with increasing P_{HCl}. Preliminary data for 300 °C suggest that Sn solubility also increases with P_{H_2O}, as in the AgCl-H_2O-HCl system (Fig. 4).

4.2.2. Wet system

4.2.1.1. CuCl - NaCl - HCl - H_2O system. The solubility of CuCl in water-saturated vapor was investigated in a series of 26 experiments conducted at temperatures of 380 and 400 °C. The concentration of

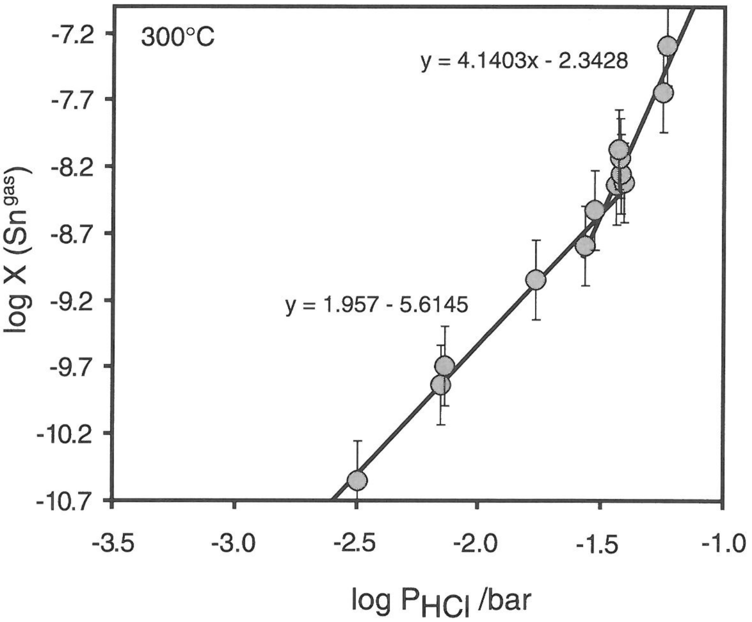

Figure 6. The mole fraction of tin in water vapor as a function of P_{HCl} in the SnO_2-H_2O-HCl system at 300 °C. The slope of the data distribution indicates that tin is present mainly as $SnCl_2 \cdot (H_2O)_n^{gas}$, and at high P_{HCl} as $SnCl_4 \cdot (H_2O)_n^{gas}$.

copper in the vapor appears to correlate negatively with total chloride concentration (Fig. 7, Table 6). We attribute this correlation to a decrease in vapor density related to a corresponding increase in the salinity of the system (cf. Bischoff, 1991). After corrections were made for vapor density, we were able to conclude to a first approximation that the copper concentration in the vapor is independent of the total Cl^- activity in the coexisting liquid at the temperatures investigated. In view of this, the Cu-Cl stoichiometry of the dominant copper gas species was interpreted to be 1:1. In contrast to its negative correlation with Cl, copper concentration correlates positively with vapor density. The significance of this correlation is discussed below.

5. DISCUSSION

The partitioning of metals into water vapor is the result of two processes that proceed in parallel, namely the dissolution of the metals, i.e., their solvation as MeL_m^{vapor} (Me refers to the metal and L to the ligand), and the development of a partial pressure of MeL_m^{gas} over the crystalline phase. As the properties of the unsolvated gaseous complexes of the metals investigated experimentally in this study are known (Pankratz 1982, 1984), the concentrations of $MeCl_m^{gas}$ can be calculated for various values of P_{H2O} and measured autoclave volumes. The calculations were made assuming inert behavior of components, and predicted maximum concentrations of the four metals (Ag, Au, Sn, and Cu) investigated that are all at least an order of magnitude lower than the analytical detection limit in our experiments. It is also known from the properties of unsolvated gaseous metal complexes that the partial pressure of $MeCl_m^{gas}$ over the crystalline phase is constant at constant temperature and constant P_{HCl} but the concentration of $MeCl_m^{gas}$ decreases with increasing P_{H2O}. By contrast the metal solubilities in the vapor phase determined experimentally increase exponentially with increasing P_{H2O} at constant temperature and fixed values of P_{HCl}. We therefore conclude that $MeCl_m^{gas}$ does not contribute significantly to the total concentration of metals in the vapor phase, and that any description of the system must also take into consideration some interaction among the components of the gaseous mixture.

5.1. Data Treatment

5.1.1. Dry systems

The interactions referred to above could be, firstly, the formation of new stable gaseous compounds with specific stoichiometry (chemical reaction), and secondly, the hydration of metal chloride by water vapor

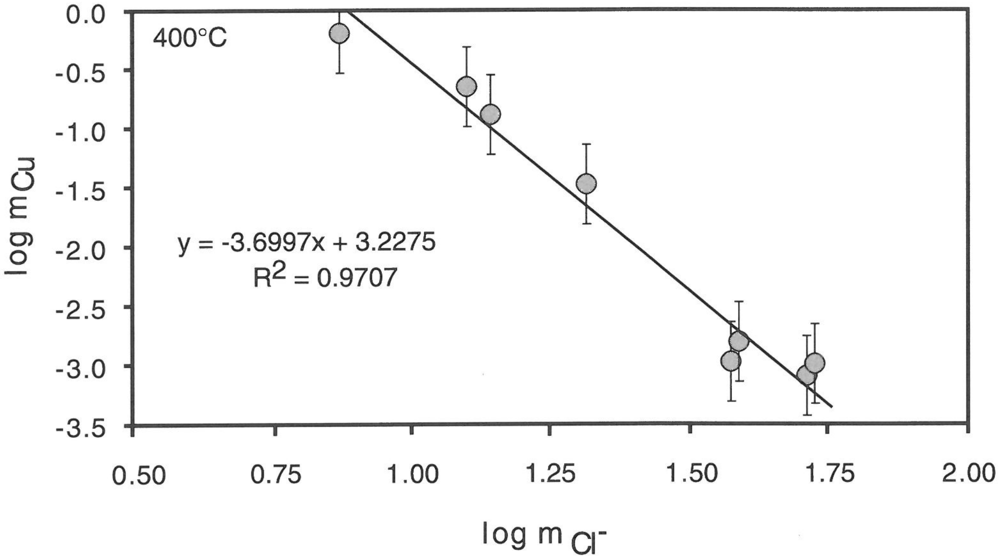

Figure 7. The concentration of copper in the vapor phase versus the total chloride concentration in the system CuCl-HCl-NaCl-H_2O at 400 °C. The negative correlation between these two parameters reflects the decreasing density of vapor due to the salinity increase.

(solubility). In both cases (chemical reaction and solubility) this process can be expressed by the following equations:

$$AgCl^{gas} + m\cdot HCl^{gas} + n\cdot H_2O^{gas} \leftrightarrow AgCl_{m+1}\cdot(H_2O)_n{}^{gas} + m/2\cdot H_2{}^{gas} \quad (3)$$

$$Au^{gas} + m\cdot HCl^{gas} + n\cdot H_2O^{gas} \leftrightarrow AuCl_m\cdot(H_2O)_n{}^{gas} + m/2\cdot H_2{}^{gas} \quad (4)$$

$$SnO_2{}^{gas} + m\cdot HCl^{gas} + n\cdot H_2O^{gas} \leftrightarrow SnCl_m\cdot(H_2O)_{n+0.5m}{}^{gas} + (2\text{-}0.5m)/2\cdot O_2{}^{gas} \quad (5)$$

The Gibbs-Pointing correction was used to account for the change in the pressure (P^o) of the component over the crystalline phase from that for a total pressure of $P = 1$ bar (standard state) to P_2 = pressure for the run as follows:

$$\ln\frac{P_2^o}{P_1^o} = \int_{P_1}^{P_2}\frac{V^o}{R\cdot T}\,dP \quad (6)$$

Given that changes in the molar volume of the crystalline phase with temperature are insignificant for the temperatures investigated, it was assumed that V^o is a constant and

$$\ln\frac{P_2^o}{P_1^o} = \frac{V^o\cdot(P_2 - P_1)}{R\cdot T} \quad (7)$$

(where V^o - is the molar volume and P_1^o, P_2^o are the pressures of this component in states 1 and 2).

