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**GOLD-CHLORIDE SPECIATION
IN HYDROTHERMAL FLUIDS :
A RAMAN SPECTROSCOPIC STUDY
AT GEOLOGICALLY RELEVANT
PRESSURES AND TEMPERATURES**

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GOLD-CHLORIDE SPECIATION IN HYDROTHERMAL FLUIDS: A RAMAN SPECTROSCOPIC STUDY AT GEOLOGICALLY RELEVANT PRESSURES AND TEMPERATURES

by

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ABSTRACT

Raman spectra have been obtained for gold-chloride solutions at elevated temperatures and pressure, at gold concentrations of 0.005-0.04M and varying pH. A hydrothermal cell has been developed, which allows Raman analyses up to 300°C and 2kbar. Using simple Au(III) chloride solutions at low pH and up to 300°C, the expected transformation to Au(I) with increasing temperature was not found, even in solutions prepared under reducing conditions. The Au(III) complex $[AuCl_4]^-$ breaks down and precipitates gold at temperatures above 250°C, but the exact temperature appears to be related to oxygen fugacity. The Raman spectra showed consistent trends in peak parameters with increasing temperature, indicating minor changes in bond lengths but no change in speciation. In the range investigated, pressure had a minimal effect on both speciation and peak frequencies. However, on heating the Au(III) complex $[AuCl_4]^-$ in the presence of metallic gold, transformation to the Au(I) form $[AuCl_2]^-$ does occur. The single Raman peak for the complex $[AuCl_2]^-$ was recorded at $327cm^{-1}$ at 250°C. A previously described peak for this species was probably an artefact of the peak fitting process. The importance of comparing trends in peak parameters to determine optimal peak fitting is highlighted. Solutions at pH values of 5.75 and 6.5, which had different mixed chloro-hydroxy complexes at ambient temperature, showed changes in speciation with increasing temperature. In the lower pH solution $(OH)^-$ groups were replaced by Cl^- ligands on heating, resulting in a transformation from $[AuCl_3(OH)]^-$ to $[AuCl_4]^-$. In the higher pH solution there was initially an increase in the number of $(OH)^-$ ligands, from $[AuCl_2(OH)_2]^-$ to a mixture with $[AuCl(OH)_3]^-$ at 75-100°C, but with increasing temperature this trend was reversed and $[AuCl_4]^-$ became dominant. No effect of pressure on the chloro-hydroxy speciation was observed.

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GOLD-CHLORIDE SPECIATION IN HYDROTHERMAL FLUIDS: A RAMAN SPECTROSCOPIC STUDY AT GEOLOGICALLY RELEVANT PRESSURES AND TEMPERATURES

INTRODUCTION

The chemical speciation of metals such as gold in hydrothermal fluids is important in understanding the controls on metal precipitation, and thus ore deposit formation, under varying geochemical and geophysical conditions. Knowledge of the exact speciation of metals is necessary for the determination and use of thermodynamic data for the relevant system. Although gold is generally accepted to be transported as a reduced sulphur-bearing complex under most conditions pertinent to hydrothermal fluids (e.g. $[Au(HS)_2]^-$, Shenberger and Barnes, 1989; $[HAu(HS)_2]^0$, Hayashi and Ohmoto, 1991; $[AuHS]^0$, Benning and Seward, 1996) there is increasing interest in the role of gold-chloride complexes in certain geochemical environments, particularly in highly oxidised fluids of high salinity and low reduced sulphur content. Recent discussions on the possible role of chloride complexes in gold transport and/or deposition include environments such as gold-rich copper porphyry deposits (Gammons and Williams-Jones, 1997), unconformity-related U-Au-Pt-Pd deposits (references in Gammons et al., 1997), and gold-rich VMS deposits (Huston and Large, 1989; Murphy and Meyer, 1998). Two simple chloride complexes of gold are known: the auric Au(III) square-planar complex $AuCl_4^-$, and the aurous Au(I) linear complex $AuCl_2^-$. Both complexes are hydrolysed at neutral to high pH, resulting in complexes of the forms $[AuCl_x(OH)_{4-x}]^-$ (Baes and Mesmer, 1976; Bjerrum, 1948) and $[AuCl_x(OH)_{2-x}]^-$ (Gadet and Pouradier, 1972) (or $AuOH \cdot H_2O$, Vlassopoulos and Wood, 1990). It is generally accepted that, while the Au(III) form $AuCl_4^-$ is stable relative to $AuCl_2^-$ under ambient conditions, it is the Au(I) form which predominates at high temperature, as has been demonstrated in solubility experiments (e.g., Gammons and Williams-Jones, 1995; Gammons et al., 1997; Zotov et al., 1991).

Raman spectroscopy is an ideal technique for studying metal complexes in solution as, with suitable equipment, Raman analyses can be carried out over a range of geologically relevant temperatures and pressures. This allows direct observation of speciation under the conditions of interest, rather than the interpretation of speciation from solubility measurements and calculated activities etc., which is the approach used in solubility experiments. Unlike the complementary vibrational technique of infrared absorption spectroscopy, the spectrum of water is unlikely to interfere with the Raman spectrum of the solute. The peaks in a Raman spectrum represent vibrational modes within the molecule, with the number of peaks being dependent on the symmetry of the molecule, and their frequencies being dependent on the bond force constants and therefore the atoms involved. As a result, different gold complexes will have different Raman spectra, and the number, frequencies and polarisation characteristics of the peaks in a Raman spectrum can serve to identify the species under consideration, or to determine the molecular structure. For example, for the square-planar $[AuCl_4]^-$ complex, three Raman peaks are observed: two are due to Au-Cl stretching (B_{2g} and A_{1g} at frequencies of 324

and 348cm^{-1} respectively), and one to Cl-Au-Cl bending (B$_{1g}$, 171cm^{-1}). A number of other vibrational modes are either active in infrared absorption, or inactive under both techniques.

Pan and Wood (1991) used Raman spectroscopy to study simple [AuCl$_4$]$^-$ solutions at very low pH (m_{HCl} 2-5), temperatures up to 300°C and pressures along the liquid-vapour curve. They fitted peaks to their spectra and found that, in addition to the two Au-Cl stretching peaks for [AuCl$_4$]$^-$, a third peak was necessary to describe their data at high temperature. They stated that, without this third peak, one of the two Au-Cl peaks became excessively wide. The new peak, at 332cm^{-1}, was attributed to the linear Au(I) complex [AuCl$_2$]$^-$, and the conclusion was that [AuCl$_4$]$^-$ was at least partially transformed to [AuCl$_2$]$^-$ with increasing temperature. This was consistent with the interpretations of solubility data, and was believed to be the first direct observation of the Au(I) complex.

The aim of this work is to test the effects of pressure together with temperature on Au-Cl solutions over a range of pH values. The paper presents data from Raman analyses of gold chloride solutions conducted using a new hydrothermal cell specifically designed for Raman analyses, under conditions up to 300°C and 2kbar. This forms an extension of an earlier study on the effects of pH, chloride and gold concentration on speciation at low temperature (Murphy and LaGrange, 1998), and the data collected necessitate a re-evaluation of the Raman spectra obtained in previous studies.

EXPERIMENTAL METHODS

Analyses were carried out both in simple sealed silica glass tubes at pressures along the H$_2$O liquid-vapour curve, in a method similar to the experiments of Pan and Wood (1991), and at higher pressures in a specially designed pressure vessel.

Low-pressure Experiments

For analyses at pressures along the H$_2$O liquid-vapour curve, samples were held in silica glass tubes and wrapped in a simple resistance-wire heating-element, with the Raman laser focused through a gap in the wire in the central part of the tube. Temperature measurement was via a type K thermocouple and a MULTICAL® digital temperature indicator. The thermocouple was located directly adjacent to the tube, within a few mm of the analysis point. The tube was angled so that the vapour bubble was above the path of the laser. This set-up allowed direct observation of the fluid for any changes in colour or any precipitation. A thermal gradient was present along the tube, which resulted in boiling of the solution at high temperatures. In addition the size of the vapour bubble varied slightly from sample to sample, which resulted in changes in the observed behaviour of the fluid, as detailed below. For these reasons, the analyses carried out at low pressure are of largely qualitative interest, but some important observations were made which necessitate their inclusion in this paper.

