

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/222493428>

# The solubility of chlorargyrite (AgCl) in water vapor at elevated temperatures and pressures

Article in *Geochimica et Cosmochimica Acta* · November 1999

DOI: 10.1016/S0016-7037(99)00213-6

CITATIONS

73

READS

623

3 authors, including:



**Artas Migdisov**

Los Alamos National Laboratory

100 PUBLICATIONS 2,828 CITATIONS

SEE PROFILE



**Anthony E. Williams-Jones**

McGill University

344 PUBLICATIONS 10,175 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



Archean tectonic processes and mineralization [View project](#)



Multi-scale analysis of multiparameter geophysical & geochemical data from active volcanic system [View project](#)



PII S0016-7037(99)00213-6

## Solubility of chlorargyrite (AgCl) in water vapor at elevated temperatures and pressures

ART. A. MIGDISOV,<sup>1,\*</sup> A. E. WILLIAMS-JONES,<sup>1</sup> and O. M. SULEIMENOV<sup>2</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, McGill University, Montréal, Quebec, Canada H3A 2A7

<sup>2</sup>Institut für Mineralogie und Petrographie, Eidgenössische Technische Hochschule, ETH-Zentrum, CH-8092, Zürich, Switzerland

(Received December 23, 1998; accepted in revised form June 10, 1999)

**ABSTRACT**—The solubility of chlorargyrite (AgCl) in undersaturated water vapor was investigated at temperatures of 300 to 360°C and pressures up to 180 bars. It was shown that the presence of water vapor increases the concentration of AgCl in the gas (vapor) phase by between 1.5 and 2 orders of magnitude. This phenomenon is attributed to the formation of hydrated gaseous particles. Silver chloride dissolved in water vapor without changing its stoichiometry (congruent dissolution,  $Ag:Cl = 1:1$ ). On the basis of the experimental data obtained in this study, the process of chlorargyrite dissolution, and the formation of hydrated gaseous particles in water vapor can be described by the reaction:



Considering that Ag is coordinated by three molecules of water and one molecule of chlorine in the  $AgCl \cdot (H_2O)_3^{gas}$  particle, it was assumed that the silver atom is in fourfold coordination. The properties of the  $AgCl \cdot (H_2O)_3$  particle were refined using *ab initio* molecular orbital calculations, and the stable geometry of the particle was deduced to have C3 symmetry.

The temperature dependence of the equilibrium constant for the reaction controlling the formation of  $AgCl \cdot (H_2O)_3^{gas}$  is described by the equation:

$$\log K_{(P=1bar)} = (22.578 \pm 5.505) - (0.0255 \pm 0.0045) \cdot TK - (11987.6 \pm 658.5)/TK$$

Preliminary calculations suggest that water vapor can transport significant quantities of silver, and that such transport may play an important role in mobilizing silver in natural hydrothermal systems. Copyright © 1999 Elsevier Science Ltd

### 1. INTRODUCTION

An important characteristic of silver-depositing hydrothermal systems is that there is extensive boiling (Sherlock et al., 1995; Marshall et al., 1993; Norman et al., 1991; Ruvalcaba-Ruiz and Thompson, 1988). Moreover, it has been argued, from a knowledge of the chemistry of these systems and recent experimental/theoretical studies, that boiling is the principal mechanism for silver precipitation and accumulation (Marshall et al., 1993; Norman et al., 1991; Spycher and Reed, 1989). Proponents of this depositional mechanism, in most cases, have assumed that metal transport is via the liquid phase. However, in a small number of cases, significant concentrations of silver have been detected in the gaseous emissions from volcanoes (Menyailov and Nikitina, 1980; Joron et al., 1982; Olmez et al., 1986; Crowe et al., 1987; Quisefit et al., 1989). For example, Gemmel (1987) and Quisefit et al. (1989) report silver concentrations in condensates collected from Momotombo volcano in Nicaragua of 10–15 ppb and 5–8 ppb, respectively (the corresponding gas temperatures were 450–770°C and 886°C). Comparable silver concentrations (2 ppb) have also been reported (Christenson and Wood, 1993) for condensates collected from Ruapehu volcano, New Zealand; the gas temperature was 354°C. Additional support for the idea that silver can be transported by vapor in appreciable concentrations is provided by analyses of sublimates from volcanic gases. For example, sublimates from

Merapi volcano in Indonesia have been shown to contain up to 100 ppm Ag (Kavalieris, 1994). Other volcanoes producing sublimates with high concentrations of silver include Mount St. Helens, New Tolbachik, Momotombo and Etna (Symonds and Reed, 1993; Novgorodova et al., 1997; Menyailov and Nikitina, 1980; Quisefit et al., 1989; Joron et al., 1982).

A number of researchers have attempted to use thermodynamic modeling to estimate metal concentrations in volcanic gases (Symonds et al., 1987; Spycher and Reed, 1989; Symonds and Reed, 1993; Getahun et al., 1996). The common assumption of the modeling is that the metals are transported as simple chloride or fluoride species ( $CuCl^{gas}$ ,  $AgCl^{gas}$ ,  $CsCl^{gas}$ , etc.). However, these studies modeled the behavior of the gas species using component fugacities, and did not take into account reactions between the trace components dissolved in the gas and the gas-solvent. This approach successfully describes high-temperature (800–400°C) gaseous transport of metals, but because solvation (hydration in the case of an aqueous solvent) is ignored, the approach underestimates the capacity of the gas phase to transport metals at lower temperature (100–400°C).

Inasmuch as silver is present mainly as chloride (and sulfide) species in the aqueous phase of natural hydrothermal systems, it is reasonable to predict that a high proportion of the silver in the vapor phase of such systems is present as silver chloride species. Several groups of researchers have reported experimental data on the partial pressures of silver chloride compounds over crystalline and liquid AgCl (Hildebrand and Lau, 1996; Tagirov et al., 1993; Gräber and Weil, 1972; Visnapuu

\*Author to whom correspondence should be addressed (artas@eps.mcgill.ca).

and Jensen, 1970; Chang and Toguri, 1974), but published data on the behavior of silver in water vapor are restricted to *ab initio* calculations (Martinez et al., 1997; Shevkunov, 1996; Shevkunov and Al'mukhrez, 1994). These latter studies have predicted the coordination of silver in the first and second hydration shells, and have estimated the energy of hydration, but they have not deduced the basic thermodynamic properties of the silver compounds in the vapor phase. The goal of the present work was to obtain thermodynamic information on soluble silver chloride species in water vapor at temperatures up to 360°C and pressures up to 200 bars.

## 2. EXPERIMENTAL METHOD

The experimental method is similar to that used by Migdisov et al. (1998). Experiments were carried out at temperatures between 300 and 360°C (Table 2) in an electric furnace (internal diameter 15 cm, height 50 cm) equipped with large 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 three thermocouples, located at the top, bottom, and center of the furnace. The vertical temperature gradient during a run was typically in the range 1.0 to 2.5°C/m, but during the first 2 to 3 h it was between 8 and 20°C/m due to the initially cold state of the autoclave. Temperature during runs 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*) in water vapor. The autoclaves were constructed from titanium alloy (grade 2 ASTM B348, Fig. 1). Each autoclave was conditioned initially with nitric acid to produce a protective layer of  $TiO_2$  on the internal surface. Autoclave volumes (100 cm<sup>3</sup>) 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  $\pm 0.1$  g. Autoclaves were loaded with pre-weighed platinum or quartz ampoules containing single crystals of *AgCl* (nitrate, copper, and iron concentrations  $< 0.001\%$ ).

The ampoule was suspended near the top of the autoclave using a titanium spring or quartz needle (Fig. 1). A known mass of distilled nanopure water was placed in the bottom of the autoclave using a syringe in order to prevent contact of solid *AgCl* with liquid  $H_2O$ . The mass of the water was determined by weighing the syringe before and after introducing the water into the autoclave, and was accurate to  $\pm 0.05$  g. Care was taken to ensure that the introduced mass did not saturate the system with liquid at the experimental conditions, and that *AgCl* solubility was restricted to the vapor. Due to the extremely low vapor pressure of silver chloride 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).