It was further assumed from Raoult's Law that:

$$\log P_{MeCl} = \log X_{MeCl} + \log P_{H_2O} \quad (8)$$

Finally, assuming that the partial pressure of HCl is close to its fugacity at the experimental conditions, and taking into account the fact that the equilibrium constant of a homogeneous gaseous reaction is independent of the total pressure in the system, the stoichiometric ratio *Me:Cl* for the hydrated gaseous species was derived from the equilibrium expression for the corresponding reaction as follows:

$$\left(\frac{\partial\log X_{AgCl_{m+1}\cdot(H_2O)_n}}{\partial\log P_{HCl}}\right)_{T,P_{H_2O},P_{H_2}} \cong m+1 \quad (9)$$

$$\left(\frac{\partial\log X_{AuCl_m\cdot(H_2O)_n}}{\partial\log P_{HCl}}\right)_{T,P_{H_2O},P_{H_2}} \cong m \quad (10)$$

$$\left(\frac{\partial\log X_{SnCl_m\cdot(H_2O)_{n+0.5m}}}{\partial\log P_{HCl}}\right)_{T,P_{H_2O},P_{H_2}} \cong m \quad (11)$$

The approach employed here is similar to one developed by Marshall (1972) for treating liquid aqueous solutions and extended to solutions involving vapor by Armellini and Tester (1993). One of the limitations of this approach is that there is commonly considerable difficulty in assigning appropriate standard states to components if the system is heterogeneous (comprises more than one state). Application of the Gibbs-Pointing correction to our two-state (solid-vapor) systems overcame this limitation by making them effectively homogeneous.

The stoichiometric relationship Me:Cl was determined from the slope of the trend of log $X_{MeCl_m \cdot (H_2O)_n}$ versus log P_{HCl}, which was essentially linear for each of the metals investigated; the experiments were conducted at constant partial pressure of water and hydrogen, and constant temperature. Based on equations (9-11) the stoichiometry of the dominant silver and gold species was interpreted to be $AgCl \cdot (H_2O)_n{}^{gas}$ and $AuCl \cdot (H_2O)_n{}^{gas}$, respectively. Tin was interpreted to be present mainly as $SnCl_2 \cdot (H_2O)_n{}^{gas}$, and at high P_{HCl} as $SnCl_4 \cdot (H_2O)_n{}^{gas}$. Significantly, whereas the Me:Cl ratio of the species interpreted to be dominant in the AgCl-HCl-H_2O and SnO_2-HCl-H_2O systems is the same as in the corresponding H_2O-free systems, that for Au is different (1:1 vs 1:3). This indicates that the presence of water vapor increases the stability of gold chloride (I) in gaseous solutions with respect to that of gold chloride (III).

The hydration number (n) of the dominant species in our experiments was determined from the relationship between log $X_{MeCl_m \cdot (H_2O)_n}$ and log P_{H_2O}, which is given by the following equations derived from the expression for the equilibrium constant of the corresponding reactions:

$$\left(\frac{\partial \log X_{AgCl \cdot (H_2O)_n}}{\partial \log P_{H_2O}}\right)_T \cong n-1 \tag{12}$$

$$\left(\frac{\partial \log X_{AuCl \cdot (H_2O)_n}}{\partial \log P_{H_2O}}\right)_{T, P_{HCl}, P_{O_2}} \cong n-1-\frac{m}{2} \tag{13}$$

$$\left(\frac{\partial \log X_{SnCl_m \cdot (H_2O)_{n+0.5m}}}{\partial \log P_{H_2O}}\right)_{T, P_{HCl}, P_{O_2}} \cong n-1 \tag{14}$$

In the case of Ag, the slope of log $X_{MeCl_m \cdot (H_2O)_n}$ versus log P_{H_2O} is ~2 for each of the temperatures investigated (Fig. 8). As this slope represents the term "*n-1*", we therefore conclude that the above complex has a hydration number of 3. However, it should be noted that the magnitude of the experimental error only permits estimation of the hydration number (n) to a precision of one integer. We interpret this complex to be $AgCl \cdot (H_2O)_3{}^{gas}$

$$AgCl^{cryst} + 3 \cdot H_2O^{gas} = AgCl \cdot (H_2O)_3{}^{gas} \tag{15}$$

Considering that silver is coordinated by three molecules of water and one of chlorine in the species $AgCl \cdot (H_2O)_3{}^{gas}$, it also seems reasonable to predict that the silver is in four-fold coordination.

Unfortunately, the system AgCl-HCl-H_2O was the only dry system investigated, in which the solid dissolved congruently and there was no dependence on f_{O_2}. Investigation of the other systems required that f_{O_2} be buffered, which introduced experimental problems in the runs conducted at constant P_{HCl}. Reaction of HCl with the assemblage MoO_2/MoO_3, which was used to buffer f_{O_2}, although not appreciable, was sufficient to cause some variation in P_{HCl}. In order to estimate the hydration number n for the gold and tin species, it was necessary to replace the graphical method used for silver (Fig. 8) by a numerical approach. Values of n were calculated for each temperature by minimizing the value of the error, using the equation:

$$\mathrm{ERROR} = X_{MeCl}{}^{experimental} - X_{MeCl}{}^{calculated}(n) \tag{16}$$

where $X_{MeCl}{}^{experimental}$ are the values obtained in the runs, and $X_{MeCl}{}^{calculated}$ (n) are the values calculated using the constants obtained for different n. This minimization algorithm is based on a golden section search and parabolic interpolation, and was implemented using a computer program similar to that of Forsythe et al (1976). On the basis of the data presently available from our experiments, gold is tentatively predicted to dissolve in the vapor phase as $AuCl \cdot (H_2O)_3$ and tin as $SnCl_2 \cdot (H_2O)_4$, and possibly as $SnCl_4 \cdot (H_2O)_2$ at low and high partial pressures of HCl, respectively.

5.1.2. *Wet system*

As discussed above, the Cu:Cl stoichiometry of the dominant copper species in the vapor was 1:1. The solubility of copper in the vapor phase may therefore be described by the reaction:

$$CuCl^{aq} + nH_2O^{vapor} = CuCl \cdot (H_2O)_n{}^{vapor} \tag{17}$$

or

$$CuCl^{solid} + nH_2O^{vapor} = CuCl \cdot (H_2O)_n{}^{vapor} \tag{18}$$

Reaction (18) is identical to reaction (17), except for the phase designation of the reactant copper species.

As discussed earlier, one of the difficulties in treating heterogeneous systems (more than one state) is assigning appropriate standard states to components. In the case of the heterogeneous dry systems (solid-vapor), we were able to overcome this difficulty by applying the Gibbs-Pointing correction, thereby making them effectively homogeneous. Unfortunately this solution is not available to us for our wet system (solid-liquid-vapor). However, several studies of the NaCl-H_2O system have shown that the solubility of NaCl in the vapor phase can be modeled semi-empirically using a relationship derived from classic equilibrium thermodynamics and based on the density of water vapor (Martynova, 1964; Styrikovich, 1969;