High-pressure Experiments: The Hydrothermal Raman Cell

A cell was developed to allow Raman spectroscopic analyses under hydrothermal conditions. The cell consists of a conventional cold seal pressure vessel, modified to accommodate a conical sapphire window at one end (Fig.1). The laser is focused through the window into a glass sample chamber within the pressure vessel, and collected in a 180° back-scattering arrangement via the same lens. The sample chamber consists of a syringe-like apparatus, with the sample contained within a flat-ended glass tube sealed by a close-fitting sliding glass plunger. The fluid sample is therefore completely isolated from all metallic components of the pressure vessel, within a glass vessel capable of adjusting to changes in the external pressure. The pressure medium is distilled water, which completely surrounds the sample holder. Pressure measurement is via a HEISE® bourdon tube gauge. The laser path length through the fluid is ≈1cm, sufficient to produce good signal/noise even at low concentrations. The sapphire window introduces a number of peaks into the Raman spectrum but these are narrow, sharply defined and do not interfere with the crucial portions of the AuCl spectra. The pressure vessel is encased in a simple resistance furnace. Temperature measurement is via a type K thermocouple located inside the pressure vessel, directly adjacent to the sample capsule and a TEMPERATURE CONTROLS® solid state temperature controller with integral ice point. The furnace temperature is measured and controlled by an identical device. Temperatures at the sample capsule are readily maintained at ±1°C for the duration of an experiment. The Raman pressure cell has been tested to 350°C and 2kbar concurrently.
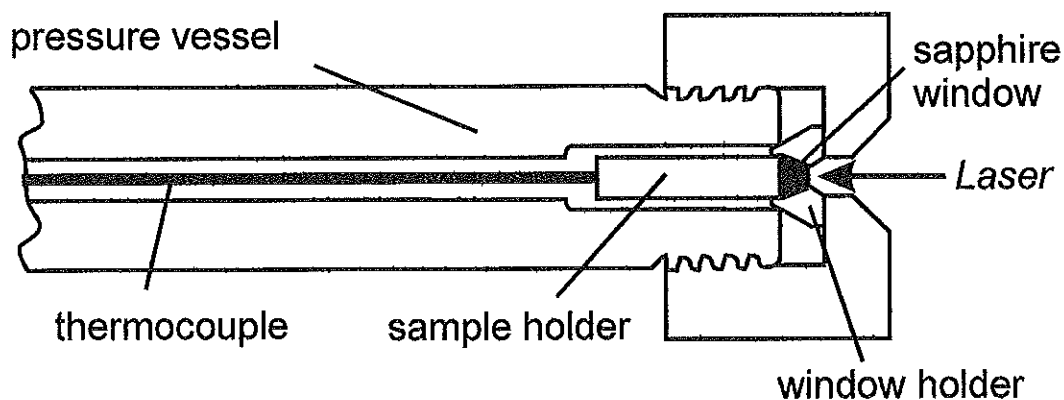

Figure 1: Schematic diagram of the hydrothermal Raman cell used for high pressure experiments.

Analytical Conditions

Raman analyses were carried out on a Jobin-Yvon T-64000 instrument in single spectrograph mode, using a single holographic grating of 1800g/mm together with a

holographic notch filter to reject the laser light. An entrance slit of 50μm gave a resolution (defined as the full width at half maximum height of the 546.07nm line of a mercury lamp) of <2 cm^{-1}. Spectra were recorded using a liquid nitrogen cooled Spectrum One CCD detector, giving a frequency range for each analysis from 200 to 850cm^{-1}. The precision of this set-up is better than ± 0.2 cm^{-1} for well-defined peaks. The 514.5nm line of a Coherent Innova 308 argon ion laser was used with a power at the sample of 50mW or less. In general, an interference filter was not used to remove laser plasma lines. Since the main plasma lines did not interfere with the sample spectra, but occurred at known points within the range studied (520.3 and 266.3 cm^{-1}), they allowed an excellent control on the wavelength calibration. Variation in the frequency of these plasma lines was <0.2cm^{-1} during the course of an experiment. The sapphire window of the hydrothermal cell affects the polarisation of both the incident and scattered light preventing polarisation measurements in the high pressure experiments. In the low pressure analyses, using glass tubes, no polarisation was applied to the scattered light for normal analyses, but several solutions were tested using both parallel and perpendicular polarisation to determine the depolarisation ratios of the peaks. Analysis times were typically 2 minutes, with 2 spectra being averaged and any cosmic rays rejected. Plating out of gold, due to photo-decomposition of the sample after long analysis (Peck et al., 1991), was not observed. However, Peck et al. (1991) described this plating out after many hours of laser illumination, whereas the samples in this study were only subjected to laser illumination for a few minutes at a time, which may explain the difference.

Sample Preparation

For the low-pressure analyses, the solutions were prepared by dissolving hydrated tetrachloroauric acid (HAuCl$_4$·4H$_2$O) in de-ionised water, resulting in a solution with total chloride concentration exactly four times that of gold, as described by Murphy and LaGrange (1998). For the high-pressure analyses, a new solution was used, made by diluting a standard Au(III) solution (supplied by MERCK®, 1g gold in 50ml 12.7% HCl) to 250ml with de-ionised water. This gave a concentration of approximately 0.02M Au, with a total chloride content of 0.78M. This solution had a pH of <0.5 and showed a darker-yellow colour than that for a 0.02M solution prepared directly from the salt. This difference is likely to be due to a minor amount of hydrolysis in the first solutions, which is not present in the later solutions, as a result of both the reduced pH and increased chloride content (Murphy and LaGrange, 1998). The solutions were prepared, and where relevant the tubes sealed, in air. In certain samples the solution was saturated in either nitrogen or hydrogen by bubbling the relevant gas through the solution for 30-60 minutes before loading into the sample capsule.

Peak Fitting and Peak Parameters

When considering changes in the spectra, a number of different variables must be considered. In the hydrolysis sequence [AuCl$_x$(OH)$_{4-x}$]$^-$ it was found that the difference between complexes in each hydrolysis step could not always be discerned from peak position

alone, due to very minor frequency shifts, but that the use of peak widths and relative proportions allowed different complexes to be distinguished (Murphy and LaGrange, 1998). Peak fitting is therefore essential in order to determine not only the positions (frequencies), but also the peak widths and relative intensities. The relative peak intensity and other spectral features can give important information as to the relative abundances of the species under consideration. However, although the intensity of a peak is proportional to the concentration of the species producing that peak, a direct comparison of concentrations between species is not usually possible. For example, as noted by Pan and Wood (1991), the Au-Cl stretching peaks are likely to be more intense in [AuCl$_4$]$^-$, which contains four Au-Cl bonds, than in [AuCl$_2$]$^-$, which contains only two.

For each spectrum in this study, a number of parameters were determined. Peaks were fitted to the data in the Au-Cl stretching region, with a commercial statistical package (MicroCal Origin 4.1) using a least-squares fitting method. A Lorentzian function was found to give a better fit than a Gaussian, and provided the central peak position, the full width at half maximum height ("width"), integrated area ("intensity") and height for each peak. Use of a Gaussian function did not significantly change the trends in parameters with temperature. Throughout this paper peaks are referred to by their approximate wavenumber position at room temperature. This is not ideal, since the peak frequency changes with increasing temperature, and is also slightly different between studies by different groups. For example the A$_{1g}$ totally symmetric Au-Cl stretch for the [AuCl$_4$]$^-$ is recorded at around 349cm^{-1} in this study, but was reported by Pan and Wood (1991) at 347cm^{-1}. However, use of the term A$_{1g}$ to describe this peak presupposes the symmetry and species present, and becomes confusing when other species are considered.

RESULTS

Low-pressure Experiments at Very Low pH

Analyses at saturated vapour pressure were conducted on a number of solutions ranging from 0.04-0.001M Au and at temperatures from 25-250°C. For the 0.04M solution, two separate experiments were conducted on identical solutions, but with different liquid/vapour ratios in the sealed tubes. The parameters obtained from the spectra are shown in Figure 2. In both cases, changes in the peak parameters occur with increasing temperature, principally a downwards shift in the frequency of both the 349 and 325cm^{-1} peaks of approximately 2cm^{-1}, and an increase in the width of the 325 peak, particularly in relation to the 349cm^{-1} peak. In the 0.02M solution, similar changes in the spectral parameters were observed. Changes in the frequency of Raman peaks with pressure are commonly seen in crystalline materials (typically increases in frequency with increasing pressure). Similarly, the observed downwards shift in frequency with increasing temperature is commonly reported, and in this case can also be seen in the peaks from the sapphire window, which show changes in both width and frequency, of varying magnitude for the different peaks. In both cases the

shift is likely to be due to changes in the bond lengths and/or strengths within the molecule as a result of thermal and/or volumetric changes.
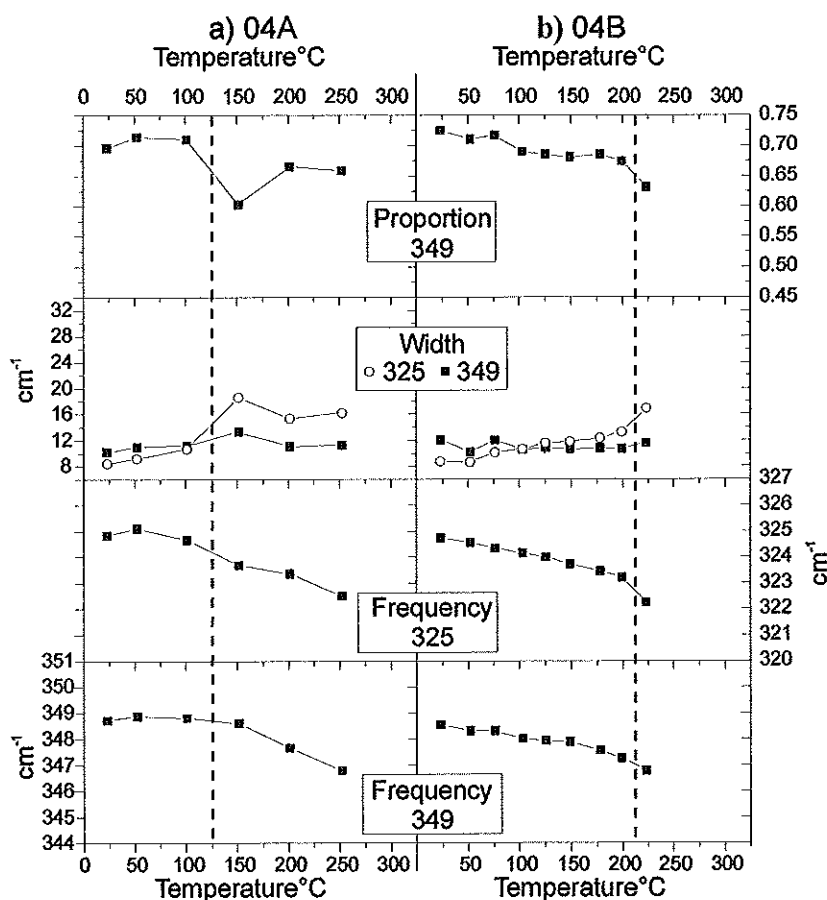