Before each run, a current of nitrogen was passed through the autoclave for 20 to 40 min to remove atmospheric gases. After the run, the autoclave was air-cooled down to room temperature, and the condensates were collected as samples. The ampoule was dried at 120°C for 1 to 2 h to remove water condensed on its walls and on the *AgCl* crystal, and was then re-weighed. *AgCl* condensed on the walls of autoclave was dissolved using 3 to 7 ml of nitric acid (pH = 0.5). The concentrations of dissolved silver in the condensates and washing solutions were determined by AA spectroscopy in graphite sample tubes using a Zeeman 5100 spectrometer (Perkin Elmer) and ICP-MS (Activation Laboratories Ltd., Ancaster, Canada).

Due to the fact that gaseous compounds with unusual stoichiometry are commonly described for solid-vapor systems (Gräber and Weil, 1972; Visnapuu and Jensen, 1970; Chang and Toguri, 1974), the stoichiometry of the gaseous silver species was investigated by varying the quantity of *HCl* employed in experiments. The *HCl* was added in quantities that yielded solutions with pH values of 1.5, 2.5, 3.7, and 4.0. Experiments were carried out at pressures close to that of saturated water vapor and at temperatures of 330 and 360°C. Partial pressures of

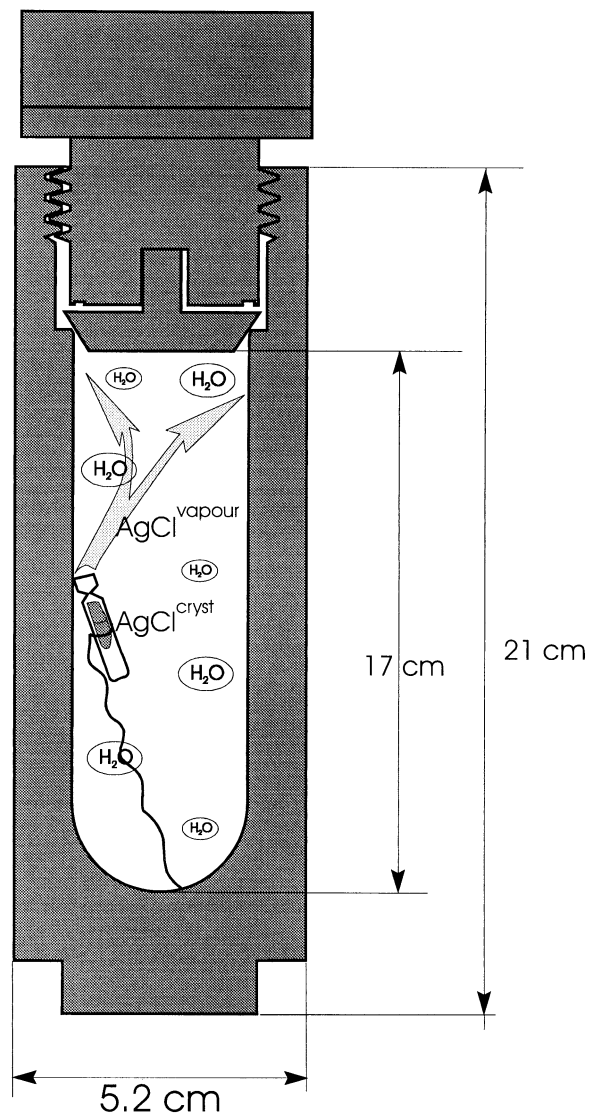


Fig. 1. A section through a titanium autoclave of the type used in this study. The autoclave contains a chlorargyrite-bearing platinum capsule.

$HCl^{gas}$  and water vapor in the runs were calculated using the P-V-T relations for hydrogen chloride-water mixtures at temperatures up to 500°C and pressures up to 1500 bars, reported by Bach et al. (1977).

A potential source of error in the method is condensation of *AgCl* on the cold parts of the autoclave during runs. The latter may occur if the chlorargyrite is at a higher temperature than other internal parts of the autoclave, notably the walls, and could lead to considerable overestimation of the solubility of *AgCl* 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 chlorargyrite was located in the coldest part of the autoclave. Thus, it is very unlikely that any condensation occurred during heating and at the experimental temperature. However, additional *AgCl* could have been released from the solid during quenching, and condensed on the cooler walls of the autoclave together with the *AgCl* which had been dissolved in vapor at the end of the experiment. Another possible source of error is partitioning of *AgCl* from the vapor phase into the liquid (water) during heating or quenching. Owing to the much higher solubility of *AgCl* in the liquid phase (several orders of magnitude higher), this could result in gross overestimation of the solubility of *AgCl* in the vapor phase.

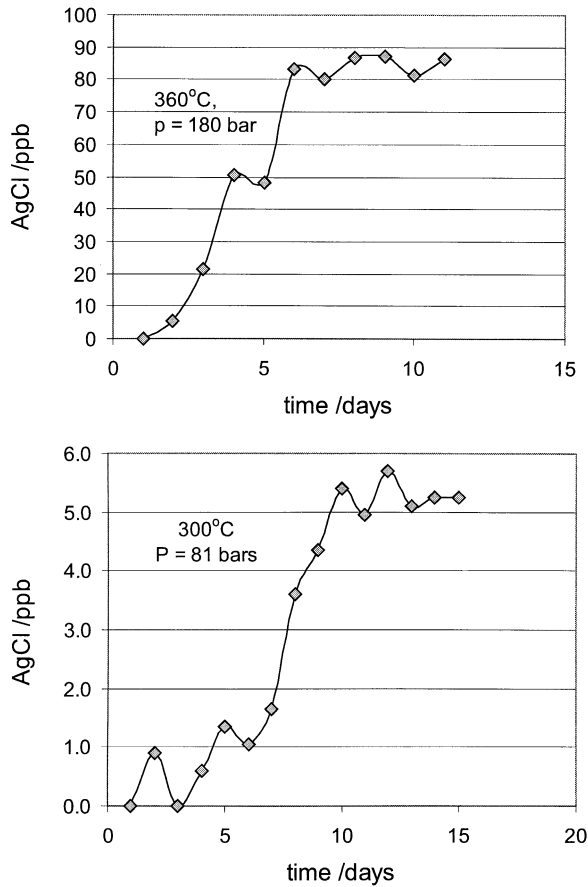


Fig. 2. The solubility of  $AgCl$  in the vapor phase as a function of time. The data suggest that equilibrium was attained after 7 days at  $360^{\circ}C$ . Two extra days were required to attain equilibrium at  $300^{\circ}C$ .

The issue of experimental error is discussed additionally in the next section.

### 3. RESULTS

In order to investigate the possibility of significant experimental error due to condensation of  $AgCl$  on the walls of the autoclave, we undertook a series of 10 blank experiments in an atmosphere free of water vapor (nitrogen atmosphere,  $p = 1-80$  bar). The mass of  $AgCl$  transported in each of these experiments was less than the detection limit ( $<0.1$  ppb) of the analytical techniques (graphite furnace AA and ICP-MS), thereby eliminating the possibility of error due to  $AgCl$  condensation. The issue of experimental error, particularly due to partitioning of  $AgCl$  into the water, was further investigated through a series of "kinetic runs". Twenty-six experiments (11 runs at  $360^{\circ}C$  and 15 at  $300^{\circ}C$ ) were carried out under constant water pressure (close to the liquid/vapor phase boundary) for durations ranging from 1 to 15 days. At  $360^{\circ}C$ , equilibrium was attained after 7 days, whereas at  $300^{\circ}C$  the time required to reach equilibrium was 8–9 days (Fig. 2, Table 1).

As is clear from Fig. 2, and Table 1, once equilibrium was attained (runs of longer than 8 and 9 days duration at 360 and  $300^{\circ}C$ , respectively),  $AgCl$  solubilities were reproducible to approximately  $\pm 15\%$  of the absolute value. If there had been

Table 1. Solubility of  $AgCl$  in the vapor phase as a function of time.