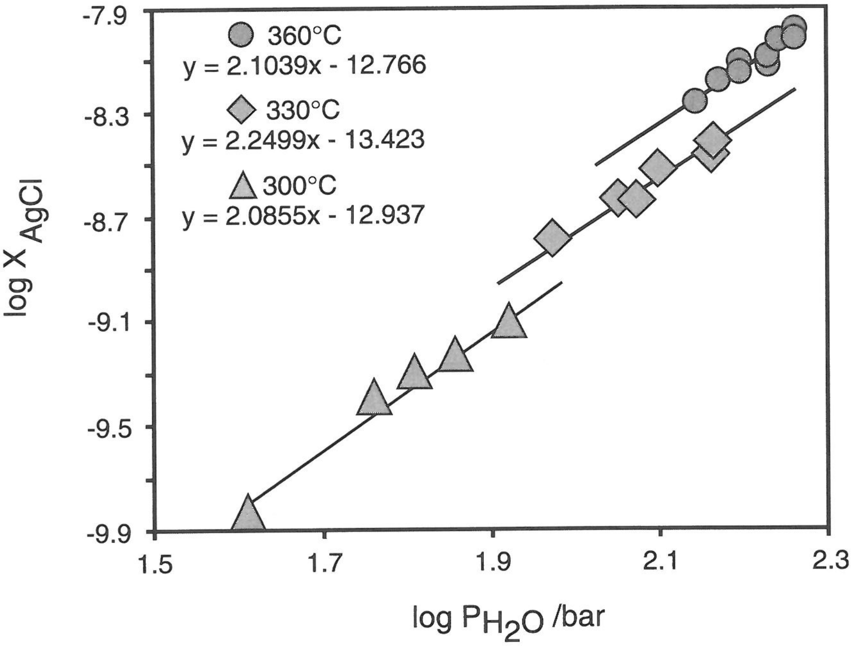

Figure 8. Logarithm of the mole fraction of $AgCl\cdot(H_2O)_n$ versus the logarithm of the partial pressure of H_2O for experiments run at 300, 330 and 360 °C. The slope of ~2 for each these temperatures suggests the stoichiometry $AgCl\cdot(H_2O)_3$.

Galobardes et al., 1981; Armellini and Tester, 1993). The model assumes that equilibrium between solid NaCl and water vapor is achieved through a solvation-type reaction:

$$NaCl^{solid} + nH_2O^{vapor} = NaCl\,(H_2O)_n{}^{vapor} \quad (19)$$

and that, due to the low density of the water vapor, its solvation power is low and the dissolved NaCl occurs as ion pairs (Mesmer et al., 1988). The equilibrium relationship for reaction (19) is:

$$K_c = \frac{a_{NaCl(H_2O)_n}}{a_{NaCl^{solid}} \cdot a^n_{H_2O^{vapor}}} \approx \frac{C_{NaCl}}{\rho^n_{H_2O^{vapor}}} \quad (20)$$

i.e.,

$$\log C_{NaCl} = n \cdot \log \rho_{H2O} + \log K_c = n \cdot \log \rho_{H2O} - \frac{A}{T} + B \quad (21)$$

where C_{NaCl} is the concentration of NaCl in the vapor phase (ppm or ppb) and A and B are constants. Armellini and Tester (1993) assumed that the stoichiometric coefficient *n* was also a constant based on a review of the literature, which indicated that it varied minimally with temperature and density.

Because, in the present experiments, the pressure change is very small (around 3-5 bars), the fugacity of $CuCl^{gas}$ is directly related to its concentration in the vapor. The equilibrium relationship therefore can be approximated as described above for NaCl:

$$\log K_c = \log m_{CuCl\cdot(H_2O)_n} - n \cdot \log \rho_{H_2O} \quad (22)$$

where K_c is the equilibrium relationship and ρ_{H_2O} is the density of water vapor.

Rewriting equation (22), we obtain:

$$\log m_{CuCl\cdot(H_2O)_n} = n \cdot \log \rho_{H_2O} + \log K_c \quad (23)$$

and differentiating equation (23) with respect to log ρ_{H_2O}, we have :

$$\left(\frac{\partial \log m_{CuCl\cdot(H_2O)_n}}{\partial \log \rho_{H_2O}} \right)_{T.} \cong n \quad (24)$$

As the log molality of copper in the vapor and log density of water vapor were linearly related in our experiments (Fig. 9), log K_c and *n* are given by the corresponding intercept and slope, respectively. The slopes of linear regressions through the data are 3.55, and 3.78 at 380 °C, and 400 °C, respectively, and the hydration number is thus 4 at both temperatures investigated. Reaction (17) therefore becomes:

$$CuCl^{aq} + 4H_2O^{vapor} = CuCl \cdot 4H_2O^{vapor} \quad (25)$$

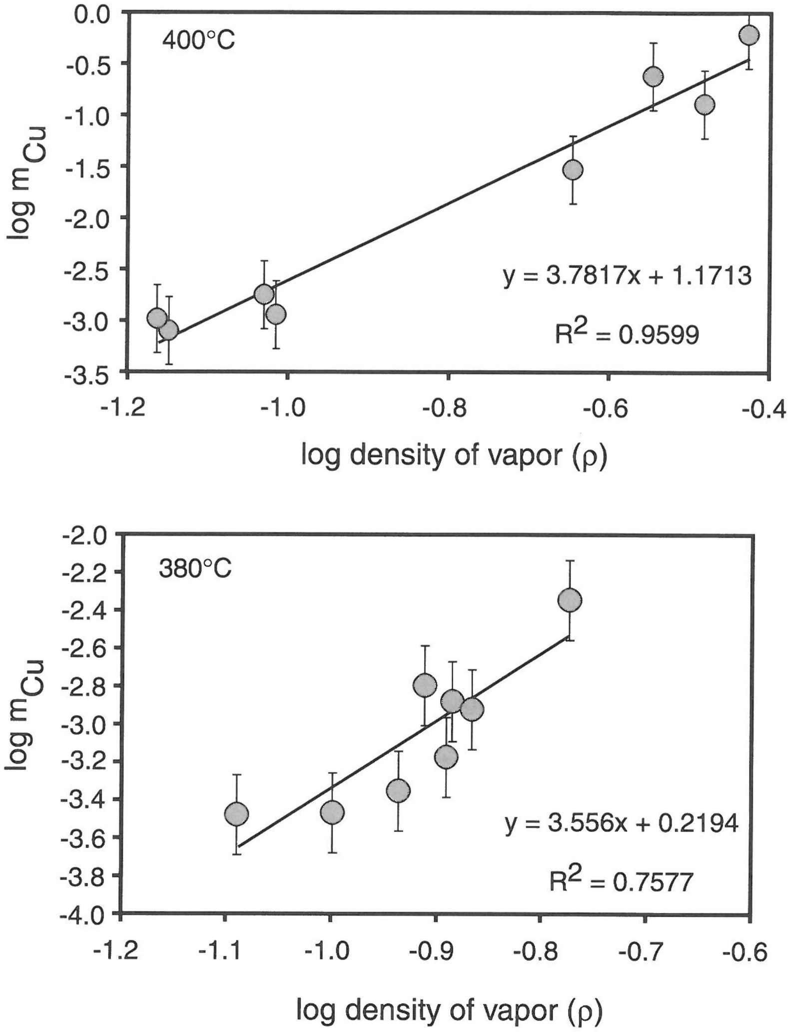

Figure 9. Concentration of copper in water vapor vs.water vapor density at temperatures of 380 and 400 °C. The linear correlation between log molality and log ρ_{H_2O} suggests that copper solubility in the vapor is controlled mainly by vapor density.

and the values of the equilibrium relationship (log K_c) are 0.22 and 1.17 at 380 and 400 °C, respectively.

5.2. Comparison of Experimental Data with Data from Natural Systems

Although the experimental data reported above are for the most part preliminary and restricted to a comparatively limited temperature range (300 and 400 °C), they do at least permit a first-order comparison with data reviewed earlier on the concentrations of the corresponding metals in natural systems. The major limitation in comparing the measured solubilities of the metals in the vapor phase to the apparent solubilities of these metals in volcanic gases is the much higher temperature of the latter. Another limitation is that, in the case of Ag and Cu, metal solubility in volcanic gases is generally controlled by saturation with respect to phases different to those employed in our experiments, e.g., native silver or argentite (Ag_2S) versus chlorargyrite (AgCl) in the case of Ag, and chalcopyrite versus nantokite (CuCl) in the case of Cu. On the other hand, HCl is generally the next most abundant component of volcanic gases after H_2O, CO_2 and SO_2, and commonly comprises several mole percent of the bulk gas, whereas H_2S typically makes up <1 mole percent of the gas.