Figure 2: Effect of temperature on Raman peak parameters for two 0.04M Au(III) chloride solutions at low pressure. Solutions have different liquid/vapour ratios: a: 04A, liquid fill 0.7, b: 04B, liquid fill 0.55. Dashed lines mark point of gold precipitation.

At elevated temperatures a red colouration was observed to form in part of each solution, together with a reduction in the intensity of the yellow colour of the rest of the sample. This occurred at 125°C in solution 04A, which contained a small bubble (liquid fill approx. 0.7) and at just over 200°C in solution 04B which contained a larger bubble (liquid fill approx. 0.55). The red colour was due to the precipitation of finely particulate gold, which began to form larger grains and could be easily identified even before cooling and opening of the sample. At the time of precipitation, a reduction in the Raman signal was recorded, but no clear change in the spectra was noted. However, changes in the peak parameters did occur, and the temperature of precipitation is marked on Figure 2. In both cases, there is an increase in the width of the 325cm^{-1} peak, which is markedly more rapid than the observed trend, and a reduction in the proportion of the 349 peak relative to that at 325cm^{-1} (a direct result of the increase in width of the latter peak). However, as the signal becomes much weaker at this

point, the changes in peak parameters are less certain, and it is possible that any changes are simply artefacts of the weaker signal. For example, as the $325cm^{-1}$ peak becomes weaker, its width is likely to be overestimated, and this will also result in an overestimation of the peak area and therefore intensity. The loss of yellow colouration is therefore interpreted to be due to the loss of $[AuCl_4]^-$ from solution, but not due to formation of $[AuCl_2]^-$. The precipitation of gold was also observed during heating with no Raman analyses, and the phenomenon cannot therefore be attributed to photodecomposition by the laser light. The gold redissolved after a period of several weeks or months at room temperature with a return of the yellow colouration of the solution, but no attempt was made to quantify the rate of dissolution. The difference in the temperature of gold precipitation between these two solutions appears to be due to the available oxygen reservoir encapsulated with the solution. In solution 04A, which contained a smaller bubble, $[AuCl_4]^-$ broke down at a lower temperature than in 04B. The transformation Au(III) to Au(I), if it were to occur, would be expected at a lower temperature in the solution with lower oxygen fugacity, and in the high-temperature experiments this may relate to the bubble size. The liquid:vapour ratio in all other solutions was maintained at $\approx$ 1:0.8 to minimise the problem of varying temperatures of precipitation. Despite the fact that the minor changes in the spectral characteristics observed during these experiments indicate that the Au(III) complex becomes less stable at high temperature, no evidence for Au(I) was seen.

Two solutions at 0.005M Au were analysed. The first (005A) was a simple diluted version of the other solutions, while the other (005B) had a small amount of HCl added, to adjust the pH down to that comparable with the 0.04M solutions, but also resulting in a slightly higher Cl/Au ratio. As discussed by Murphy and LaGrange (1998), the presence of excess chloride affects the speciation. The unadjusted 0.005M solution shows three peaks at room temperature (Fig. 3), and although two are very similar to those for $[AuCl_4]^-$, all are attributed to the hydrolysis product $[AuCl_3(OH)]^-$. The adjusted solution, with minor excess chloride, shows the two peaks typical of $[AuCl_4]^-$ seen in the more concentrated solutions. On heating, the unadjusted solution (005A) showed a decrease in peak frequencies, and an increase in the width of the $325cm^{-1}$ peak, similar to that seen in the 0.04M solutions (Fig. 3a). The third peak, at $335cm^{-1}$, became weaker with increasing temperature and was no longer observed at 100°C and above. More variation in the parameters is observed than in the more concentrated solutions, and the observed trends are not as smooth, but this is probably due to the weaker signal, along with the effects of the $[AuCl_3(OH)]^-$ complex. This is particularly true at high temperatures, when the signal was further reduced by precipitation (see below).

The solution with added HCl (005B) shows very different spectral parameters (Fig. 3b). Although the data is limited, it is clear that there is an increase in the frequency of the $349cm^{-1}$ peak with increasing temperature, in contrast to the decrease in frequency seen in all other samples. In addition, both the 325 and 349 cm^{-1} peaks increase in width, while in the other solutions only the peak at 325 cm^{-1} widens. In these 0.005M solutions the precipitation of gold at high temperature was less pronounced than at higher concentrations, but fine grains

of gold were observed after cooling and opening of the sample tube. At high temperature (>250°C) a white precipitate was observed to form on the glass of the tube, which did not re-dissolve on cooling. Like the precipitation of gold, this was observed to occur on simple heating without analysis, and is therefore not due to photodecomposition effects of the laser light.

The 0.001M solution provided very weak spectra, which became weaker with increasing temperature, allowing no conclusions to be drawn. However, the solution showed similar behaviour to the 0.005M solutions, also forming a white precipitate at high temperature.
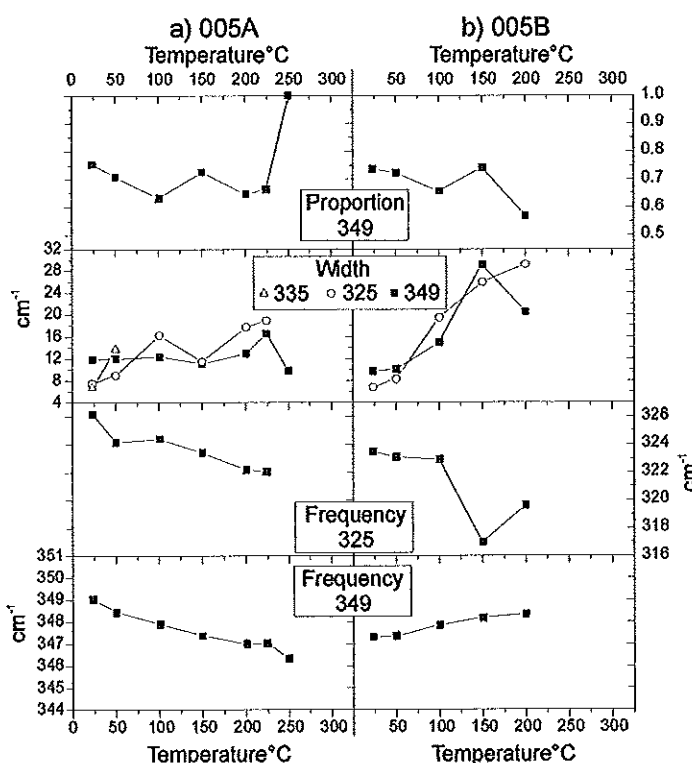

Figure 3: Effect of temperature on Raman peak parameters for two 0.005M Au(III) chloride solutions at low pressure. a: 005A, unadjusted b: 005B, pH and chloride content slightly adjusted.

The difference in behaviour between the solutions with high (0.04, 0.02M) and low concentrations (0.005, 0.001M) is likely to be related to differences observed by Murphy and LaGrange (1998). In these low-chloride, low-gold solutions, the gold is present as mixed chloro-hydroxy complexes (e.g. $[AuCl_3(OH)]^-$), which evidently behave differently from simple chlorides with increasing temperature. The white precipitate is as yet unidentified. A Raman spectrum showing a single peak at 880cm^{-1} was recorded, but it was not possible to use any other analytical methods to identify the substance. A gold-hydroxide complex is unlikely, since they are usually strongly coloured, and chlorides can be ruled out as they are

generally also strongly coloured and soluble. A mixed chloro-hydroxy solid is a possibility and it is worth noting that Peck et al. (1991) reported a white precipitate which formed on addition of excess NaOH to Au(III) chloride solutions. They suggested that this solid was a gold hydroxide, but this seems unlikely for the reasons given above. In none of the low-pressure experiments was there any evidence for the occurrence of a new peak between the two Au-Cl stretching peaks for the complex $[AuCl_4]^-$, which would be expected if the Au(III) complex transformed to Au(I). This is perhaps the most significant finding of these experiments.