Time (days)	$T^{\circ}C$	$H_2O$ (gr)	$P$ (bar)	$AgCl$ (ppb)
1	360	15	183	0.0
2	360	15	183	5.3
3	360	15	183	21.3
4	360	15	183	50.8
5	360	15	183	48.4
6	360	15	183	63.3
7	360	15	183	80.1
8	360	15	183	86.6
9	360	15	183	87.2
10	360	15	183	81.1
11	360	15	183	86.4
1	300	4	81	0.0
2	300	4	81	0.9
3	300	4	81	0.0
4	300	4	81	0.6
5	300	4	81	1.4
6	300	4	81	1.1
7	300	4	81	1.7
8	300	4	81	3.6
9	300	4	81	4.4
10	300	4	81	5.4
11	300	4	81	5.0
12	300	4	81	5.7
13	300	4	81	5.1
14	300	4	81	5.3
15	300	4	81	5.3

Experimental results of the runs under constant water pressure for durations ranging from 1 to 15 days (close to the liquid/vapor phase boundary).

significant condensation of  $AgCl$  onto the autoclave walls or partitioning of  $AgCl$  into the water during the experiments, none of the experimental results would have been reproducible, and consequently equilibrium would never have been attained.

A set of 31 experiments were conducted to evaluate vapor phase solubility in the  $H_2O-AgCl$  system at temperatures of  $300, 310, 330, 340, 350,$  and  $360^{\circ}C$  and 9 experiments in the  $H_2O-AgCl-HCl$  system at  $330$  and  $360^{\circ}C$ . Vapor pressure in the  $H_2O-AgCl$  system varied from 20 to 160 bars, and was close to that of the liquid-vapor phase boundary in the system  $H_2O-AgCl-HCl$ .

The mole fraction of  $AgCl$  in the vapor was calculated from the silver concentration in the quenched condensate (Table 2). Due to the low partial pressure of  $AgCl$ , 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 Fig. 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  $Ag:Cl = 1:1$ , i.e., the formation of other species was suppressed.

The concentrations of  $AgCl$  in the vapor phase determined

from our experiments are reported in Table 2, and shown as a function of  $P_{H_2O}$  in Fig. 4. From this figure, it can be seen that the isothermal concentration of  $AgCl$  in the vapor increases sharply with increasing  $H_2O$  pressure.

The partitioning of  $AgCl$  into the water vapor results from two processes that proceed in parallel, namely the dissolution of chlorargyrite in the vapor phase, i.e., its solvation as  $AgCl^{vapor}$ , and the development of a partial pressure of  $AgCl^{gas}$  over the crystalline phase. Concentrations of  $AgCl^{gas}$  were calculated for various values of  $P_{H_2O}$  and measured autoclave volumes. The calculations were made assuming inert behavior of components, and the results of this calculation are illustrated by the bold curves shown in Fig. 4. At  $P_{H_2O} = 0$ , the mole fraction of  $AgCl^{gas}$  in the gas phase must be equal to unity, and, in principle, its partial pressure can be estimated from data in the literature for the uni-component system. Unfortunately, there are no experimental data available on the partial pressure of  $AgCl^{gas}$  vapor at temperatures lower than the melting point of chlorargyrite (728 K or 454°C). Thus, the values for the thermodynamic parameters that must be used to calculate  $P_{AgCl}^{gas}$  are all extrapolations from values measured at high-temperature. Reliable calculation of  $P_{AgCl}^{gas}$  is further complicated by uncertainties in the high temperature data (Fig. 5), and the fact that the differences in estimated pressures increase sharply with decreasing temperature.

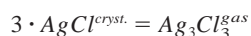
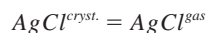
The partial pressure of  $AgCl^{gas}$  over the crystalline phase is constant at constant temperature (i.e., there is a fixed mass in the constant volume autoclave), but the concentration of  $AgCl^{gas}$  decreases with increasing  $P_{H_2O}$  (Fig. 4). By contrast  $AgCl$  solubility in the vapor phase ( $AgCl^{vapor} + AgCl^{gas}$ ) increases exponentially with increasing  $P_{H_2O}$  at constant temperature. Maximum estimates of  $P_{AgCl}^{gas}$  are provided by the equation of Tagirov et al. (1993), and, are similar to those corresponding to the analytical detection limit in our experiments (0.1–0.5 ppb). We, therefore, conclude that  $AgCl^{gas}$  does not contribute significantly to the total concentration of  $AgCl$  in the vapor phase.

Isobaric solubility trends were calculated by polynomial fits to the isothermal dependencies (Fig. 6).  $AgCl^{vapor}$  concentrations increase slowly with increasing temperature at constant pressure, whereas the  $AgCl$  solubility (a maximum value) at the investigated temperature decreases sharply with decreasing temperature once the vapor is saturated with liquid.

#### 4. DISCUSSION

##### 4.1. Vapor-phase Speciation of $AgCl$

Silver chloride evaporation in the uni-component system proceeds mainly in response to the following reactions (Hildebrand and Lau, 1996; Tagirov et al., 1993; Gräber and Weil, 1972; Visnapuu and Jensen, 1970; Chang and Toguri, 1974):



As has been demonstrated in several publications (Hildebrand and Lau, 1996; Tagirov et al., 1993; Visnapuu and Jensen, 1970),  $AgCl^{gas}$  is the dominant species in the gaseous phase, and its partial pressure is many times greater than that of  $Ag_3Cl_3$ . It was, therefore, assumed that silver chloride evapo-

Table 2. Experimental results.

T°C	H <sub>2</sub> O (g)	P (bar)	AgCl <sup>vap</sup> (ppb)	X (AgCl <sup>vap</sup> ) × 10 <sup>10</sup>	logX
360	15	182.69	94.6	119.1	-7.92
360	15	182.69	101.0	127.1	-7.90
360	13	175.14	90.9	114.4	-7.94
360	12	170.12	71.9	90.5	-8.04
360	12	170.12	78.4	98.7	-8.01
360	10	157.05	67.3	84.7	-8.07
360	10	157.05	73.8	92.9	-8.03
360	9	148.76	61.2	77.1	-8.11
360	8	139.14	50.1	63.1	-8.20
360	4	84.86	15.0	18.9	-8.72
360	3	66.74	11.2	14.1	-8.85
360	2	46.6	7.6	9.6	-9.02
350	10	161.49	71.5	90.0	-8.05
350	11	170.43	81.3	102.3	-7.99
340	6	121.64	31.1	52.2	-8.28
340	7	139.26	43.7	70.7	-8.15
340	8	146.77	51.5	81.0	-8.09
330	8	145.41	36.0	45.3	-8.34
330	8	145.41	33.1	41.7	-8.38
330	7	125.59	28.0	35.3	-8.45
330	7.5	118.70	21.3	26.8	-8.57
330	5	113.35	21.0	26.4	-8.58
330	6	104.23	16.1	20.3	-8.69
310	4	84.24	14.1	17.7	-8.75
310	3	74.46	11.0	13.8	-8.86
310	2	54.17	4.8	6.0	-9.22
300	4	81.13	5.7	7.2	-9.14
300	3	72.02	5.0	6.3	-9.20
300	3.5	64.61	4.2	5.3	-9.27
300	3	57.32	3.3	4.2	-9.38
300	2	40.83	1.2	1.5	-9.82

T°C is the temperature of the run, H<sub>2</sub>O is the mass of water added to the autoclave (amount of water in the gas phase (g)), P is the water vapor pressure ≈ total pressure (bar), AgCl<sup>vap</sup> is the concentration of dissolved AgCl in the vapor phase (ppb), X (AgCl<sup>vap</sup>) is the mole fraction of AgCl in the vapor phase, logX is the log of the AgCl mole fraction corrected using the Gibbs-Pointing relationship.

ration in the  $AgCl-H_2O$  system is mainly in the form  $AgCl^{gas}$ , and that participation of  $Ag_3Cl_3^{gas}$  is negligible. The first assumption that is conventionally made in describing a gaseous system is that of ideal behavior of the gaseous components. In the present case, this means an ideal gaseous mixture of inert components, where the concentration of  $AgCl^{gas}$  in the gaseous phase is governed by its partial pressure over the crystalline phase. As was noted previously, this partial pressure (and mass of  $AgCl$  in the gaseous phase) must be constant at constant temperature and constant autoclave volume. Therefore, the increase in the  $H_2O^{gas}$  pressure (increasing mass in an autoclave of constant volume) must be accompanied by a corresponding decrease in the mole fraction of  $AgCl$  in the gaseous phase:

$$X_{AgCl} = \frac{M_{AgCl}}{M_{H_2O} + M_{AgCl}} \cong \frac{M_{AgCl}}{M_{H_2O}} \quad (1)$$

The Gibbs-Pointing correction was used to describe the change in the fugacity ( $f^0$ ) of the crystalline phase from that for a total pressure of  $P_1 = 1$  bar (standard state) to  $P_2 =$  pressure for the run:

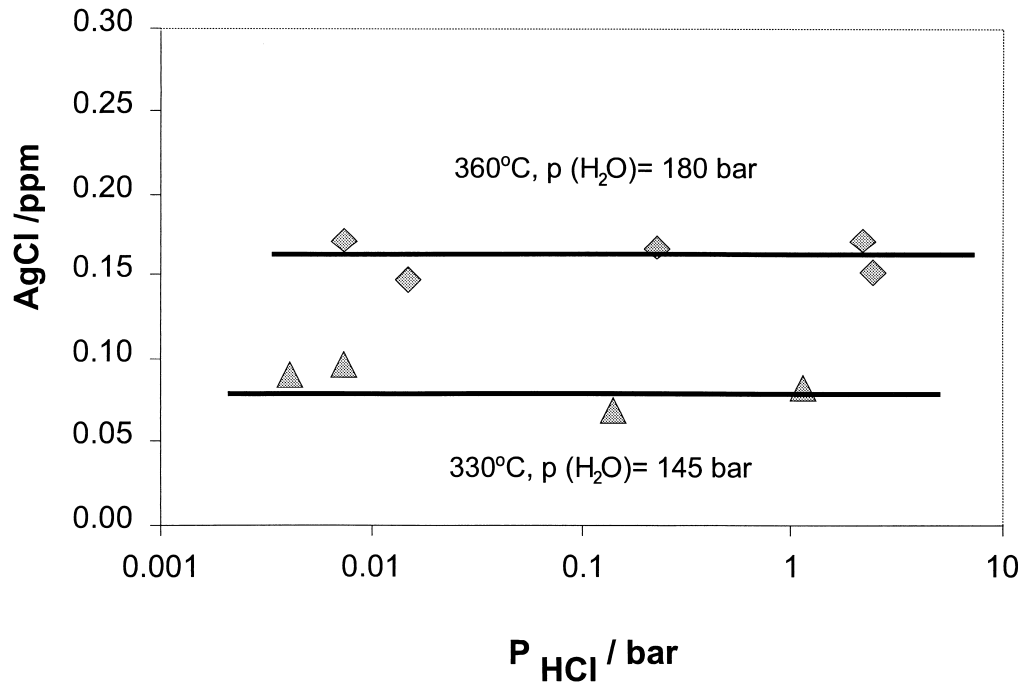


Fig. 3. Concentration of silver chloride in water vapor versus the partial pressure of  $\text{HCl}^{gas}$ . The zero slope of the data distribution indicates that  $\text{AgCl}$  solubility was independent of  $P_{\text{HCl}}$ .

$$\ln \frac{f_2^0}{f_1^0} = \int_{P_1}^{P_2} \frac{V^0}{R \cdot T} dP, \quad (2)$$

Given that changes in the  $\text{AgCl}$  molar volume with temperature are insignificant for the temperatures investigated, it was assumed that  $V^0$  is a constant and

$$\ln \frac{f_2^0}{f_1^0} = \frac{V^0 \cdot (P_2 - P_1)}{R \cdot T} \quad (3)$$

(where  $V^0$  is the molar volume of  $\text{AgCl} = 25.73 \text{ cm}^3/\text{mol}$  and  $f_1^0, f_2^0$  the fugacities of this component in states 1 and 2).

It is apparent from Fig. 4 that this assumption cannot be applied to the experimental points at the studied conditions, and that any description of the system must also take into consideration some interaction among the components of the gaseous mixture.

Possible interactions could be, firstly, the hydration of silver chloride by water vapor (solubility), and secondly, the formation of new stable gaseous chemical compounds with specific stoichiometry (chemical reaction). Given that there was no change in stoichiometry (as was demonstrated in the runs with  $\text{HCl}$ ), the silver chloride concentrations in the vapor phase can be described as resulting from dissolution of  $\text{AgCl}$  in gaseous  $\text{H}_2\text{O}$  or as the formation of hydrated  $\text{AgCl}^{vapor}$  particles (effectively the same thing).

In principle, the solubility of  $\text{AgCl}$  can be modeled using equations of state, e.g., Peng-Robinson or Benedict-Webb-Rubin. However, application of these equations of state re-

quires that the ideal gas limit of the species in question be known precisely. Unfortunately, this is not the case for  $\text{AgCl}$ , as discussed. An alternative approach to modeling  $\text{AgCl}$  solubility, which does not depend on  $P_{\text{AgCl}}^{ogas}$ , is to assume that  $\text{AgCl}$  is dissolved in the vapor phase as the hydrated complex  $\text{AgCl} \cdot (\text{H}_2\text{O})_n$ , and that the hydration number of this complex has a constant value. These assumptions lead to a relatively simple description of the dissolution of  $\text{AgCl}$  in the vapor, and this, in turn, permits reduction of the data to a form which can be easily used in thermodynamic models employed to interpret natural systems (e.g., Symonds and Reed, 1993). In theory, the hydration number may vary with temperature and pressure. However, as discussed subsequently, within the limits of error of our experiments, this value appears to be essentially constant over the range of temperature and pressure conditions investigated. This complex can be described to a first approximation as a normal gaseous particle, characterized by constant stoichiometry and having standard properties of gaseous compounds, such as partial pressure and fugacity. The  $\text{AgCl}$  solubility in water vapor is represented by the reaction



This model is semi-empirical, and based directly on classical equilibrium thermodynamics. A similar approach was used by Martynova (1964), Styrikovich (1969), Galobrades et al. (1981), Alekhin and Vakulenko (1988), and Armellini and Tester (1993) to model experimental data in the  $\text{NaCl}-\text{H}_2\text{O}$  system, and, as discussed by Armellini and Tester (1993), the solubilities predicted with this approach agree very well with

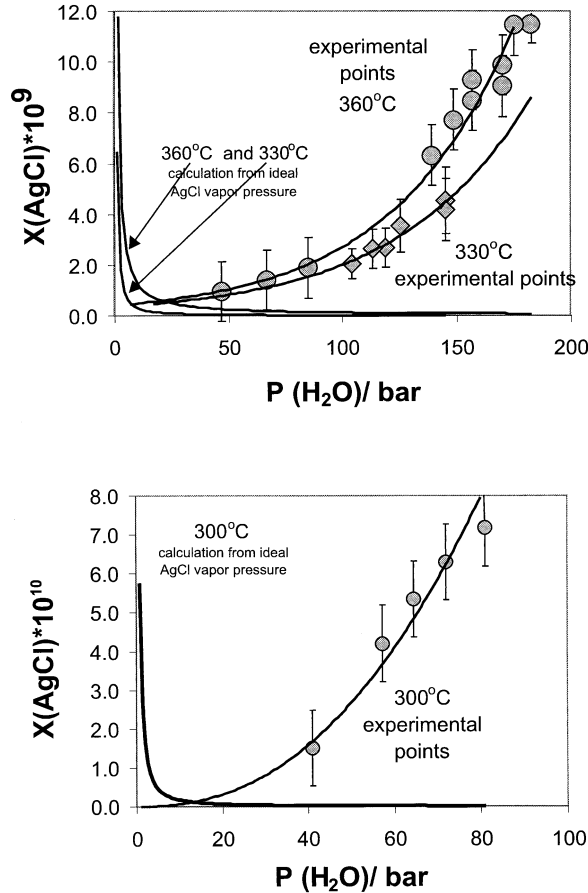


Fig. 4.  $AgCl$  concentrations in the vapor versus the pressure in the system. Due to the low partial pressure of  $AgCl^{vap}$ , the total pressure in the autoclave was effectively that of the water. The heavy solid lines show the silver chloride concentration calculated assuming no hydration of  $AgCl$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

those predicted by the more complicated Pitzer-Palaban model (Pitzer and Palaban, 1986).