The maximum concentration of Ag reported for a volcanic gas is 250 ppb, which was measured in a condensate of high-temperature (830 °C) gases collected from a fumarole at Poas (Table 2). However, if we restrict temperature to <400 °C, the highest Ag value drops to 20 ppb and corresponds to condensates of gases released at 170 °C from a fumarole at Cerro Negro (Gemmell, 1987); typically the Ag concentrations of gases at temperatures <400 °C are in the range 3 to 10 ppb (Gemmell, 1987). In our experiments, we obtained mole fractions of Ag of $7.2\text{x}10^{-10}$ and $1.27\text{x}10^{-8}$ at pressures close to water saturation and temperatures of 300 and 360 °C, respectively. These mole fractions correspond to concentrations of 6 ppb and 100 ppb, respectively, and are at least 3–4 orders of magnitude higher than those predicted thermodynamically from volatility data (Tagirov, 1993). However, as can be seen from the data reported above, they compare very favorably with the concentrations measured in condensed gases from volcanic fumaroles.

The highest concentration of Au reported in the literature for the condensate of a volcanic gas is 32 ppb collected from a fumarole on Usu volcano (Giggenbach and Matsuo, 1991). Interestingly, the temperature of the gas was only 165 °C. More typically the concentrations range between 1 and 3 ppb (Gemmell, 1987). By contrast, the concentrations corresponding to the maximum mole fractions of Au obtained in our experiments were 1.1 ppm and 175 ppb at 300 and 360 °C respectively.

Tin concentrations in volcanic gas condensates reported in the literature are significantly higher than those reported for Ag or Au, and range up to 7.2 ppm (for a condensate from a fumarole at Usu volcano degassing at a temperature of 649 °C). At temperature conditions closer to those of our experiments, the concentrations are <2 ppm, e.g., 1.4 ppm for a fumarole degassing at 344 °C (Gemmell, 1987). These concentrations are at least two orders of magnitude higher than those obtained in our experiments, which were conducted at 300 °C, and yielded a maximum mole fraction of Sn of $7.2\text{x}10^{-9}$, or a concentration of 47 ppb. The reason for this large discrepancy between nature and experiment is unclear. However, it should be emphasized that our investigation of tin solubility is at a very preliminary stage and that it is complicated by the dual valence state of Sn.

Concentrations of Cu in volcanic gases are considerably higher than those of Ag or Au, but similar to that of Sn, the highest reported value being 8.4 ppm from a high-temperature (770 °C) fumarole on Momotombo (Gemmell, 1987). For lower temperature fumaroles (< 400 °C), condensate copper concentrations are typically in the range 200 to 800 ppb. By contrast, concentrations in our experiments (water-saturated) are all substantially higher, ranging from 22 to 277 ppm at 380 °C and 250 ppm to 3.9 wt. % at 400 °C. Although the highest of these values may seem to be unreasonably high, it is interesting to note that Ulrich et al. (1999) report an average copper concentration of 3.3 wt. % for vapor-rich fluid inclusions (analysed by LAM-ICPMS) from the Bajo de la Alumbrera porphyry copper deposit, Argentina; the inclusions coexist with liquid-rich inclusions that homogenize at temperatures between 550 and 650 °C. A possible explanation for the relatively low concentrations of Cu in volcanic gases may be the nature of the saturating phase, i.e., chalcopyrite versus nantokite in our experiments. This does not, however, explain the high concentration of Cu in the porphyry inclusions, which may point to a ligand other than Cl playing an important role in metal transport in porphyry systems.

Given the relatively simple nature of the systems investigated experimentally and the preliminary state of some of these investigations, the results available to date are most encouraging. There is thus every reason to believe that as more complexity is added to these systems, it should be possible to reproduce with considerably greater accuracy the metal concentrations of natural vapors. The next obvious step in experimental investigations of the solubility of metals in aqueous vapors will be to introduce sulfur, a step that is facilitated by ongoing work in our group on the solubility of metals in H_2S (Migdisov et al., 1998, and Zakaznova-Iakovleva et al., 2001).

5.3. Role of Vapor Transport in Ore genesis

A question raised in the introduction to this paper, and one of growing interest to many researchers, in the light of recent reports of high concentrations of metals in vapor-rich fluid inclusions (Ulrich et al, 1999), is whether the concentrations of metals in natural hydrothermal vapors are sufficient to concentrate metals to potentially economic levels. Although it is clearly premature to try and answer this question rigorously, the data made available by our experiments provide an opportunity to roughly evaluate the impact of vapor transport of metals on the ore-forming process. We do this via a relatively simple thermodynamic model to track the removal of silver from rock during progressive interaction with water vapor.

For simplicity, we have restricted the system to the five elements: Ag, Cl, S, O, and H. Chloragyrite was used to represent the Ag phase, and quartz, the inert host-rock. A quartz column containing 5 ppm AgCl was subdivided into 44 segments, or reactors, each having a mass of 1 kg, and differing in temperature

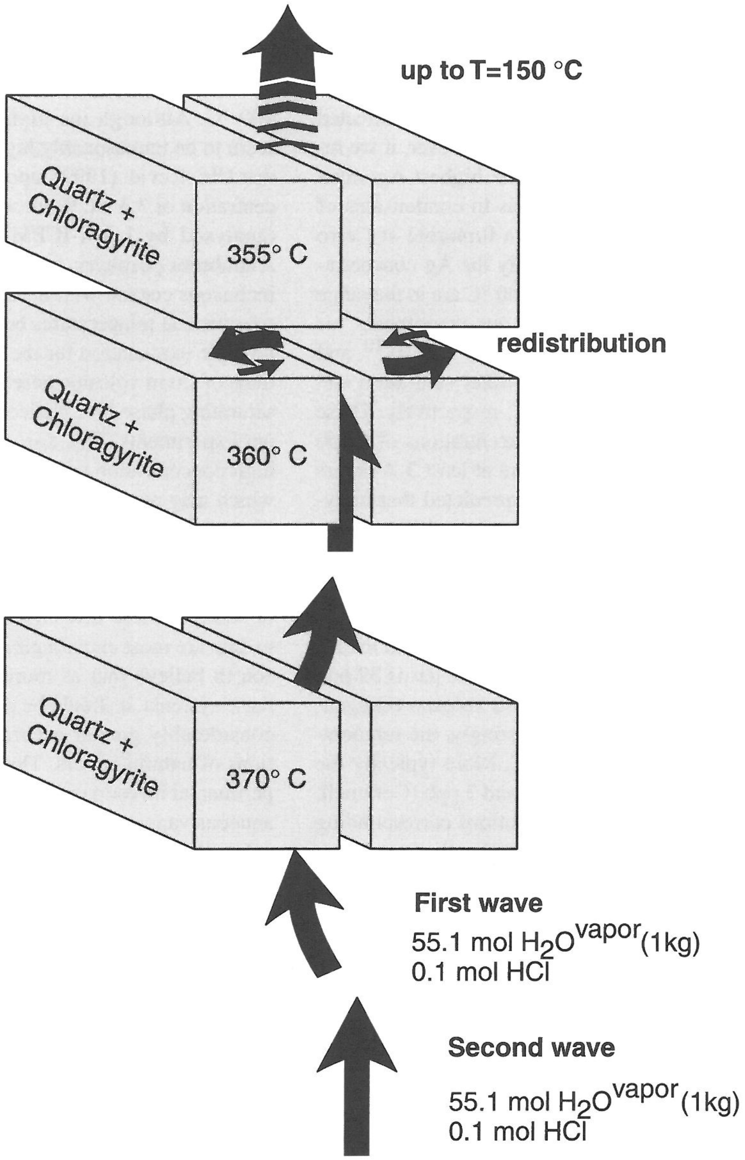

Figure 10. Schematic diagram describing a simplified thermodynamic model in which silver in a rock column composed of chloragyrite and quartz is mobilized during progressive interaction with water vapor. See text for further details.

from the preceding reactor by 5 °C; temperature ranged from 370 °C at the bottom of the column to 150 °C at the top. The pressure in each reactor was that of saturated water vapor (Figure 10). A 1-kg aliquot of water vapor was introduced at the base of the column and allowed to proceed linearly upwards, equilibrating successively with the reactors in the column. This single batch experiment simulated the alteration of the column at a fluid/rock ratio of 1:1. In order to evaluate the effects of higher fluid/rock ratios, additional 1-kg aliquots of fluid were passed through the previously altered column and brought to equilibrium with each reactor along the path.