High-Pressure Experiments

High-pressure experiments at very low pH

Experiments were conducted on gold-chloride in highly acidic HCl solution at temperatures from 25-300°C and pressures of 0.85 and 1.5 kbar (12500 and 21000psi). The Raman spectra obtained are shown in Figure 4, an example of the peaks fitted to them in Figure 5, and the parameters obtained from peak fitting in Figure 6. The data for the lowest pressure analyses (0.85 kbar) show very smooth and clear trends. Both the 325 and 349 cm^{-1} peaks shift downwards in frequency with increasing temperature, in a very smooth manner. The width of the 349 cm^{-1} peak remains constant, increasing by less than 1 cm^{-1} over the temperature range studied, while the 325 cm^{-1} peak increases in width by more than 20 cm^{-1}, to three times its original width. This increase is much more pronounced than in the low-pressure experiments. The proportion of the 349 cm^{-1} peak decreases slowly relative to the peak at 325 cm^{-1}, and drops suddenly above 250°C. This drop at high temperature was also seen in the lower-pressure solutions, and the downwards trend up to that point has a similar slope to the earlier analyses. It was not possible to observe the precipitation of gold due to the nature of the hydrothermal cell. However, a small amount of gold precipitate was present in the solutions after cooling and opening of the pressure vessel, and the solutions showed a much weaker yellow colouration. In general there was a reduction in the intensity of the signal at some high temperature, usually above 200°C, and linked to the decrease in the proportion of the 349 cm^{-1} peak and increase in the width of the 325 cm^{-1} described above. The spectra obtained above this point were identical to those obtained from the solution after cooling and depressurisation. This suggests that the gold precipitation occurred at high temperature, at the point of reduction in signal intensity, rather than during cooling or depressurisation. This is consistent with the observations made in the low-pressure experiments. An identical solution was examined at higher pressure (1.5kbar), and shows very similar trends to the lower-pressure analyses. There is, however, a slight jump in the parameters at 225°C, visible in the frequency of both peaks, and the width of the 325 cm^{-1} peak. In addition, the downwards shift in frequencies with temperature is more pronounced than at 0.85 kbar, especially for the 349 cm^{-1} peak.

In both experimental runs, there was no evidence in the spectra for the occurrence of a third peak representing $[AuCl_2]^-$. Peaks were fitted to the spectra after removing a curved background consistent with the trend of the spectra (the steep slope of a broad feature in the

spectrum of the glass sample holder). When two peaks are fitted to the spectra, and the parameters plotted against temperature, they show smooth trends with regular changes in the parameters. The peak at 325 cm^{-1} becomes very wide with increasing temperature (Fig. 5) but it does so in a regular manner, and such an increase in width with temperature is not unusual in Raman spectra. When the spectra were fitted using three peaks, each individual spectrum had an excellent fit, but the parameters no longer showed consistent trends with temperature (Fig. 7). Instead, the peak positions, widths and relative proportions of both the 325 cm^{-1} and the third peak varied widely with temperature, with the frequency of the third peak varying from 327 to 338 cm^{-1} and its width from 2 to 16 cm^{-1}. This suggests that the spectra are best represented by only two peaks.
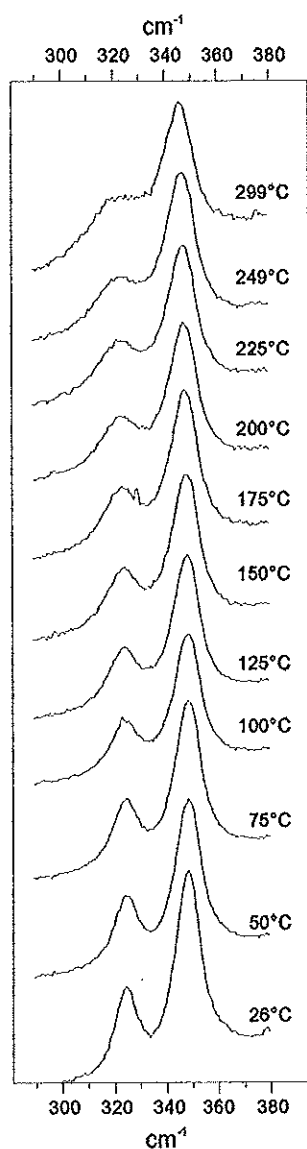

Figure 4: The effect of temperature on Raman spectra for the Au-Cl stretching region for Au(III) chloride solutions at 0.85 kbar.
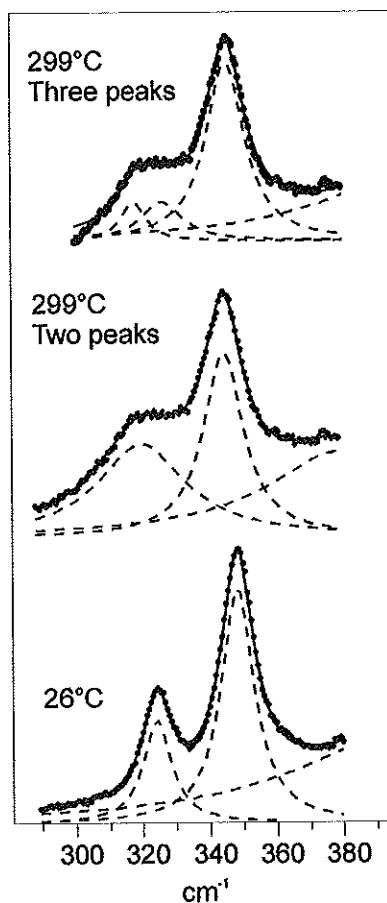
Figure 5: Peak fitting at low and high temperature for the spectra shown in Figure 4.
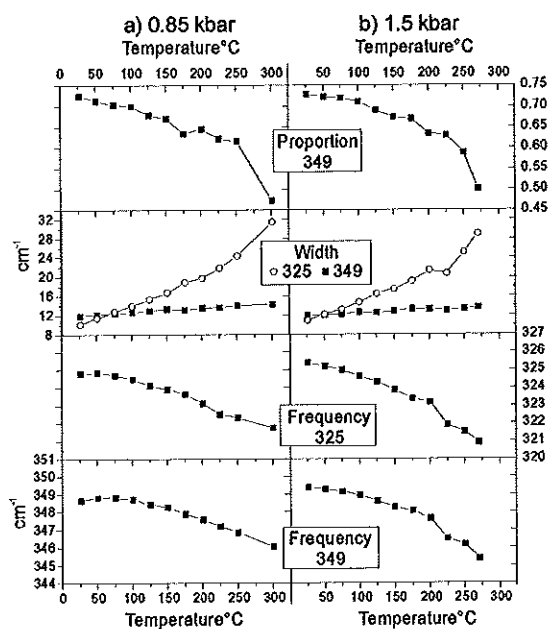

Figure 6: Effect of temperature on Raman peak parameters for two 0.02M Au(III) chloride solutions at different pressures (a) 0.85kbar and (b) 1.5kbar.
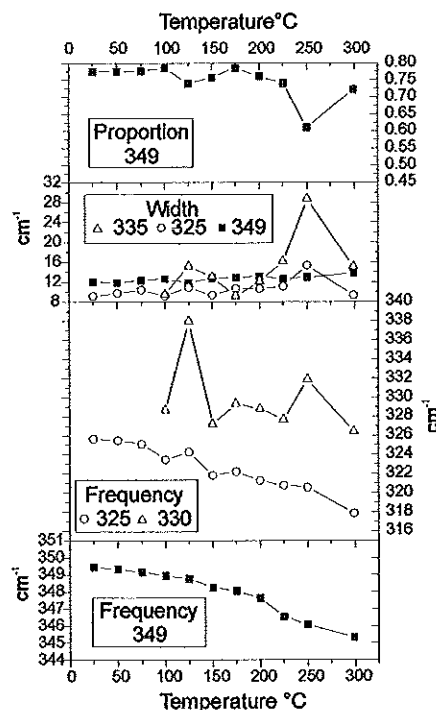
Figure 7: Peaks fitted to the spectra shown in Figure 6a, using 3 peaks instead of 2. At low temperature, no third peak is necessary, but at high temperature a third peak provides a better fit than two peaks alone. The peak parameters obtained for spectra, using third peak are very variable, particularly for the third peak at around 330cm-1. Comparison with the trends in Figure 5a suggests the third peak is an artefact, rather than a true feature.

High pressure experiments under reducing conditions

Pan and Wood (1991) showed that the peak, which they attributed to $[AuCl_2]^-$, was much stronger in a solution after bubbling hydrogen gas through the sample before analysis. In order to test the effect of more reducing conditions, two samples were therefore analysed after bubbling nitrogen and hydrogen gas through the solution. The spectra for these solutions look similar to those prepared in air (Fig. 8). With increasing temperature, the peaks again show a downwards trend in frequency. There was no significant difference between the nitrogen- and hydrogen-saturated solutions, and no evidence for a third peak, due to $[AuCl_2]^-$, was observed.