Assuming, that the fugacity of  $AgCl \cdot (H_2O)_n^{gas}$  can be approximated as:

$$f_{AgCl \cdot (H_2O)_n} \cong f_{H_2O} \cdot X_{AgCl \cdot (H_2O)_n} \quad (5)$$

where  $X_{AgCl \cdot (H_2O)_n}$  is the mole fraction of the hydrated complex and  $f_{H_2O}$  is the water fugacity, the equilibrium constant of reaction (4) can be written as:

$$\begin{aligned} \log K_4 &= \log X_{AgCl \cdot (H_2O)_n} + \log f_{H_2O} - n \cdot \log f_{H_2O} \\ &= \log X_{AgCl \cdot (H_2O)_n} - (n - 1) \cdot \log f_{H_2O} \quad (6) \end{aligned}$$

To a first, rough approximation, it can be assumed that the fugacity coefficients of the components in a vapor solution do not differ greatly from unity, and the total pressure in the system is equal to the pressure of water. The equations relating the mole fraction of  $AgCl \cdot (H_2O)_n^{gas}$ , partial pressure of water and total pressure of the system can be obtained from Eq. 6 as follows:

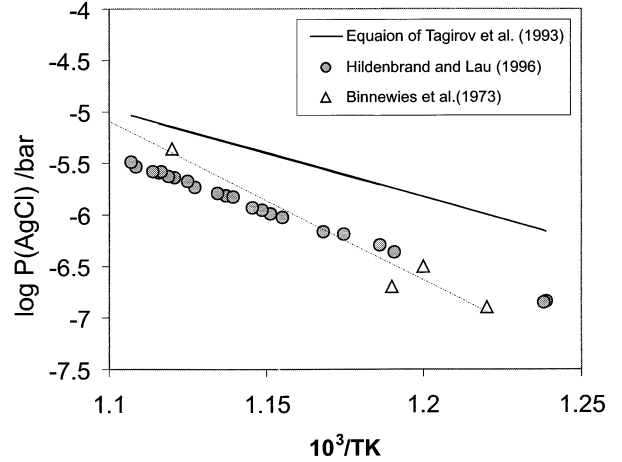


Fig. 5. Published experimental measurements and predicted values of  $P_{AgCl(gas)}$  over chlorargyrite. The diagram omits some high temperature data (1150 to 1700 K), which appear in publications between 1920 and 1952.

$$\log X_{AgCl \cdot (H_2O)_n} = (n - 1) \cdot \log f_{H_2O} + \log K_4 \quad (7)$$

$$\left( \frac{\partial \log X_{AgCl \cdot (H_2O)_n}}{\partial \log P} \right)_T \cong n - 1 \quad (8)$$

The hydration number ( $n$ ) can be determined by the slope of the trend of  $\log X_{AgCl \cdot (H_2O)_n}$  in water vapor, versus  $\log P_{H_2O}$  (Eqs. 7 and 8). This relationship is illustrated in Fig. 7.

It is evident from Fig. 7 that the slope is  $\sim 2$  for the temperatures investigated. The relatively constant slope for all these temperatures confirms, to a first approximation, the assumption of constant stoichiometry of the hydrated complex. However,

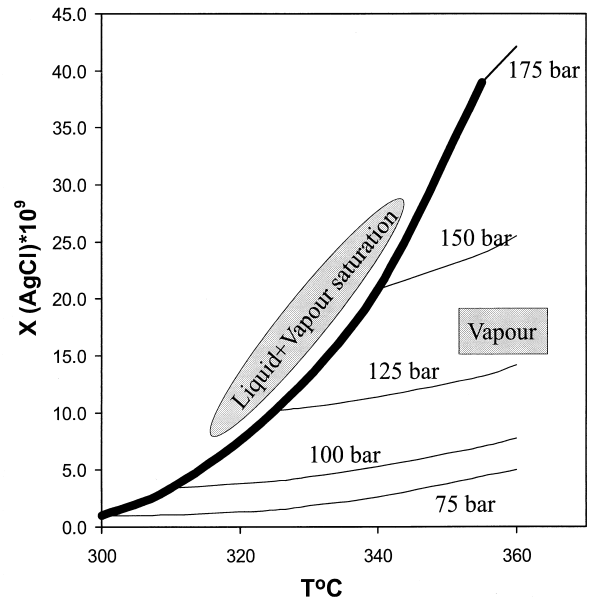


Fig. 6. Isobaric solubility trends obtained from polynomial fits of the experimental data. The heavy solid line represents liquid+vapor saturation.

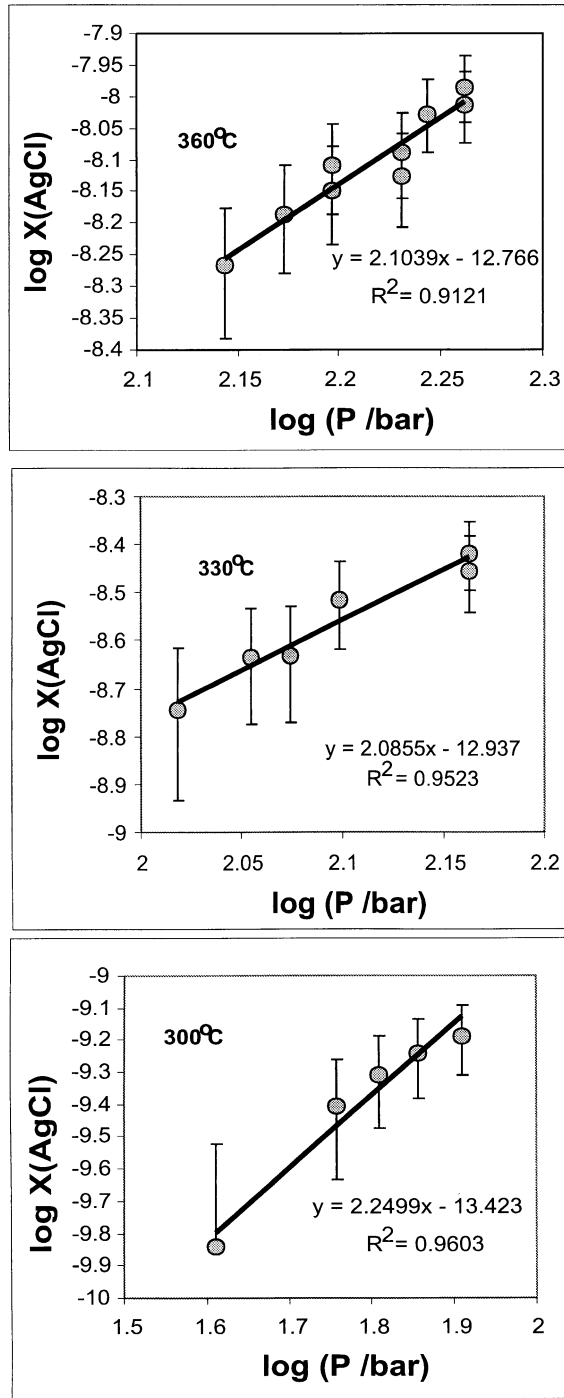


Fig. 7. Plots of values of  $\log$  of  $\log X_{\text{AgCl} \cdot (\text{H}_2\text{O})_n}$  versus  $\log P_{\text{H}_2\text{O}}$ . The bars indicate the experimental error. The slope of  $\sim 2$  for these temperatures suggests the stoichiometry  $\text{AgCl} \cdot (\text{H}_2\text{O})_3$ .

the size of the experimental error only permits estimation of the hydration number ( $n$ ) to a precision of one integer. We, therefore, cannot rule out the possibility that small variations in the hydration number ( $n$ ) of  $\text{AgCl}$  with temperature in the system investigated by our experiments were hidden by experimental error. As the slope in Fig. 7 represents the term “ $n-1$ ”, we

therefore conclude that the above complex has a hydration number of 3, and we interpret this complex to be  $\text{AgCl} \cdot (\text{H}_2\text{O})_3^{\text{gas}}$ . Identical results were obtained using vapor densities instead of partial pressures of water.



In systems of real gases, estimation of  $\text{AgCl}$  solubility is complicated by the non-ideal behavior of the components and the vapor solution. Fugacity coefficients of water at the conditions of our experiments differ from 1 and have a pressure dependence. In order to more accurately describe a system involving real gases, Eq. 8 may be replaced by the following equation:

$$\left( \frac{\partial \log X_{\text{AgCl} \cdot (\text{H}_2\text{O})_n}}{\partial \log P} \right)_T = (n-1) \left\{ 1 + \left( \frac{\partial \log \varphi_{\text{H}_2\text{O}}}{\partial \log P} \right)_T \right\} \quad (10)$$

The essential difference between the two equations is that, whereas Eq. 8 describes a linear dependence between  $\log X_{\text{AgCl} \cdot (\text{H}_2\text{O})_n}$  and  $\log P_{\text{H}_2\text{O}}$ , Eq. 10 yields a slope, the variability of which depends on the size of the term  $\left( \frac{\partial \log \varphi_{\text{H}_2\text{O}}}{\partial \log P} \right)_T$ .