The results of our simulation are shown in Figure 11. As is evident from this figure, there was appreciable mobilization of silver. After reaction with the first

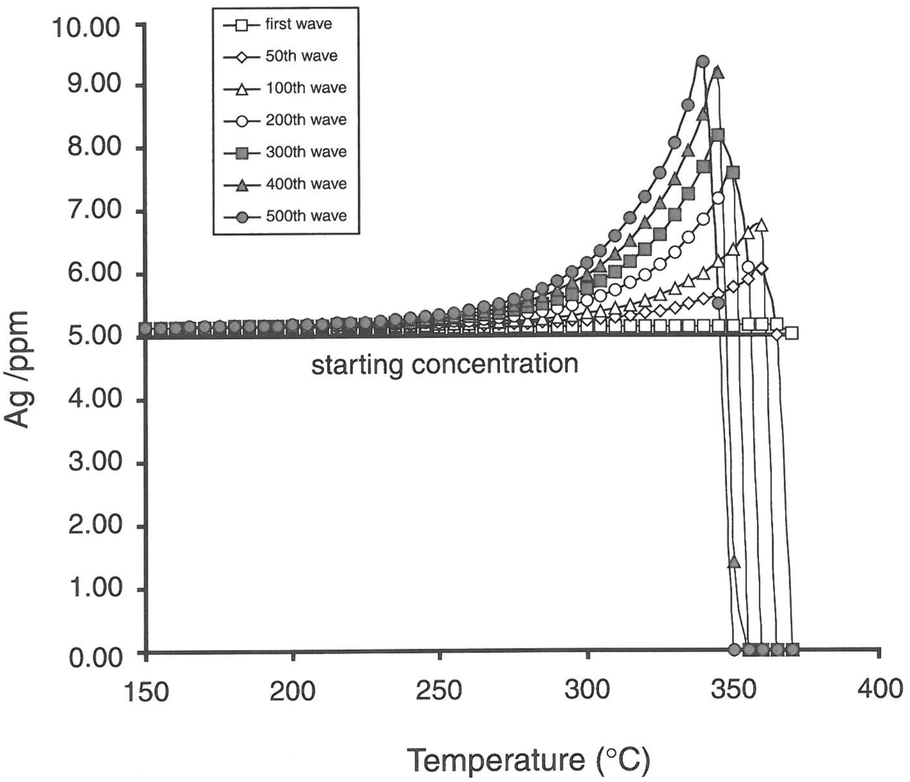

Figure 11. Results of a simulation of the reaction of water vapor with a chloragyrite-bearing quartz vein. The diagram shows the distribution of Ag concentrations in the quartz as a function of temperature at varying vapor-rock ratios (represented by the number of aliquots introduced into the vein).

batch of fluid (fluid/rock ratio, 1:1), the silver content in quartz dropped from 5 ppm to 3 ppm at the base of the column, and gradually increased with decreasing temperature upwards, to a maximum of 5.3 ppm at 365 °C and then gradually decreased to 5.1 ppm at 150 °C. After 50 aliquots of water vapor had been introduced into the column, the maximum silver content had increased to 6 ppm, and the temperature of this maximum had decreased to 355 °C. Most significantly, all the silver formerly present in reactors at 5 °C above this temperature (the first two reactors) had been removed. With further additions of fluid, the peak gradually became better defined, and continued to migrate to lower temperature; after 100 and 500 aliquots of water vapor had been introduced the maxima were 6.8 and 9.3 ppm, respectively, and the corresponding temperatures were 350 and 335 °C. Again, as noted above, all the silver had been removed from reactors at temperatures > 5 °C above those of the maxima.

Although highly idealized, the calculations presented above show that water vapor may be an effective agent for the transport of silver in vapor-dominated hydrothermal systems at temperatures above 300 °C, and an important vehicle for the redistribution of silver in many boiling hydrothermal systems.

6. CONCLUSIONS

The idea that aqueous vapors can transport metals in appreciable concentrations, and may be responsible for the formation of metallic mineral deposits has been around for over 350 years, but in the modern era has been largely ignored. Arguments put forward by Henley and McNabb in the late 1970's, and recent evidence of high concentrations of metals in vapor-rich fluid inclusions, demand that the role of vapor transport in metallic mineral concentration be further evaluated. In this paper we have summarized the data available on the concentrations of metals in volcanic gases (the best examples of possible ore-forming vapors), briefly reviewed metal speciation in gaseous solutions, and presented results of some of the first experiments to be conducted on the solubility of ore-forming metals in aqueous vapors. These experiments, while very preliminary and representing relatively simple analogues of natural systems, do suggest that aqueous vapors may be able to mobilize appreciable quantities of metals in natural hydrothermal systems. It is our hope that this review will encourage further experimentation on the solubility of metals in aqueous vapors, and lead to complementary field-based studies designed to evaluate the potential role of these vapors as agents of transport in the formation of metallic mineral deposits.

Acknowledgments—This research was supported by NSERC research and collaborative grants and an FCAR team grant to AEW-J, S.A. Wood and C.H. Gammons provided important advice on experimental techniques, S. Kecani helped in the design and construction of the analytical equipment and G. Kennedy and S. Lalli assisted in the analytical work. The manuscript was significantly improved by the thoughtful reviews of T.M. Seward, J. Webster, and T. Williams. S.A. Wood furnished important advice on both the preparation and content of the manuscript.

Editorial handling: S.A. Wood

REFERENCES

Alcock C. B., Itkin V. P., and Horrigan M. K. (1984) Vapor pressure equations for the metallic elements: 298-2500 K. *Can. Metall. Q* **23**, 309-313.

Alekhin Yu. V. and Vakulenko A. G. (1987) Solubility and thermodynamic properties of sodium chloride in water vapor at 300-500° and ≤300 bar. *Geokhimiya* **(10)**, 1468-1481.

Ambrose D. and Sprake C. H. S. (1972) Vapor pressure of mercury. *J. Chem. Thermodyn.* **4**, 603-620.

Armellini F. J. and Tester J. W. (1993) Solubility of sodium chloride and sulfate in sub- and supercritical water vapor from 450-550 °C and 100-250 bar. *Fluid Phase Equilib.* **84**, 123-142.

Barnes H. L. (1997) *Geochemistry of Hydrothermal Ore Deposits -3rd edition.* New York, John Wiley and Sons, 972 pp.

Bateman A. M. (1950) *Economic Mineral Deposits.* New York, John Wiley and Sons, 916 pp.

Bernard A. (1985) Les mecanismes de condensation des gaz volcaniques (chimie mineralogie et equilibre des phases condensees majeures et mineures). Ph.D. thesis, Univ. of Brussels, Belgium.

Bernard A. and Le Guern F. (1986) Condensation of volatile elements in high temperature gases of Mt. St. Helens. *J. Volcanol. Geotherm. Res.* **28**, 91-105.

Bischoff J. L. and Rosenbauer R. J. (1988) Liquid-vapor relations in the critical region of the system sodium chloride-water from 380 to 415°C: A refined determination of the critical point and two-phase boundary of seawater. *Geochim. Cosmochim. Acta* **52**, 2121-2126

Bischoff J. L. (1991) Densities of liquids and vapors in boiling sodium chloride-water solutions: A PVTX summary from 300° to 500 °C. *Am. J. Sci.* **291**, 309-338.