High pressure experiments at higher pH values

Several sets of analyses were conducted at higher pH values to test the effect of both temperature and pressure on the speciation of mixed chloro-hydroxy complexes. Murphy and LaGrange (1998) presented analyses at room temperature for Au-Cl complexes with varying pH, and found a general trend of successive replacement of Cl$^-$ ligands by (OH)$^-$ ligands with increasing pH, in the Au(III) hydrolysis sequence $[AuCl_x(OH)_{4-x}]^-$. The Raman bands identified for each species are given in Table 1.
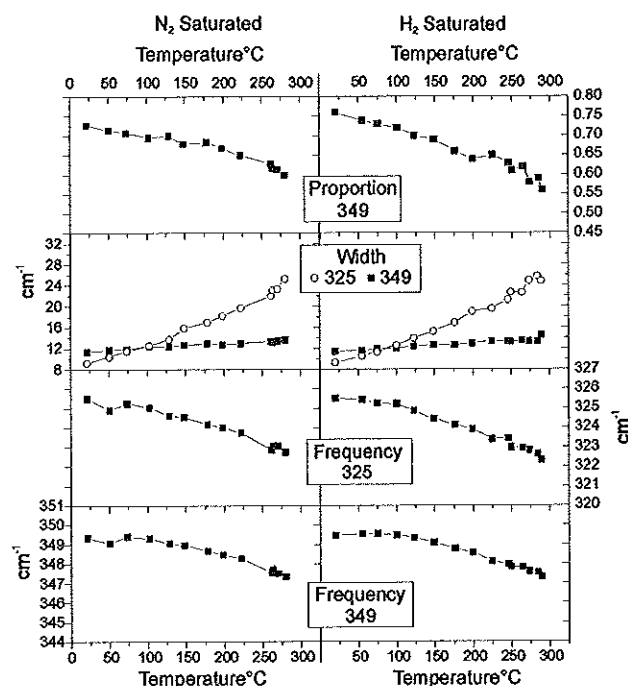
Figure 8: Effect of temperature on Raman peak parameters for N_2 saturated and H_2 saturated 0.02M Au(III) chloride solutions at 1kbar.

Table 1: Predicted numbers of Raman peaks, Raman frequencies, and experimental data for Au-chloro and chloro-hydroxy complexes: (1) Tossell (1996); (2) Peck et al. (1991); (3) Pan and Wood (1991); (4) Braunstein and Clark (1973) (for [AuCl₂]⁻ in crystalline salt) *. For these vibrations Tossell (1996) recorded vibrational modes without distinguishing which were Raman active. For both Au-Cl and Au-OH only one of the given frequencies is Raman active

Complex	Predicted Frequencies (1)		Experimental		Murphy and LaGrange (1998)	
	Au-Cl	Au-OH	Au-Cl Stretch	Au-OH Stretch [2]	Au-Cl Stretch	Au-OH Stretch
[AuCl₄]⁻	353 323		347 324 [2]		348 325	
[AuCl₃(OH)]⁻	352 341 324	624	339 [2]	569	348 335 325	566
[AuCl₂(OH)₂]⁻ *cis*	328 317	640 617			354 337	568 580
[AuCl₂(OH)₂]⁻ *trans*	343* 322*	623* 614*	356 [2]	576		
[AuCl (OH)₃]⁻	321	635 616 596	366 [2]	553	356	565 579 ?
[Au (OH)₄]⁻				580		
[AuCl₂]⁻ *(hydrated)*	269 (273)		329 [4] 332 [3]			
[Au(OH)₂]⁻		533 502				
[AuCl(OH)]⁻	285	510	339 [3]			

pH 5.75, 1kbar, 25-250°C

At pH 5.75, at room temperature, the solution showed 3 Raman peaks (Fig. 9a), at approximately 350, 336, and 326 cm^{-1}. A weak, broad peak is also visible at around 566 cm^{-1} (Fig. 9b), attributed to an Au-OH stretch, but it is partially obscured by a peak from the sapphire window at 576 cm^{-1}. These peaks are consistent with the [AuCl$_3$(OH)]$^-$ complex described by Murphy and LaGrange (1998) as the first stage of hydrolysis of [AuCl$_4$]$^-$ at low to neutral pH. With increasing temperature the peak parameters show a marked change at 150°C (Fig. 9c). At and above this temperature, the third peak is no longer discernable, but is likely to be present although its continued existence can be recognised by a sudden increase in both frequency and width of the "325" peak at 150°C and 175°C. At higher temperatures the peak parameters return to the overall trend, of a gradual decrease in frequency and increase in width, which is similar to that seen in the low-pH solutions. The two remaining peaks are at the frequencies expected for the simple Au(III) chloride at this temperature. Note that the final analysis, at 250°C, was very weak, and the departure of the peak parameters from the overall trend is probably not real. Thus the observed spectra indicate that at this pH, increase in temperature results in replacement of (OH)$^-$ ligands by Cl$^-$, and a return to the simple chloride complex [AuCl$_4$]$^-$.
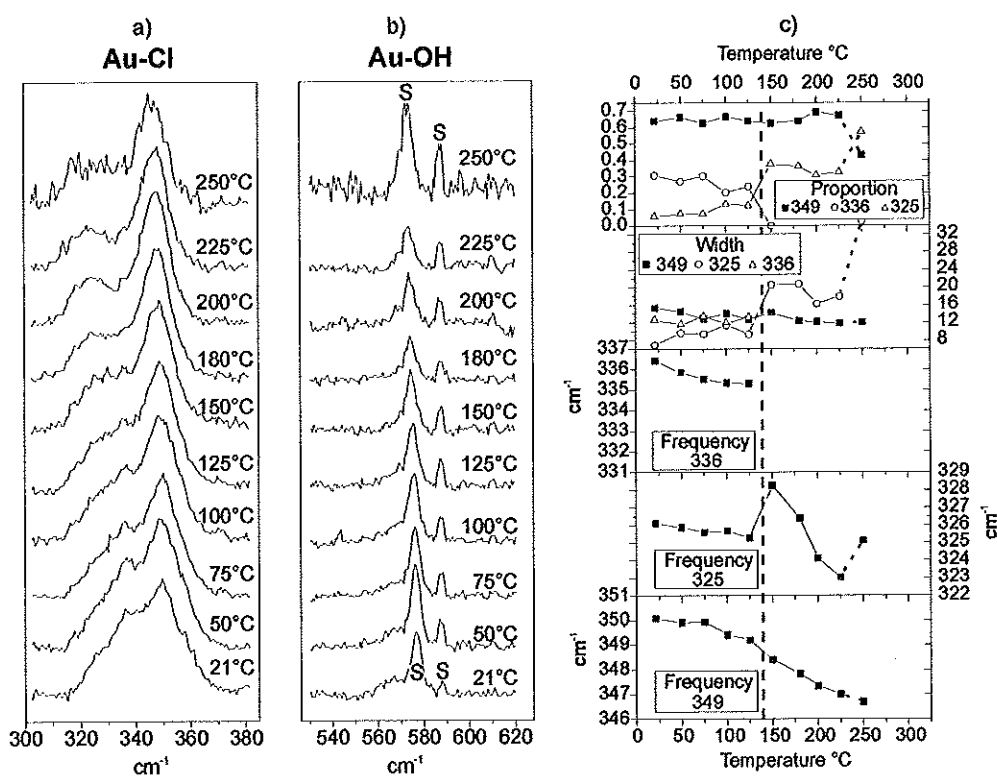

Figure 9: Effect of temperature on 0.02M Au(III) chloride solutions at pH 5.75: (a) spectra for the Au-Cl stretching region; (b) the Au-OH stretching region from the same spectra. Peaks marked S = sapphire; and (c) peak parameter obtained from the spectra. Peak proportions = Area$_{peak}$/ Area$_{total peaks}$.