Interpreting our data using this equation and the equation of state for water of Kestin et al. (1984), we obtain hydration numbers  $n$ , of  $3.2 \pm 0.7$  at  $300^\circ\text{C}$  and  $4.2 \pm 0.7$  at  $360^\circ\text{C}$ ,

Considering that silver is coordinated by three or four molecules of water and one of chlorine in the species  $\text{AgCl} \cdot (\text{H}_2\text{O})_3^{\text{gas}}$ , it seems reasonable to predict that the silver is in five- or fourfold coordination. Significantly, tetrahedral or fourfold coordination has been interpreted for  $\text{Ag}^+$  in both water vapor and aqueous solutions. In the case of univalent ion hydration in the vapor phase, the coordination has been modeled by Monte Carlo and molecular dynamic simulations (Martinez et al., 1997; Shevkunov, 1996; Shevkunov and Al'mukhrez, 1994; Abraham and Matteoli, 1983). In the aqueous phase, the coordination of the first hydration shell around the univalent silver ion has been shown to be tetrahedral using electron spin echo modulation (Kevan et al., 1977; Narayana et al., 1978), ultraviolet spectroscopy (Texter et al., 1983) and X-ray absorption (EXAFS) spectroscopic studies (Seward et al., 1996; Yamaguchi et al., 1984). In view of the above discussion, further interpretation of the nature of the  $\text{AgCl} \cdot (\text{H}_2\text{O})_n^{\text{gas}}$  species assumes that Ag is in fourfold coordination.

#### 4.2. Ab initio calculations

The structure of  $\text{AgCl} \cdot (\text{H}_2\text{O})_3^{\text{gas}}$  was refined with the aid of *ab initio* molecular orbital calculations conducted at the MP2(FULL)/LanL2DZ level of theory. The calculations were carried out using the Gaussian 94 (1995) suite of programs on DEC 8400 5/30 and SGI Origin 2000 workstations. Vibrational frequencies were obtained from numerical second derivatives calculated at the MP2(FULL)/LanL2DZ level of theory, in order to verify that the structures computed were local minima on the potential energy surface. Starting with different initial geometries, two potentially stable structures (structure I and structure II) were identified and their geometries optimized (Fig. 8). The vibrational analysis confirmed that the structures represent local minima on the potential energy surface. For the singlet states considered, the zero-point corrected electronic



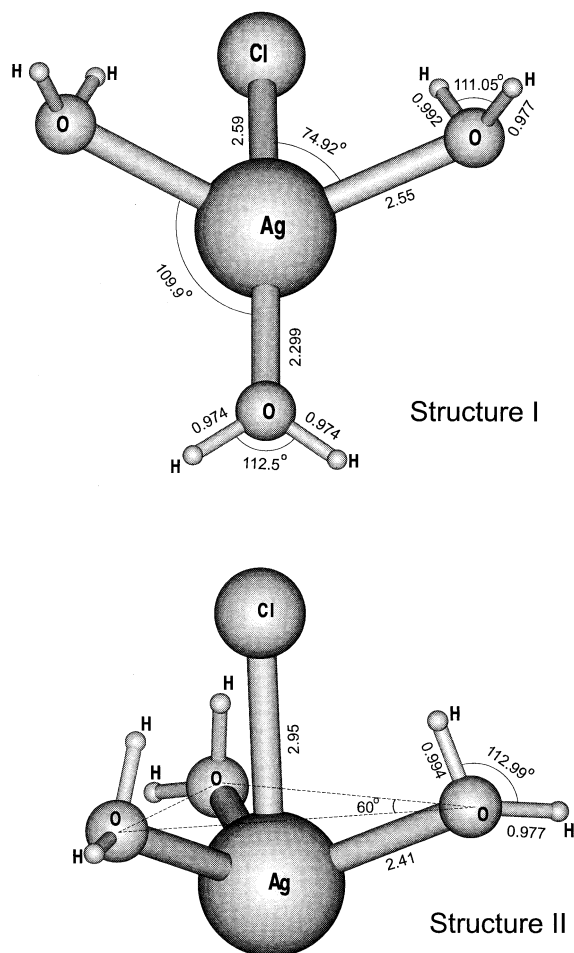


Fig. 8. Illustrations of the results of *ab initio* molecular orbital calculations of the optimal geometry of  $AgCl \cdot (H_2O)_3^{gas}$ .

energy is 0.8 kcal/mol lower for structure II, suggesting that this structure have the more stable form.

Structure I can be derived from that of  $Ag(H_2O)_4^+$ , in which water molecules coordinated to the silver atom occupy the vertices of a regular tetrahedron. Replacement of one of these water molecules by a chlorine atom gives rise to structure I, which has distorted tetrahedral symmetry. As a result of this replacement, water molecules closest to the chlorine atom display a significant OH stretch ( $0.992 \pm$  compared with 0.97 for isolated water), appreciable opening of the HOH angle and a tilt angle (i.e., angle between Ag-O bond and the water plane) of  $49^\circ$ . The water molecule opposite the chlorine atom has a tilt angle of  $8.3^\circ$ . Structure II has  $C_3$  symmetry, the water molecules are slightly more distorted compared to those of the first structure (OH stretch  $0.994 \pm$  and HOH angle  $113^\circ$ ), and the tilt angle is  $34^\circ$ . Net charges on the silver atoms indicate that, in both structures, a significant amount of charge is transferred to the silver atoms from the coordinated solvent molecules. This suggests that the interaction of silver with the ligands is not entirely electrostatic. The energy required to promote the  $AgCl \cdot (H_2O)_3$  cluster from the solution to the gas phase was estimated using the Onsager reaction field model. At the ex-

Table 3. Values of  $\log K_f$ , calculated from the experimental data for the reaction  $AgCl^{cryst} + 3 \cdot H_2O^{gas} + AgCl \cdot (H_2O)_3^{gas}$ .

T°C	$\log K_f$ experimental	$\log K_f$ fitted	$\pm$ error
360	-12.53	-12.525	-0.005
350	-12.537	-12.573	0.036
340	-12.507	-12.632	0.125
330	-12.707	-12.700	-0.007
310	-12.668	-12.871	0.203
300	-12.975	-12.975	0

perimental temperatures, these energies are 9.1–8.5 kcal/mol for structure I and 2.5–2.3 kcal/mol for structure II. The lower energy associated with structure II can be attributed to a lower dipole moment and lower solvent polarization energy. From the various lines of evidence discussed above, it seems likely that silver dissolved in the vapor phase as  $AgCl \cdot (H_2O)_3^{gas}$  occurs dominantly as structure II, and that the thermodynamic properties, which have been derived for this species refer to a conformer with the geometry of structure II.

#### 4.3. Thermodynamic data and application to natural systems

Equilibrium constants for reaction (9) were calculated from the experimental data described earlier and are presented in Table 3 (for  $P_{total} = 1$  bar). The temperature dependence of the  $\log K$  of reaction (9) at a pressure of 1 bar is given by the following equation, which was fitted to the experimental data:

$$\log K_{(p=1bar)} = (22.578 \pm 5.505) - (0.0255 \pm 0.0045) \cdot TK - (11987.6 \pm 658.5)/TK \quad (11)$$

The Gibbs free energies of  $AgCl \cdot (H_2O)_3^{gas}$  were calculated from the  $\log K$  values obtained from Eq. 11. Thermodynamic data for  $H_2O^{gas}$  were taken from Kestin et al. (1984) and the properties of chlorargyrite were obtained from Robie et al., (1978).

The entropy and heat capacity of  $AgCl \cdot (H_2O)_3^{gas}$  were calculated using the following equations:

$$\left( \frac{\partial \Delta G_f^0}{\partial T} \right) = -S \quad (12)$$

$$\left( \frac{\partial S_f^0}{\partial T} \right) = \frac{C_p}{T} \quad (13)$$

The standard thermodynamic properties of  $AgCl \cdot (H_2O)_3^{gas}$  particle were estimated as  $\Delta G_{298}^0 = -678303$  J/mol,  $S_{298}^0 = 573.5$  J/(mol · K). It should be noted that these estimates are based on experimental data collected over a narrow temperature range, i.e., 300 to 360°C, and that significant errors may be associated with the calculation of free energies outside this temperature range.