Blades A. T., Jayaweera P., Ikonomou M. G., and Kebarle P. (1990) Ion-molecule clusters involving doubly charged metal ions (M^{2+}). *Int. J. Mass Spectrom. Ion Processes* **102,** 251-267.

Blades A. T., Klassen J. S., and Kebarle P. (1995) Free energies of hydration in the gas phase of the anions of some oxo acids of C, N, S, P, Cl, and I. *J. Amer. Chem. Soc.* **117**, 10563-10571.

Brewer L. and Lofgren N. L. (1950) The thermodynamics of gaseous cuprous chloride, monomer and trimer. *J. Amer. Chem. Soc.* **72,** 3038-3045

Brimhall G. H. and Crerar D. A (1987) Ore Fluids: Magmatic to Supergene. In *Thermodynamic Modeling of Geological Materials: Minerals, Fluids and Melts* (eds. I.S.E. Carmichael and H.P. Eugster), Reviews in Mineralogy **17**, 235-321.

Brittain R. D., Lau K. H. and Hildenbrand D. L. (1983) The vaporization of realgar, arsenic sulfide (As_4S_4). *J. Electrochem. Soc.* **130**, 1206-1210.

Brown J. S. (1948) *Ore genesis; a metallurgical interpretation, an alternative to the hydrothermal theory.* Hopewell, N.J., Hopewell Press, 204 pp.

Bunsen M. R. (1853) Recherches sur la formation des roches volcaniques en Islande. *Ann. Chim. Phys. 3rd Series* **38**, 215-289.

Chang S. K. and Toguri J. M. (1974) Effect of temperature and electron energy on mass-spectrum of silver chloride. *J. Less-Common Metals* **38**, 187-192.

Charpentier J. F. W. (1778) Mineralogische Geographie der Chursächsischen Lande. Leipzig.

Charpentier J. F. W. (1799) Beobachtung über die Lagerstätte der Erze, hauptsächlich aus den sächsischen Gebirgen. Leipzig.

Cordes H., Dost L. and Cammenga H. K. (1971) Thermodynamic properties of metal vapors. II. Mercury. *Z. Metallk.* **62**, 915-925.

Daubrée A. (1841) Mémoire sur le gisement, la constitution et l'origine des amas de minerai d'étain. *Annales des mines - 3^e^ série* **XX**, 65-112.

Daubrée A. (1849) Recherches sur la production artificielle de quel-ques espèces minérales cristallines particulièrement de l'oxyde d'étain des filons titanifères des Alpes. *Annales des Mines, 4^e^ série* **XVI**, 129-155.

Davidson W. R. and Kebarle P. (1976) Binding energies and stabilities of potassium ion complexes from studies of the gas phase ion equilibriums $K^+ + M = K^+M$. *J. Am. Chem. Soc.* **98**, 6133-6138.

Descartes R. (1644) *Principia Philosophae,* Amsterdam, I. Rieuwertsz (Publisher), 388 pp.

Deville C. S. (1862) Lettre à M. Elie de Beaumont sur les phénomènes éruptifs de l'Italie méridionale. *Compt. Rend.* **54**, 99-483.

Dienstbach F., Emmenegger F. P. and Schlaepfer C. W. (1977) Vaporization of copper(II) chloride and the structure of the vapor studied using UV/visible and Raman spectroscopy. *Inst. Anorg. Anal. Chem. Helv. Chim. Acta* **60**, 2460-2470.

Drummond S. E. and Ohmoto H. (1985) Chemical evolution and mineral deposition in boiling hydrothermal systems. *Econ. Geol.* **80**, 126-147.

Elie de Beaumont L. (1847) Voyage métallurgique en Angleterre, ou Recueil de mémoires sur le gisement, l'exploitation et le traitement des minerais de fer, étain, plomb, cuivre et zinc, dans la Grande-Bretagne. A. Dufrénoy and L. Élie de Beaumont, Paris, Bachelier, 1837-1839.

Ewing C. T. and Stern K. H. (1974) Equilibrium vaporization rates and vapor pressures of solid and liquid sodium chloride, potassium chloride, potassium bromide, cesium iodide, and lithium fluoride. *J. Phys. Chem.* **78**, 1998-2005.

Faure F. M., Mitchell M. J., and Bartlett R. W. (1972) Vapor pressure study of stibnite (Sb_2S_3). *High Temp. Sci.* **4**, 181-191.

Faure F. M., Mitchell M. J., and Bartlett R. W. (1973) Vapor pressure study of arsenic trisulfide. *High Temp. Sci.* **5**, 128-137.

Ferro D., Piacente V., and Scardala P. (1989) Vaporization enthalpies of black and red mercury sulfides and their heat of transition from vapor pressure measurements. *J. Less-Common Met.* **147**, 1-8.

Forsythe G. E., Malcolm M. A. and Moler C. B. (1976) Computer Methods for Mathematical Computations, Prentice-Hall.

Fulignati P. and Sbrana A. (1998) Presence of native gold and tellurium in the active high-sulfidation hydrothermal system of the La Fossa volcano (Vulcano, Italy). *J. Volcanol. Geotherm. Res.* **86**, 187-198.

Galobardes J. F., Van Hare D. R., and Rogers L. B. (1981) Solubility of sodium chloride in dry steam. *J. Chem. Eng. Data* **26**, 363-366

Gemmell J. B. (1987) Geochemistry of metallic trace elements in fumarole condenstates from Nicaraguan and Costa Rican volcanoes. *J. Volcanol. Geotherm. Res.* **33**, 161-181.

Getahun A., Reed M. H., and Symonds R. (1996) Mount St. Augustine volcano fumarole wall rock alteration: mineralogy, zoning, composition and numerical models of its formation process. *J. Volcanol. Geotherm. Res.* **71**, 73-107

Giggenbach W. F. and Matsuo S. (1991) Evaluation of results from Second and Third IAVCEI Field Workshops on Volcanic Gases, Mt Usu, Japan, and White Island, New Zealand. *Appl. Geochem.* **6**, 125-141.

Gmelin Handbuch der anorganischen Chemie. (Gmelin handbook of inorganic chemistry.) Gmelin - Institut fur Anorganische Chemie und Grenzgebiete in der Max-Planck-Gesellschaft zur Forderung der Wissenschaften. Berlin, Verlag Chemie.

Gospodinov G. G., Pashinkin A. S., Boncheva-Mladenova Z. and Novoselova A. V. (1970) The determination of solid antimony sulphide vapour pressure. *Izvestia Akademii Nauk SSSR, Neorganicheskie Materiali* **4**, 1242 – 1247.

Gräber P. and Weil K. G. (1972) Mass-spectrometric investigations of silver halides. 1. Mass-spectrum appearance potentials, and fragmentation scheme of silver chloride. *Ber. Bunsengeschaft Phys. Chem.* **B 76 (6)**, 417-425.

Guilbert J. M. and Park C. F. Jr. (1986) *The Geology of Ore Deposits*. W. H. Freeman and Company, New York, 985 pp.

Hedenquist J. W., Aoki M., and Shinohara H. (1994) Flux of volatile and ore-forming metals from the magmatic-hydrothermal system of Satsuma Iwojima volcano. *Geology* **22**, 585-588.

Heinrich C. A., Günther D., Audétat A., Ulrich T., and Frischknecht R. (1999). Metal fractionation between magmatic brine and vapor, determined by microanalysis of fluid inclusions. *Geology* **27**, 755-758.

Heinrich C. H., Ryan C. G., Mernagh T. P., and Eadington P. J. (1992) Segregation of Ore Metals between magmatic brine and vapor: A fluid inclusion study using PIXE microanalysis. *Econ. Geol.* **87**, 1566-1583.