pH 6.5, 1kbar, 25-250°C

At pH 6.5 and ambient temperature the solution shows two peaks, a strong one at 339 cm^{-1} and a weaker one at 355 cm^{-1}(Fig. 10a). A strong Au-OH stretching peak is also observed at 567 cm^{-1}. With increasing temperature two changes are seen (Fig. 10b). Between 25 and 75°C there is a very rapid decrease in the frequency of the 355 cm^{-1} peak (Fig 10c), and an increase in its area relative to the peak at 339 cm^{-1}. There is also a brief increase in its width, which may be due to the presence of two unresolved peaks (presumably at 355 and 351 cm^{-1}). The 339 peak also shows a relatively rapid decrease in frequency over this range, to 336cm^{-1}, although it is less pronounced. From 75 to 150°C the parameters remain relatively stable with a gradual increase in width and decrease in frequency of both. Above 150°C there is another change: the 336 peak (which is now at 334 cm^{-1}) begins to decrease rapidly in frequency, and shows a sudden increase in width followed by a relatively steady decline. The 355 peak (now at 350 cm^{-1}) shows a sudden decrease in frequency, and a somewhat irregular decrease in width.
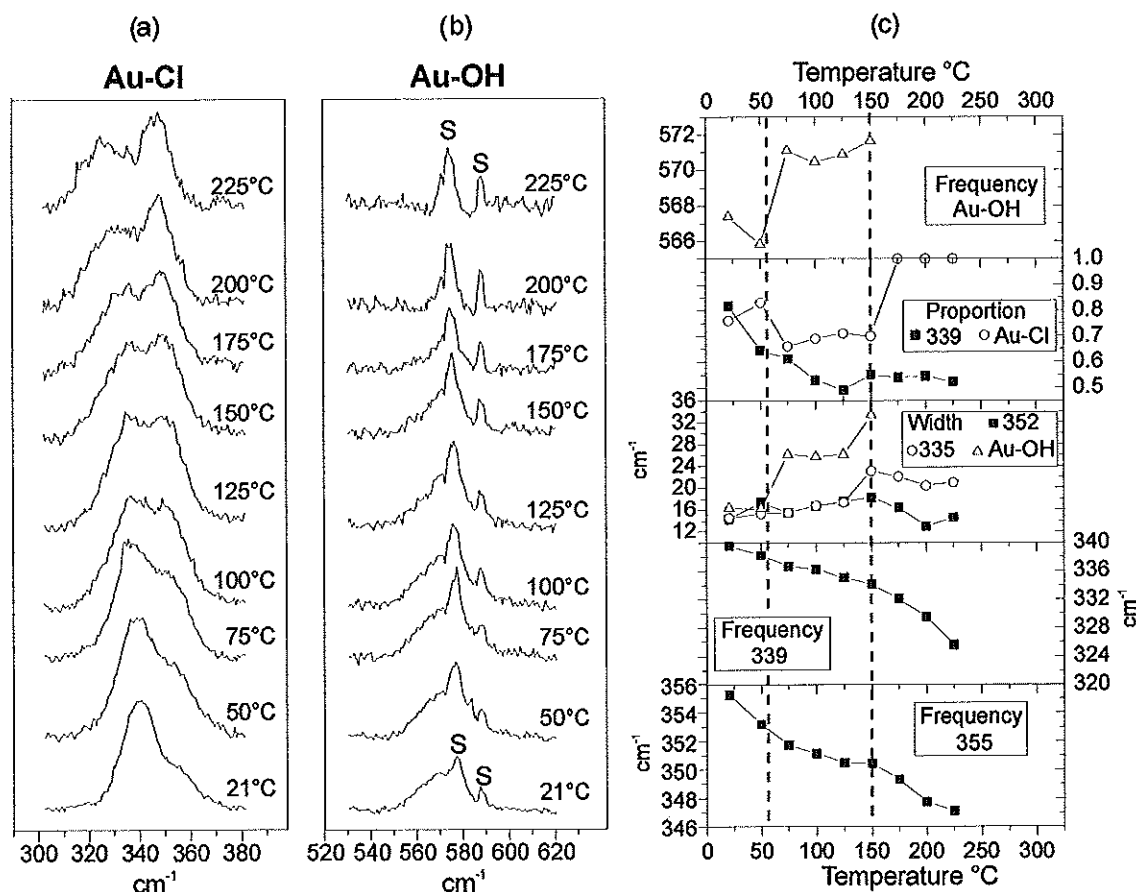

Figure 10: Effect of temperature on 0.02M Au(III) chloride solutions at pH 6.5: (a) spectra for the Au-Cl stretching region; (b) the Au-OH stretching region from the same spectra. Peaks marked S = sapphire; and (c) peak parameter obtained from the spectra. Peak proportions = Area$_{339}$/ Area $_{all\ Au-Cl\ peaks}$, Area $_{AuCl}$/Area $_{(Au-Cl+Au-OH)}$.

It is also important to consider the behaviour of the Au-OH stretching peaks. The peak at 567 cm^{-1} shows no change from 25-50°C, but from 75-150°C it is both wider, and has a larger area relative to the Au-Cl stretching region, indicating an increase in the proportion of Au-OH bonds. The increase in width may be due to the presence of two peaks, which are unresolvable due both to their width (as described by Murphy and LaGrange, 1998) and to the interference of the sapphire peak. Above 150°C, the Au-OH peak first reduces sharply in intensity relative to the Au-Cl region, and then disappears altogether. These data suggest that the original complex is initially undergoing replacement of Cl$^-$ ligands by (OH)$^-$ groups, but then (above 150°C) the (OH)- groups are lost. The peak positions are slightly higher than those described by Murphy and LaGrange (1998), but the peak proportions and relative positions are consistent with a change from the complex [AuCl$_2$(OH)$_2$]$^-$ at room temperature, to a mixture with [AuCl (OH)$_3$]$^-$ at 75-150°C, then a return to [AuCl$_4$]$^-$ at higher temperatures. However, the complex that is present at high temperature does not appear to be simply the [AuCl$_4$]$^-$ complex that might be expected, based on earlier results. The relative proportions of the two peaks are not correct (compare the spectrum at 225°C in Fig. 10a with that in Fig. 4, the normal [AuCl$_4$]$^-$ complex at the same temperature and pressure) and the peak which is now at 323cm^{-1} would be expected to be around 320cm^{-1} at this temperature. It is likely that the peak parameters are distorted by a minor amount of another complex such as [AuCl$_3$(OH)]$^-$, which at room temperature has peaks at 349, 335 and 325cm^{-1}. If this were the dominant complex, it would be expected that the 335 peak appears as a resolvable band, but if it is a minor component alongside [AuCl$_4$]$^-$ it is likely to appear only as a distortion of the 325 peak.

Effect of pressure

Two solutions were analysed for the effects of pressure on both peak parameters and speciation. A solution of 0.02M Au at pH=0 was pressurised to 1.5kbar, and the solution repeatedly analysed with reducing pressure. No change in peak parameters was observed until below 0.7 kbar. The pressure was released to ambient, since the gauge measurement was less accurate in this range. A shift in frequency of <1cm^{-1} downwards was observed between the ambient and the high-pressure analyses, but no further change was seen between 0.7 and 1.5kbar.

The same experiment was repeated with a solution of pH 6.5, showing peaks characteristic of the [AuCl$_2$(OH)$_2$]$^-$ complex at room temperature. No change was observed with release of pressure.

Why is Au(I) Not Observed?

It is generally assumed that the dominant chloride complex of gold under hydrothermal conditions will be [AuCl$_2$]$^-$. Solubility work (e.g. Gammons and Williams-Jones, 1995; Hayashi and Ohmoto, 1991; Wood et al., 1987) has shown that Au(I) complexes replace Au(III) with increasing temperature and are significant by 150°C and dominant at 300°C.

Gammons et al. (1997) have studied the disproportionation of Au(I) chloride to Au(III) chloride on cooling from high temperatures. However, in these experiments no evidence for the presence of Au(I) complexes was found. There are three possible explanations for the difference between this study and previous work.

1.   Previous solubility work mistakenly identified Au(I) complexes. This is extremely unlikely given the volume of data. Although the determination of speciation from solubility data alone can result in some ambiguity (see Tossell, 1994, for a discussion of this), the presence of Au(I) can also be confirmed by visual observations, such as the change in colour from colourless to yellow, with associated precipitation of gold, as high temperature Au(I) disproportionates to Au(III) (Gammons et al., 1997).

2.   [AuCl$_2$]$^-$ was present in the solutions of the present study, but was undetected. This is also unlikely, given the strength of the signal in most of the analyses. In addition, the observation of the bright yellow colour, which persisted in the solutions to high temperatures, until the precipitation of gold, indicates that any transformation of Au(III) to Au(I) was very minor.

3.   Assuming both that Au(I) was indeed present in solubility experiments by previous workers, and that it was not present in the samples from this study, then variations in analytical procedure or sample composition must be responsible for the difference.

The last-mentioned possibility appears to be the most likely. However, the differences between solutions in this study and in previous work are relatively minor. The concentration of gold in solution was similar (0.005-0.02M, compared to 0.002-0.016M in Gammons et al., 1997), as was chloride content. One major difference is equilibration time: in this study solutions were analysed with no specific equilibration time other than that necessary to allow temperature stabilisation (typically 10 to 15 minutes), whereas solubility studies are carried out over long time periods (typically 7-30 days) to allow equilibrium between solid and fluid to be reached. However, in this study, where all the components are in solution, equilibration time is not expected to be a significant factor. Murphy and LaGrange (1998) showed that changes in gold chloro-hydroxy speciation with pH were almost instantaneous, as evidenced by rapid colour changes, and this was also observed by Gammons et al. (1997) in the rapid appearance of yellow colouration on addition of an oxidising agent to a colourless Au(I) solution. Without addition of oxidising agents, those authors recorded that equilibrium in the disproportionation reaction was reached within 4 hours of quenching. Although analyses in this study were not subject to several hours equilibration time, at the end of an experimental run the solution had been held at temperatures above 150°C for several hours. If transformation was to occur it should have been observed. Thus, it appears that the failure to observe the transformation of Au(III) to Au(I) with increasing temperature should not be significantly affected by equilibration time. The only other significant difference is that the solutions in this study were prepared by dissolution of a gold-chloride salt, while the solubility studies, by definition, concerned the dissolution of metallic gold (or in the case of Gammons and Williams-Jones, 1995, the Au-Ag alloy electrum).