In order to facilitate the application of our data to natural systems, we calculated the liquid-vapor partition coefficient (D) for the  $AgCl^{cryst} - H_2O^{liquid} - H_2O^{vapor}$  system at the experimental temperatures and saturated water vapor pressure. Partition coefficient calculations were performed using the HCh computer code, which uses an algorithm, based on Gibbs free

energy minimization (Shvarov 1976, 1978). The data on aqueous Ag species were taken from SUPCRT 92 (Johnson et al., 1992). The results of our calculations are presented as mass distribution coefficients ( $Ag^{\text{vapor}} \text{ mol} \cdot \text{l}^{-1} / Ag^{\text{aqueous}} \text{ mol} \cdot \text{l}^{-1}$ ), and were fitted by the following equation:

$$D = (-0.10 \pm 0.01) + (9.64 \cdot 10^{-4} \pm 9.3 \cdot 10^{-5}) \cdot T^{\circ}\text{C} - (3.1 \cdot 10^{-6} \pm 2.8 \cdot 10^{-7}) \cdot T^{\circ}\text{C}^2 + (3.32 \cdot 10^{-9} \pm 2.8 \cdot 10^{-10}) \cdot T^{\circ}\text{C}^3$$

All coefficients calculated are in the range of  $1.78 \cdot 10^{-5}$  to  $5.12 \cdot 10^{-4}$ , meaning that silver concentrations in the vapor phase are  $\sim 4$ – $5$  orders of magnitude less than those calculated for liquid water.

Although these data indicate that  $AgCl$  partitions strongly into the liquid phase, they suggest, nevertheless that appreciable quantities of silver may be transported in the vapor phase of natural hydrothermal systems. It should be noted, however, that the silver concentrations of the experimental condensates (up to 100 ppb) are 1–1.5 orders of magnitude greater than those reported for volcanic fumaroles (5–10 ppb) (Gemmel, 1987; Quisefit et al., 1989). This can be attributed, both to the fact that the pressure of the water vapor in such fumaroles is typically lower than that of liquid-saturated water vapor, and that the dissolved silver is unsaturated with respect to  $AgCl(s)$ . However, it is important to note that chlorargyrite occurs mainly as a secondary mineral formed by weathering, and that fumarolic vapors may be close to saturation with other silver phases, e.g., argentite/acanthite ( $Ag_2S$ ). This could be readily determined by calculating the saturation indices of these minerals from knowledge of their solubility, and data on the concentrations of components involved in transport and deposition, such as  $Cl$  and  $S$ .

In order to illustrate the possible role of the vapor phase in silver transport, we have developed a thermodynamic model to track the removal of silver from rock during progressive interaction with water vapor. Speciation calculations were performed using the HCh computer code (see previous text). For simplicity, we have restricted the system to the five elements:  $Ag$ ,  $Cl$ ,  $S$ ,  $O$ , and  $H$ . Chlorargyrite 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 from the preceding reactor by  $5^{\circ}\text{C}$  temperature ranged from  $370^{\circ}\text{C}$  at the bottom of the column to  $150^{\circ}\text{C}$  at the top. The pressure in each reactor was that of saturated water vapor. A 1 kg aliquot of water vapor was introduced at the base of the column and allowed to proceed linearly upward, 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 Fig. 9. As it is evident from this figure, there is appreciable mobilization of silver. After reaction with the first 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 upward, to a maximum of 5.3 ppm at  $365^{\circ}\text{C}$  and then gradually decreased to 5.1 ppm at  $150^{\circ}\text{C}$ . 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  $355^{\circ}\text{C}$ . Most significantly, all the silver formerly present in reactors at  $5^{\circ}\text{C}$  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  $335^{\circ}\text{C}$ . Again, as noted previously, all the silver had been removed from reactors at temperatures  $>5^{\circ}\text{C}$  above those of the maxima.

Although, highly idealized, the calculations presented above are supported by data for natural systems. For example, Joron et al. (1982) have shown, in a series of silica tube experiments at Etna, that the silver content of sublimates reaches a peak value, increasing from approximately 0.2 ppm at  $860^{\circ}\text{C}$  to a maximum of 35 ppm at a temperature of  $\sim 300^{\circ}\text{C}$ . We, therefore, conclude that water vapor is an effective agent for the transport of silver in vapor-dominated hydrothermal systems at temperatures above  $300^{\circ}\text{C}$ , e.g., fumarolic systems where concentrations up to 100 ppm have been reported in sublimates (Kavalieris, 1994), and an important vehicle for the redistribution of silver in many boiling hydrothermal systems.

## 5. CONCLUSIONS

We have shown experimentally that significant concentrations of  $AgCl$  can be transported in water vapor, and that these concentrations are 1.5–2 orders of magnitude greater than those for the water-free system are. The silver chloride is interpreted to be present in the vapor phase as a species having the stoichiometry  $AgCl \cdot (H_2O)_3^{\text{gas}}$ . This species, in turn, is interpreted to have been produced in our experiments via the reaction:



The equilibrium constant for this reaction can be calculated from the relationship:

$$\log K_{(p=1\text{bar})} = (22.578 \pm 5.505) - (0.0255 \pm -0.0045) \cdot TK - (11987.6 \pm 658.5)/TK.$$

Within the limits of experimental error, the behavior of  $AgCl \cdot (H_2O)_3^{\text{gas}}$  approximates that of an ideal gaseous particle, and, based on *ab initio* calculations, this particle is interpreted to have a pseudo-bipyramidal form with  $C_3$  symmetry.

An idealized model developed using our data for the solubility of chlorargyrite in water vapor suggests that water vapor is an effective agent for the transport of silver in vapor-dominated hydrothermal systems, and an important vehicle for the redistribution of silver in many boiling hydrothermal systems.

*Acknowledgments*—This research was made possible through grants from NSERC and FCAR to AEW-J, and assistance of S. Kecani in the design of the autoclaves used in the experiments. Critical reviews by Dr. Khodakovsky and two GCA referees provided important comments that helped improve the manuscript significantly.

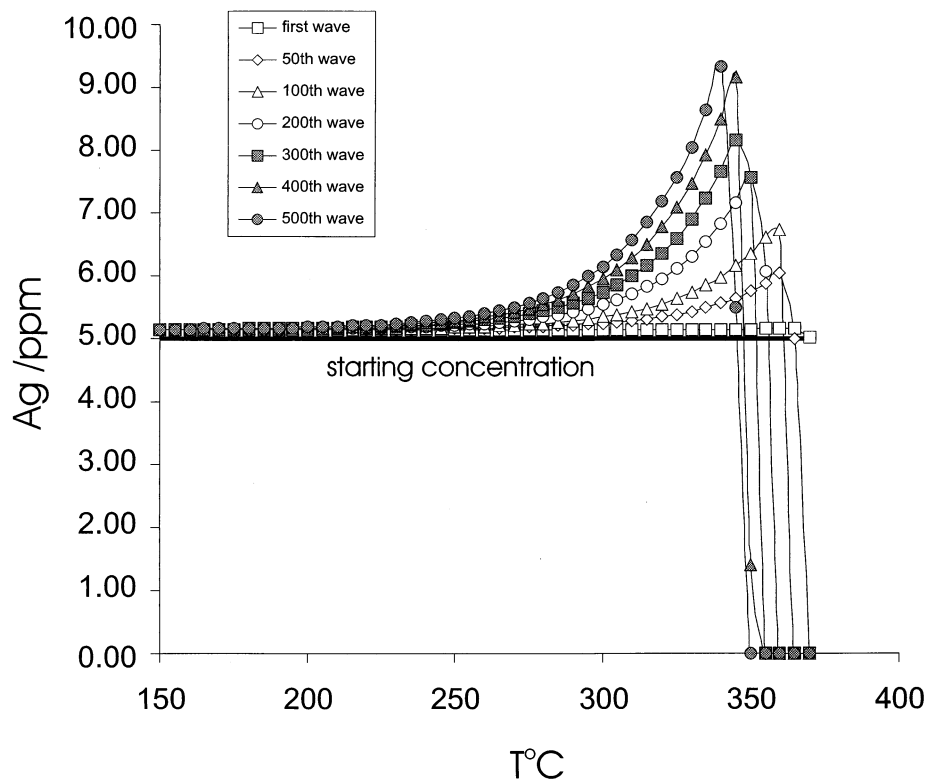


Fig. 9. Results of a simulation of the reaction of water vapor with a chloragyrite-bearing quartz vein. The diagram shows the distribution of Ag concentration in the quartz as a function of temperature at varying vapor-rock ratios (represented by the number of aliquots introduced into the vein).