Henley R. W. and McNabb A. (1978) Magmatic vapor plumes and ground-water interaction in porphyry copper emplacement. *Econ. Geol.* **73**, 1-20.

Hildenbrand D. L. and Lau K. H. (1996) Thermochemistry of gaseous AgCl, Ag_3Cl_3 and CuCl. *High Temp. Mater. Sci.* **35**, 11-20.

Hsiao C. M. and Schlechten A. W. (1952) Volatility and Stability of Metallic Sulphides, *Journal of Metals* **Jan.**, 65-69

Hubbard S. R. and Ross R. G. (1982) Slope anomaly in the vapor pressure curve of mercury. *Nature* **295**, 682-683.

James S. E. and Hager J. P. (1978) High temperature vaporization chemistry in the gold-chlorine system including formation of vapour complex species of gold and silver with copper and iron. *Metall. Trans.* ***9B***, 501-508.

Kavalieris I. (1994) High Au, Ag, Mo, Pb, V, and W content of fumarole deposits at Merapi volcano, central Java, Indonesia. *J. Geochem. Explor.* **50**, 479-491.

Kebarle P. (1975) Thermochemical information from gas phase ion equilibria. NATO Adv. Study Inst. Ser., Ser. B, B6 (Interact. Ions Mol.), 459-87

Kebarle P., Davidson W. R., French M., Cumming J. B., and McMahon T. B. (1977) Solvation of negative ions by protic and aprotic solvents. Information from gas phase ion equilibria measurements. *Faraday Discuss. Chem. Soc.* **64**, 220-229.

Kestin J., Sengers J. V., Kamgar-Parsi B., and Levelt Sengers J.M.H. (1984) Thermophysical Properties of Fluid H_2O. *J. Phys. Chem. Ref. Data* **13**, 175-183.

Korzhinsky M. A., Tkachenko S. I., Schmulovich K. L., Taran Y. A., and Steinberg G. S. (1994) Discovery of a pure rhenium mineral at Kudriavy volcano. *Nature* **369**, 51-52.

Krauskopf K. B. (1957) The heavy metal content of magmatic vapor at 600°C. *Econ. Geol.* **52**, 786-807.

Krauskopf K. B. (1964). The possible Role of volatile metal compounds in ore genesis. *Econ. Geol.* **59**, 22-45.

Kulakov M. P. (1975) Melting point and vapor pressure of mercury(II) sulfide. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **11**, 553-554.

Kvande H. (1979) Determination of the average molar mass of the vapor above molten sodium chloride by the transpiration method. *Acta Chem. Scand.* **A33**, 407-412.

Lacroix A. (1907) Les mineraux des fumerolles de l'eruption du Vesuve en Avril 1906. *Bull. Soc. Min. Fran.* **30**, 219-266.

Lau K. H., Brittain R. D., and Hildenbrand, D. L. (1982) Vaporization of arsenic trisulfide and the dissociation energy of arsenic monosulfide. *J. Phys. Chem.* **86**, 4429-4432.

Le Guern F. (1988) Ecoulements gazeux reactifs à hautes temperatures, mesures et modelisation. Ph.D. thesis, University of Paris, 314 pp.

Le Guern F. and Bernard A. (1982) A new method for sampling and analyzing sublimates. Application to Merapi Volcano, Java. *J. Volcanol. Geotherm. Res.* **12**, 133-146.

Le Guern F., Gerlach T.M. and Nohl A. (1982) Field gas chromatograph analyses of gases from a glowing dome at Merapi volcano, Java, Indonesia, 1977, 1978, 1979. *J. Volcanol. Geotherm. Res.* **14**, 223-245.

Lenian P., Picquenard E., Corset J., Jensen D.and Stendel R. (1988) Raman spectrometric study of the composition of sulfur vapor at temperatures up to 700° C. *Ber. Bunsenges. Phys. Chem.* **92**, 859-870.

Lindgren W. (1933) *Mineral Deposits, 4th ed.* New York, McGraw-Hill, 930 pp.

Lukashenko E. E., Korobeinikov A. P. and Khomaiko I. A. (1970) Saturated vapor pressure and enthalpies of vaporization of individual sodium and potassium chlorides. *Zh. Fiz. Khim.* **44**, 341-343.

Marshall W. L. (1972) A further description of complete equilibrium constants. *J. Phys. Chem.* **76**, 720-731.

Martynova O. I. (1964) Some problems of the solubility of involatile inorganic compounds in water vapor at high temperatures and pressures. *Russ. J. Phys. Chem.* **38**, 587-592

Menyailov I. A. and Nikitina L. P. (1980) Chemistry and metal contents of magmatic gases: the new Tolbachik volcanoes gas (Kamchatka). *Bull. Volcanol.* **43**, 197-207.

Mesmer R. E., Marshall W. L., Palmer D. A., Simonson J. M., and Holmes H. F. (1988) Thermodynamics of aqueous association and ionization reaction at high temperatures and pressures. *J. Sol. Chem.* **17**, 699-718.

Migdisov Art A., Suleimenov O. M., and Alekhin Yu. V. (1998) Experimental study of polysulfane stability in gaseous hydrogen sulfide. *Geochim. Cosmochim. Acta* **62**, 2627-2635.

Migdisov Art. A., Williams-Jones A. E., and Suleimenov O. M. (1999) The solubility of chlorargyrite (AgCl) in water vapor at elevated temperatures and pressures. *Geochim. Cosmochim. Acta* **63**, 3817-3827.

Mills K. C. (1974) *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*. National Physical Laboratory, Teddington, Middlesex, London Butterworths, 844 pp.

Munir Z. A., Street G. B., and Winters, H. F. (1971) Mass-spectrometric and vapor pressure studies on the sublimation of realgar (As_4S_4). *J. Chem. Phys.* **55**, 4520-4527.

Naboko S. I. (1964) Contemporary volcanoes and gas hydrothermal activity. *Geologiya SSSR* **31**, 323-387.

Nemoto, T., Hayakawa, M., Takahashi, K., and Oana, S. (1957) Report on the geology, geophysical, and geochemical studies of of Usu volcano (Showashinzan). *Rept. Geol. Surv. Japan* no. 170, p. 1-149.

Novoselova A. V. and Pashinkin A. S. (1978) *Vapour pressure of volatile metals sulphides*. Moscow, Nauka, 112 pp.

Ozin G.A. (1969) Gas-phase Raman spectroscopy of phosphorus, arsenic, and saturated sulfur vapors. *J. Chem. Soc. D* **(22)**, 1325-1327.

Pankratz L. B. (1982) Thermodynamic properties of elements and oxides. United States Dept. of the Interior, Bureau of Mines: Washington, D.C.

Pankratz L. B. (1984) Thermodynamic properties of halides. United States Dept. of the Interior, Bureau of Mines: Washington, D.C.

Pankratz L. B. (1987) Thermodynamic properties of sulfides. United States Dept. of the Interior, Bureau of Mines: Washington, D.C.

Park C. F. and McDiarmid R. A. (1975) *Ore Deposits-3rd Edition*, New York, McGraw-Hill, 522 pp.

Pashinkin A. S., Izergin A. A., Amirov R. A., Alikhanyan A. S., and Steblevskii, A. V. (1982) Saturated vapor pressure and heat of formation in arsenic sulfide (As_4S_4). *Izv. Akad. Nauk SSSR, Neorg. Mater.* **18**, 1253-1256.

Pashinkin A. S., Molodyk A. D., Belousov V. I., Strel'chenko S. S., and Fedorov, V. A. (1974) Composition of arsenic (III) sulfide vapor. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **10**, 1600-1602.

Pitzer K. S. (1996) Sodium chloride vapor at very high temperatures: linear polymers are important. *J. Chem. Phys.* **104**, 6724-6729.

Pitzer K.S. and Palaban R.T. (1986) Thermodynamics of NaCl in steam. *Geochim. Cosmochim. Acta* **50**, 1445-1454

Pryce W. (1778) *Mineralogia Cornubiensis*. London, J. Phillips (Printers), 331 pp.