The Au(I) complex is known to break down on cooling to form the Au(III) complex and metallic gold – this, according to the reaction

$$3AuCl_2^- = 2Au_{(s)} + AuCl_4^- + 2Cl^- \tag{1}$$
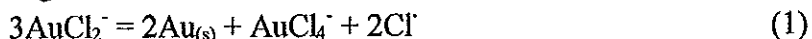
This disproportionation reaction was studied in detail by Gammons et al. (1997), who described a change in the solution from colourless to yellow, alongside gold precipitation. The observed precipitation of gold in this study, which occurs on heating of the Au (III) complex, and is associated with a loss of yellow colour, is clearly not due to the same reaction. However, if reaction (1) is responsible for the disproportionation of Au(I) to Au(III) on cooling, then the inverse reaction

$$2Au_{(s)} + AuCl_4^- + 2Cl^- = 3AuCl_2^- \tag{2}$$
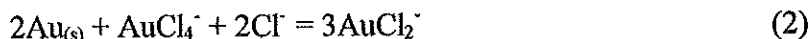
can be invoked to describe the transformation on heating. This indicates a problem with the experimental system used thus far, in that although abundant excess chloride is present, no metallic gold is available. The transformation cannot therefore proceed via this route. This could explain the difference between the current study and previous ones: in the solubility experiments the addition of excess gold would have allowed the transformation to take place, whereas in the current study this was not possible.

Experiments in the Presence of Metallic Gold

To test this hypothesis, the Au(III) chloride solution was heated in the presence of metallic gold. Initially this was carried out in the simple tube furnace, allowing observation of the solution during the experiment. The transformation should be identifiable visually, as Au(III) chloride solutions are bright yellow in colour, while Au(I) chloride is colourless (Gammons et al., 1997). The solution was sealed in the tube with several small strips of gold foil and then heated slowly. The colour of the solution began to fade visibly above 230°C, and at 250°C was almost colourless. Unlike the experiments in the absence of metallic gold, no gold precipitation was observed at high temperature. However, a small volume of solution was trapped behind the vapour bubble. In this small part of solution, a red colouration was observed as gold began to precipitate, but this redissolved immediately on shaking the tube. Evidently, this small volume of solution was effectively isolated from the metallic gold, and behaved as in the previous experiments. On cooling, the solution slowly regained its yellow colour, and fine particulate gold was observed to precipitate. This gold appeared to have dissolved from the gold foil during heating, and was reprecipitated during the disproportionation reaction on cooling (equation 1). This disproportionation occurred rapidly, which is consistent with the observation by Gammons et al. (1997) that the addition of gold foil could increase the rate reaction (1) during cooling. After several days at room temperature the particulate gold had disappeared, but the surface of the gold foil had become covered in fine crystals, indicating that the gold had recrystallized on this surface. These observations are consistent with the transformation of Au (III) chloride to Au(I) at high temperature, according to reaction (2). This experiment was then repeated in the hydrothermal cell, with a small amount of finely particulate gold being added to the fluid in the glass sample chamber. Raman analyses were carried out and the resulting spectra are shown in Figure 11a. Until

temperatures above 200°C the spectra show the same features as those for the solutions in the absence of metallic gold. However, at 225°C the 325cm^{-1} peak is slightly larger than expected, and at slightly higher frequency (Fig. 11b), and with increasing temperature, it becomes clear that a new peak is present at ≈326 cm^{-1}, which is likely to represent [AuCl$_2$]$^-$. The peaks due to [AuCl$_4$]$^-$ become weaker while this peak grows, and by 275°C the new peak is dominant (Fig. 11b). This is consistent with the observation that the solution above 250°C was very pale yellow in colour, but not completely colourless, indicating the continued presence of a small amount of Au (III). In fact, the spectra measured at 250 and 275°C in Figure 11 were acquired over more than double the time of the earlier spectra (300s x 2, as opposed to 120s x 2), although the total solubility of gold is much higher at this temperature, as evidenced by the precipitation of gold during cooling. Thus the Raman spectrum of [AuCl$_2$]$^-$ is many times weaker than that for [AuCl$_4$]$^-$, an observation predicted by Pan and Wood (1991) given the lower number of Au-Cl bonds contributing to the peak intensity. The position of this new peak, which presumably represents the symmetric Σ_g^+ Au-Cl stretch of the linear [AuCl$_2$]$^-$ complex, is much higher than that predicted by Tossell (1996), but is very close to that described by (Braunstein and Clark, 1973) for salts containing the [AuCl$_2$]$^-$ ion (329 cm^{-1}). Tossell (1996) noted that the difference in the degree of error between his predicted frequencies and those measured experimentally for the Au(I) and Au(III) complexes was likely to be due to differences in electron correlation effects.
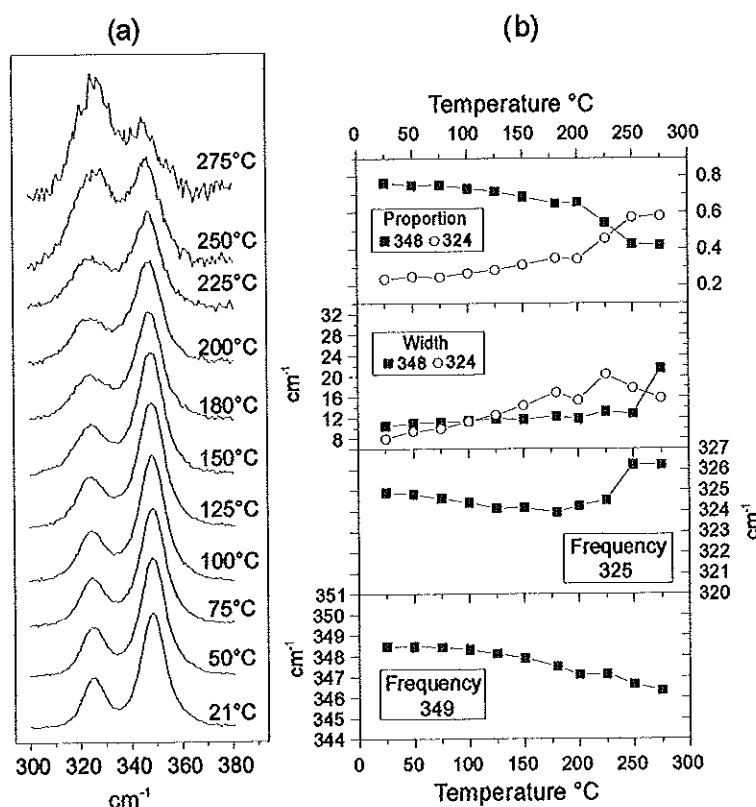

Figure 11: Effect of temperature on 0.02M Au(III) solution containing gold foil; (a) Raman spectra for Au-Cl stretching region (N.B. spectra at 250 and 275°C recorded at longer integration times than other spectra); (b) Peak parameters obtained from spectra.

DISCUSSION

The data presented in this study are very different from those of Pan and Wood (1991), who found evidence for the partial transformation of $[AuCl_4]^-$ to $[AuCl_2]^-$ at high temperature in simple Au(III) chloride solutions in the absence of metallic gold. However, the Raman spectra do not differ that markedly between the two studies, at least for the simple temperature analyses without adjustment of redox conditions.

Contrast with Pan and Wood (1991): Simple Solutions

The spectra of Pan and Wood (1991) do not clearly show the presence of a third peak, but rather a merging between the two peaks at 347 and 323 cm^{-1}. The presence of a third peak at 332 cm^{-1} was interpreted from peak fitting, because the authors stated that without a third peak the 323 cm^{-1} peak became "excessively wide". The assignment of this new peak to the symmetric stretch of $[AuCl_2]^-$ was based on a number of sources of evidence. The Au(I) complex $[AuCl_2]^-$ would be expected to replace $[AuCl_4]^-$ at high temperature, making the Au(I) complex the most obvious candidate for the appearance of any new peak. The presence of a single peak suggests a very simple complex, such as the linear $[AuCl_2]^-$ ion which has only one Raman active vibration, a symmetric Au-Cl stretch. The peak was in a similar position to that predicted for the $AuCl_2^-$ ion in salts as described by Braunstein and Clark (1973). More importantly, experiments were conducted with a solution under reducing conditions, and the 332 cm^{-1} peak was observed much more strongly, and could clearly be identified even without peak fitting techniques. More reducing conditions would be expected to increase the degree of transformation from Au(III) to Au(I), supporting assignment of this peak to the Au(I) complex. The polarisation characteristics of this stronger peak were consistent with a totally symmetric stretch. Therefore, the occurrence of the peak at 332 cm^{-1} and its assignment to the totally symmetric stretch of the $[AuCl_2]^-$ complex seemed well founded.

Note that the spectra in this study appear slightly different to those of Pan and Wood (1991), in that the ratio of the peak intensities 349/325cm^{-1} is lower in this study. This is due to different polarisation conditions, which slightly reduce the 349cm^{-1} peak. Our parallel-polarised spectra look identical to those of Pan and Wood (1991), and the lower intensity of the 325cm^{-1} peak emphasises the "merging" effect with increasing temperature. The similarity between the spectra in the two studies, and the fact that spectra in this study required only the two peaks due to $[AuCl_4]^-$, calls into question the validity of the third peak described by Pan and Wood (1991).