#### REFERENCES

- Abraham M. H. and Matteoli E. (1983) Calculation of the thermodynamics of solvation of gaseous univalent ion in water from 273 to 573 K. *J. Chem. Soc. Farad. Trans. I* **79**, 2781–2800
- Alekhin Y. V. and Vakulenko A. G. (1988) Thermodynamic parameters and solubility of NaCl in water vapor at 300–500°C up to 300 bar. *Geochem. Int.* **25**(5), 97–110.
- 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 Equilibria*. **84**, 123–142
- Bach R. W., Friedrichs H. A., and Rau H. (1977) p-V-T relations for hydrogen chloride-water mixtures up to 500°C and 1500 bars. *High Temp. High Pressures* **9**(3), 305–312.
- 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**(2/3), 187.
- Christenson B. W. and Wood C. P. (1993) Evolution of a vent-hosted hydrothermal system beneath Ruapehu Crater Lake, New Zealand. *Bull. Volcanol.* **55**(8), 547–565.
- Crowe B. M., Finnegan D. L., Zoller W. H., and Boynton W. V. (1987) Trace element geochemistry of volcanic gases and particles from 1983–1984 eruptive episodes of Kilauea volcano. *J. Geophys. Res.* **92**(B13), 13708–13714.
- Galobrades 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.
- Gaussian 94 (1995) Revision C. 3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA.
- Gemmel B. J. (1987) Geochemistry of metallic trace elements in fumarolic condensates 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.
- 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. Bunsengesellschaft Phys. Chem.*, **B 76**(6), 417–425.
- Hildenbrand D. L. and Lau K. H. (1996) Thermochemistry of gaseous AgCl, Ag<sub>3</sub>Cl<sub>3</sub>, and CuCl. *High Temp. and Material Sci.* **35**, 11–20.
- Johnson J. W., Oelkers E. H., and Helgeson H. C. (1992) SUPCRT 92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0° to 1000°C. *Comput. Geosci.* **18**(7), 899–947.
- Joron J. L., Le Guern F., and Treuil M. (1982) Geochemical study of elements condensed during cooling of a gaseous volcanic phase: Mount Etna in 1976. *Bull. Volcanol.* **45**(3), 167–172.
- Kavalieris I. (1994) High Au, Ag, Mo, Pb, V and W content of fumarolic deposits at Merapi Volcano, central Java, Indonesia. *J. Geochem. Explor.* **50**(1–3), 479–491.
- Kestin J., Sengers J. V., Kamgar-Parsi B., and Levelt Sengers J. M. H. (1984) Thermophysical Properties of Fluid H<sub>2</sub>O. *J. Phys. Chem. Ref. Data* **13**(1), 175–183.
- Kevan L., Hase H., and Kawabata K. (1977) Silver atom solvation and desolvation in ice matrices: Electron spin resonance studies of radi-

- ation-produced silver atoms formed at 4 K. *J. Chem. Phys.* **66**, 3834–3835.
- Marshall D. D., Diamond L.W., and Skippen G. B. (1993) Silver transport and deposition at Cobalt, Ontario, Canada: Fluid inclusion evidence. *Econ. Geol.* **88(4)**, 837–854.
- Martinez J. M., Pappalardo R. R., and Marcos E. S. (1997) Study of the  $\text{Ag}^+$  hydration by means of a semicontinuum quantum-chemical solvation model. *J. Phys. Chem. A*, **101**, 4444–4448.
- 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 case (Kamchatka) [USSR], *Bull. Volcanol.* **43(1)**, 197–205.
- Migdisov A. A., Suleimenov O. M., Alekhin Y. V. (1998) Experimental study of polysulfane stability in gaseous hydrogen sulfide. *Geochim. Cosmochim. Acta* (**62**)**15**, 2627–2635.
- Narayana P. A., Becker D., and Kevan L. (1978) Electron spin echo modulation studies of silver atom solvation and desolvation in ice matrices. *J. Chem. Phys.* **68**, 652–654.
- Norman D. I., Harrison R. W., and Andres C. B. (1991) Geology and geochemical analysis of mineralizing fluids at the St. Cloud and U.S. treasury mines, chloride mining district, New Mexico, *J. Geochem. Explor.* **42(1)**, 61–89.
- Novgorodova M. I., Generalov M. E., and Glavatskikh S. F. (1997) Native aluminum from gas exhalations of active volcanoes and from ancient basaltic diatremes: Similarity of composition and origin, *Dokl. Akad. Nauk.* **354(4)**, 524–528.
- Olmez I., Finnegan D. L., and Zoller W. H. (1986) Iridium emissions from Kilauea volcano. *J. Geophys. Res.* **91(B1)**, 653–663.
- Pitzer K. S. and Palaban R. T. (1986) Thermodynamics of NaCl in steam. *Geochim. Cosmochim. Acta* **50**, 1445–1454.
- Quisefit J. P., Toutain J. P., Bergametti G., Javoy M., Cheynet 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.
- Robie R. A., Hemingway B. S., and Fisher J. R. (1978) Thermodynamic properties of minerals and related substances at 298.15°K and 1 bar ( $10^5$  Pascals) pressure and higher temperatures. *Geological Survey Bull.* 1452, Washington.
- Ruvalcaba-Ruiz D. C., and Thompson T. B. (1988) Ore deposits at the Fresnillo mine, Zacatecas, Mexico. *Econ. Geol.*, **83(8)**, 1583–1596.
- Seward T. M., Henderson C. M. B., Charnock J. M., and Dobson B. R. (1996) An X-ray absorption (EXAFS) spectroscopic study of aquated  $\text{Ag}^+$  in hydrothermal solutions to 350°C. *Geochim. Cosmochim. Acta* **60(13)**, 2273–2282.
- Sherlock R. L., Tosdal R. M., Lehrman N. J., Graney J. R., Losh S., Jowett E. C., and Kesler S. E. (1995) Origin of the McLaughlin mine sheeted vein complex-metal zoning, fluid inclusion, and isotopic evidence. *Econ. Geol.* **90(8)**, 2156–2181.
- Shevkunov S. V., and Al'mukhrez A. A. (1994) Microstructure of a nucleus for the dense phase of  $\text{H}_2\text{O}$  in an interior space  $\text{Ag}^+$ ,  $\text{I}^-$  in an equilibrium with vapor. Monte Carlo method calculation. *Khim. Fiz.* **13(11)**, 117–27.
- Shevkunov S. V. (1996) The numerical modeling of the  $\text{Ag}^+$  and  $\text{I}^-$  ion hydration in a wide temperature interval. *Russ. J. Electrochem. (Transl. of Elektrokhimiya)* **32(8)**, 867–878.
- Shvarov Y. V. (1976) Algorithm for calculation of the equilibrium composition in a multicomponent heterogeneous system. *Dokl. Akad. Nauk SSSR.* **229**, 1224–1226.
- Shvarov Y. V. (1978) Minimization of the thermodynamic potential of an open chemical system. *Geochem. Int.* **15**, 200–203.
- 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.
- Styrikovich M. A. (1969) Steam solutions. *Vestnik Akad. Nauk SSSR* **39(12)**, 70–77 (in russian).
- 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(8)**, 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.
- 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.
- Texter J., Hastrelter J. J., and Hall J. L. (1983) Spectroscopic confirmation of the tetrahedral geometry of  $\text{Ag}(\text{H}_2\text{O})_4^+$ . *J. Phys. Chem.* **87**, 4690–4693.
- Visnapuu A. and Jensen J. V. (1970) Composition and properties of vapors over molten silver chloride. *J. Less-Common Metals* **76(20)**, 141.
- Yamaguchi T., Lindquist O., Boyce J. B., and Claeson T. (1984) Determination of the hydration structure of silver ion in aqueous silver perchlorate and nitrate solutions from EXAFS using synchrotron radiation. *Acta Chem. Scand.* **A38**, 423–428.