Quisefit J. P., Toutain J. P., Bergametti G., Javoy M., Cheyet B., and Person A. (1989) Evolution versus cooling of gaseous volcanic emissions from Momotombo Volcano, Nicaragua: Thermochemical model and observations. *Geochim. Cosmochim. Acta* **53**, 2591-2608.

Rau H., Kutty T.R.N., and Guedes de Carvalho J.R.F (1973) High temperature saturated vapor pressure of sulfur and estimation of its critical quantities. *J. Chem. Thermo.* **5**, 833

Rivkin S. L. (1988) *Thermodynamic properties of gases*. (ed, D. D. Wagman) 4th ed., New York: Hemisphere Pub. Corp.

Rogstad A. (1972) High-temperature laser Raman spectroscopic study on mixtures of arsenic and sulfur vapors. *J. Mol. Struct.* **14**, 421-426.

Shmulovich K. I. and Churakov S. V. (1998) Natural fluid phases at high temperatures and low pressures. *J. Geochem. Explor.* **62**, 183-191.

Shpil'rain E. E. and Nikanorov E. V. (1971) Experimental study of mercury vapor pressure by the boiling point method. *Teplofiz. Vys. Temp.* **9(3)**, 640-643.

Smith C.L., Ficklin W.H., and Thompson J.M. (1987) Concentrations of arsenic, antimony, and boron in steam and steam condensate at the Geysers, California. *J. Volcanol. Geotherm. Res.* **32**, 329-341

Sourirajan S. and Kennedy G. C. (1962) The system H_2O-NaCl at elevated temperatures and pressures. *Am. J. Sci.* **260**, 115-141

Spycher N. F. and Reed M. H. (1989) Evolution of a Broadlands-type epithermal fluid along alternative P-T path; Implications for the transport and deposition of base, precious and volatile metals. *Econ. Geol.* **84**, 328-359

Steblevskii A. V., Alikhanyan A. S., Pashinkin A. S. and Malyusov V. A. (1986) Vapor composition in the arsenic-sulfur system. *Zh. Neorg. Khim.* **31**, 2451-2456.

Steno N. S. (1669) *De Solido intra Solidum Naturaliter Contento.* Florence.

Steudel R. (1984) Elemental sulfur and related homocyclic compounds and ions. In *Sulfur - Its significance for chemistry, for the geo-, bio- and cosmosphere and technology,* vol. **3**, A. Müller and B. Keeds (Eds), Elsevier, Amsterdam. 3-37.

Steudel R. (1987) Sulfur homocycles. In *The chemistry of inorganic homo and heterocycles*, vol. **2**, J. Sowerby and I. Haiduc (Eds), Academic Press. London, 737-739.

Stoiber R. E. and Rose W. I. Jr. (1974) Fumarole incrustations at active Central American volcanoes. *Geochim. Cosmochim. Acta* **38**, 495-510.

Styrikovich M.A. (1969) Steam solutions. *Vestnik Akad. Nauk SSSR* **39**, 70-77

Sullivan C. L., Prusacryk J. E., and Carson K. D. (1970) Molecules in the equilibrium vaporisation of antimony sulfide and selenide. *J. Chem. Phys.* **53**, 1289-1290

Sunner J., Magnera T. F., and Kebarle P. (1981) Ion-molecule equilibrium measurements by high-pressure mass spectrometry. Some recent advances in concepts and technique. *Can. J. Chem.* **59**, 1787-1796.

Symonds R. B. (1992) Getting the gold from the gas: How recent advances in volcanic-gas research have provided new insight on metal transport in magmatic fluids. Rept. Geol. Surv. Japan, No. 279, 170-175.

Symonds R. B. and Reed M. H. (1993) Calculation of multicomponent chemical equilibria in gas-solid-liquid systems: calculation methods, thermochemical data, and applications to studies of high-temperature volcanic gases with examples from Mount St. Helens. *Am. J. Sci.* **293**, 758-864.

Symonds R. B., Rose W. I., Reed M. H., Lichte F. E., and Finnegan D. L. (1987) Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia. *Geochim. Cosmochim. Acta.* **51**, 2083-2101

Symonds R. B., Reed M. H. and Rose W. I. (1992) Origin, speciation, and fluxes of trace-element gases at Augustine volcano, Alaska: insights into magma degassing and fumarolic processes. *Geochim. Cosmochim. Acta* **56**, 633-657

Symonds R. B., Rose W. I., Gerlach T. M., Briggs P. H., and Harmons, R. S. (1990) Evaluation of gases, condensates and SO_2 emissions from Augustine Volcano, Alaska: the degassing of a Cl-rich system. *Bull. Volcanol.* **52**, 355-374.

Symonds R. B., Rose W. I., Bluth G. J. S., and Gerlach T. M. (1994) Volcanic-gas studies: Methods, results and applications. In *Volatiles in Magmas* (eds. M. R. Carroll and J. R. Holloway). Reviews in Mineralogy **30**, 1-66.

Tagirov V. K., Makarov V. A., and Brukvin V. A. (1993) Vapor composition and pressure over chlorides of silver and gold. *Metalli* **5**, 67-71.

Taran Y. A., Bernard A., Gavilanes J-C., and Africano F. (2000) Native gold in mineral precipitates from high-temperature volcanic gases of Colima volcano, Mexico. *Appl. Geochem.* **15**, 337-346.

Taran Y. A., Hedenquist J. W., Korzhinsky M. A., Tkachenko S. I., and Shmulovich K.I. (1995) Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands. *Geochim. Cosmochim. Acta* **59**, 1749-1761.

Tedesco D. and Totain J-P. (1991) Chemistry and emission rate of volatiles from White Island volcano (New Zealand). *Geophys. Res. Let.* **18**, 113-116.

Toutain J. P., Aloupogiannis P., Delorme H., Person A., Blanc P., and Robaye G. (1990) Vapor deposition of trace elements from degassed basaltic lava, Piton de la Fournaise volcano, Reunion Island. *J. Volcanol. Geotherm. Res.* **40**, 257-268.

Ulrich T., Gunther D., and Heinrich C. A. (1999) Gold concentrations of magmatic brines and the metal budget of porphyry copper deposits. *Nature* (London) **399**, 676-679.

Ustyugov G. P., Kudryavtsev A. A., and Kuadzhe B. M. (1968) Saturated vapor pressure of arsenic sulfides. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **4**, 1338-1339.

Visnapuu A. and Jensen, J. V. (1970) Composition and properties of vapors over molten silver chloride. *J. Less-Common Metals.* **76**, 141.

Wagman D. D., Evans W. H., and Parker V. B. (1982*) The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C_1 and C_2 organic substances in SI units*. Washington, Amer. Chem. Soc.; New York: Amer. Inst. of Physics, 392 pp.

Walker A. L. and Walker W. J. (1956) *The origin and nature of ore deposits*. Colorado Springs, Walker Associates.

Wood S. A. (1987) Thermodynamic calculations of the volatility of the platinum group elements (PGE): The PGE content of fluids at magmatic temperatures. *Geochim. Cosmochim. Acta* **51**, 3041-3050.

Wood S. A. and Samson I. M. (1998) Solubility of ore minerals and complexation of ore metals in hydrothermal solutions. In *Techniques in Hydrothermal Ore Deposits* (eds. J. P. Richards and P. B. Larson). Reviews in Economic Geology **10**, 33-80.

Zakaznova-Iakovleva V. P., Migdisov Art. A., Suleimenov O. M., Williams-Jones A. E. and Alekhin Yu. V. (in press) Experimental study of stibnite solubility in gaseous hydrogen sulphide. *Geochim. Cosmochim. Acta*, **65**, 289-298.

Zeis E. G. (1929) The Valley of 10,000 Smokes, the fumarolic incrustations and their bearing on ore deposition. *National Geographic Society Technical Paper* **1**, 61-79.