Returning to the data of Pan and Wood (1991), the data given for their fitted peaks give no consistent trends when plotted against temperature (Fig. 12). The frequency of their 347cm^{-1} peak shows a slight downwards trend (1cm^{-1} over 300°C), and the 332cm^{-1} peak also shows a smooth downward trend in frequency after its appearance (2 cm^{-1} from 150-300°C). However, the 323cm^{-1} peak shows a more variable frequency, with a sudden jump from 325 to

320 cm^{-1} between 200 and 250°C, coincident with the appearance of the 332 cm^{-1} peak. Similarly, the widths of the three peaks do not show consistent trends. In particular, the 332 peak had a width of <2cm^{-1} when it was first recorded, then 4cm^{-1} at 200°C, both of which are very low for a Raman peak in a system such as this one. Such low widths are generally only recorded for peaks in perfectly crystalline materials such as defect-free diamond, or gas emission lines. In theory, the appearance of a single peak representing [AuCl$_2$]$^-$ should not significantly affect the peak positions or parameters of the existing peaks. However, in practice errors of peak fitting before the new peak can be resolved may cause a shift towards the new peak position (i.e. an increase in the frequency of the 323cm^{-1} peak) and an increase in width. Once the new peak can clearly be resolved, these errors should not persist. In the data of Pan and Wood (1991), the decrease in frequency of the 323 cm^{-1} peak is the opposite of that which would be expected. Comparison with the data from this study suggests that the 332cm^{-1} peak described by Pan and Wood (1991) is in fact an artefact of the peak-fitting process. It is suggested that their spectra would be better described, as in this study, by a simple increase in the width of the 323cm^{-1} peak with increasing temperature.

Contrast with Pan and Wood (1991): Reducing Solutions

Pan and Wood (1991) also presented spectra from a solution under reducing conditions at high temperature, in which a peak at around 332 cm^{-1} was clearly present. In the reducing solutions analysed in this study, no evidence of this peak was observed. As the solutions and techniques used in both cases were similar, we currently have no explanation for why the spectra of Pan and Wood (1991) were not replicated in this study. The only apparent difference is that the solutions in this study were measured at higher pressure (1kbar, as opposed to <150bar). The peak described in this study, in the presence of metallic gold, does not appear to be the same as that described in the reducing solutions of Pan and Wood (1991). The difference in frequency between the two peaks ($\approx$326 cm^{-1} and 332 cm^{-1}) is too large to be explained by slight errors due to the difficulties of fitting peaks to overlapping bands.

The spectra presented by Pan and Wood (1991) for their reducing solutions appear to show a slight downwards shift in the frequency of the 348 peak, as would be predicted with increasing temperature. However, the shift in position of the 325 cm^{-1} peak is much more pronounced, and the peak occurs at well below 320 cm^{-1} at 300°C. This downwards shift is much greater than that observed in this study. When the "332 cm^{-1}" peak is first shown (in Pan and Wood's Fig. 5) it is several wavenumbers higher than in the other spectra, which suggests the peak fitting for this spectrum is not exact. The peak positions of the spectra presented are, therefore, not in complete agreement with the peak expected for the [AuCl$_4$]$^-$ complex. Any change in peak positions other than the minor changes due to slight errors in peak fitting, suggest that the peaks do not represent the simple Au(III) complex.
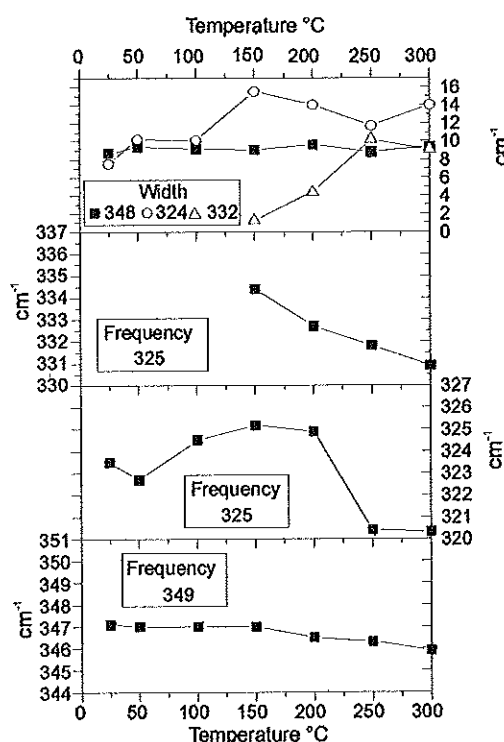
Figure 12: Peak parameters given by Pan and Wood (1991) for their spectra with increasing temperature.

Effect of pH on Speciation

Although no change in speciation was observed with increasing temperature for the low pH solutions, very clear changes were observed at higher pH showing that temperature does have a major effect on mixed chloro-hydroxy complexing. The results are consistent with the preliminary EXAFS and XANES results of Schofield et al. (1998), at temperatures up to 175°C. That study indicated that, while at low pH there was no change in complexing with temperature, at moderate pH increasing temperature caused removal of OH⁻ ligands. However, they found that at higher pH the reverse was true, and increasing temperature encouraged the replacement of Cl⁻ ligands by OH⁻. In the present study it can be seen that for high pH solutions at temperatures above 175°C, the trend is reversed, and Cl⁻ begins once more to replace OH⁻ groups. The exact pH ranges of the analyses in each study were different, but as shown by Murphy and LaGrange (1998), chloride and gold concentration can have an important effect on the pH of transitions between the various mixed chloro-hydroxy complexes, and there is no reason to suppose that this will be any different at high temperatures. Therefore, probable differences in these factors between the two studies can explain the occurrence of the described behaviour at different pH values. However, the important fact is that the trends observed in both studies are identical.

The unadjusted 0.005M low chloride solution (pH circa. 3) showed a third peak at room temperature, which decreased in intensity with increasing temperature. This behaviour was identical to that observed in the high-chloride pH 5.75 solution, supporting the interpretation by Murphy and LaGrange (1998) that in this solution $[AuCl_4]^-$ was partially hydrolysed to $[AuCl_3(OH)]^-$. The previous work found that hydrolysis begins at much lower pH in low chloride-low gold solutions. The similarity between the behaviour of the two solutions with increasing temperature indicates that the complex present in both is indeed the same.

Geological Implications

The observation that Au(III) chloride only converts to Au(I) in the presence of metallic gold could have important implications for the behaviour of gold in certain hydrothermal fluids. Such fluids are not necessarily in contact with metallic gold. In experimental studies, the solubility of gold in hydrothermal fluids has always been measured as total solubility, including Au(I), as metallic gold is always present in such experiments. In the absence of metallic gold, with Au present only as Au(III) the solubility may be somewhat different from that measured experimentally. However, it has been shown that at high temperatures, if Au(III) chloride cannot convert to Au(I) because of a lack of Au, it will break down, precipitating gold and severely limiting the gold solubility. It remains to be seen whether a hot fluid, in contact with Au-bearing minerals, would dissolve gold as Au(I) or Au(III) complexes. In most geological situations, the auriferous minerals would be likely to be sulphides, and the resulting complexes probably sulphur-bearing, rather than chloride. However, the behaviour of gold in hydrothermal fluids is still not completely understood, and the importance of metallic gold for allowing a change in complex speciation must also be investigated in other ligand systems. Without such systems, it may be that data from spectroscopic techniques (e.g. EXAFS and XANES as well as Raman) will not be directly comparable with speciation assessments based on solubility experiments.

There are a number of aspects which require further investigation, particularly the precipitation of gold (and in the case of low concentration, low-chloride concentrations, a white precipitate) at high temperature.

CONCLUSIONS

1.   No evidence was found for the occurrence of Au(I) complexes on heating simple Au(III)chloride solutions to 300°C and 0.85-1.5 kbar. However, when the same solution was heated in the presence of metallic gold, the Au(I) complex$[AuCl_2]^-$ was observed, with the Raman spectrum showing a single Au-Cl stretching band at $326cm^{-1}$.

2.   A re-evaluation of the spectra of Pan and Wood (1991) indicates that the Au(I) chloride complex was not present in the majority of their solutions. The peak described by those authors at 332 cm^{-1} and attributed to $[AuCl_2]^-$ is believed to be an artefact of the peak

fitting process. This work highlights the importance of careful peak fitting and assessment of trends in peak parameters when interpreting Raman spectra.

3.   The effect of pressures up to 1.5kbar on the speciation of gold chloride and mixed chloro-hydroxy complexes is minimal.

4.   The effect of temperature on the Cl^-/OH^- ratio of mixed chloro-hydroxy complexes varies with pH, but in general, at high temperature, the simple Au (III) chloride complex is dominant, indicating a net loss in hydroxide ligands with increasing temperature. It will be necessary to study the effect of temperature on moderate to high pH solutions in the presence of metallic gold.

ACKNOWLEDGEMENTS

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