

# Thallium (I) chloride complexing in aqueous media to 200°C

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## Introduction

Thallium occurs in hydrothermal ore deposits where it is frequently associated with arsenic, antimony and gold mineralization. Many epithermal gold deposits contain appreciable concentrations of thallium, often as discrete minerals. In recent years, thallium minerals have also been identified in the upper portions of the large Precambrian gold deposit at Hemlo (Harris, 1990). In addition, large concentrations (up to 0.5 wt%) occur in some gold-containing hot spring and well discharge precipitates associated with active geothermal systems (e.g. Krupp and Seward, 1987). The coordination chemistry of thallium in hydrothermal solutions is unknown. We report here our preliminary results from a study of chloridothallium (I) complexes up to 200°C and at equilibrium vapour pressures. Experiments to extend these data to higher temperatures are currently underway. The aim of this study is to gain insight into the aqueous chemistry of thallium at elevated temperatures and pressures as a first step forward trying to understand the association of thallium with gold, arsenic, antimony ( $\pm$  Ag, Hg, Ga, etc).

## Experimental Methods

The complexing of  $Tl^+$  with chloride ligands was studied spectrophotometrically using a gold-lined titanium cell with silica glass windows. The solutions were only in contact with gold and silica. Digitised spectra of solutions containing  $2 \times 10^{-4}$  mol  $dm^{-3}$  thallium,  $1 \times 10^{-3}$  mol  $dm^{-3}$  HCl and varying NaCl concentrations up to 3.00 mol  $dm^{-3}$  were recorded at 0.1 nm intervals using a Cary5 spectrophotometer. The spectra (Fig. 1) were corrected for window, solvent and chloride ion absorbance. The deconvolution of the spectra and computation of the equilibrium formation constants were performed using a modified version of the computer program, SQUAD (Leggett, 1985). A non-linear least squares refinement of the  $\beta_{mn}$  in the extended form of Beer's law as expressed by:

$$A = \sum_{m=1}^m \sum_{n=0}^n \beta_{mn} [Tl^+]^m [Cl^-]^n \gamma_{Tl^+}^m \gamma_{Cl^-}^n \gamma_{mn}^{-1} \epsilon_{mn} l$$

was performed, where  $\beta_{mn}$  are the cumulative equilibrium formation constants for the species  $T_m Cl_n^{m-n}$  and  $\gamma_{Tl^+}$ ,  $\gamma_{Cl^-}$  and  $\gamma_{mn}$  are the individual

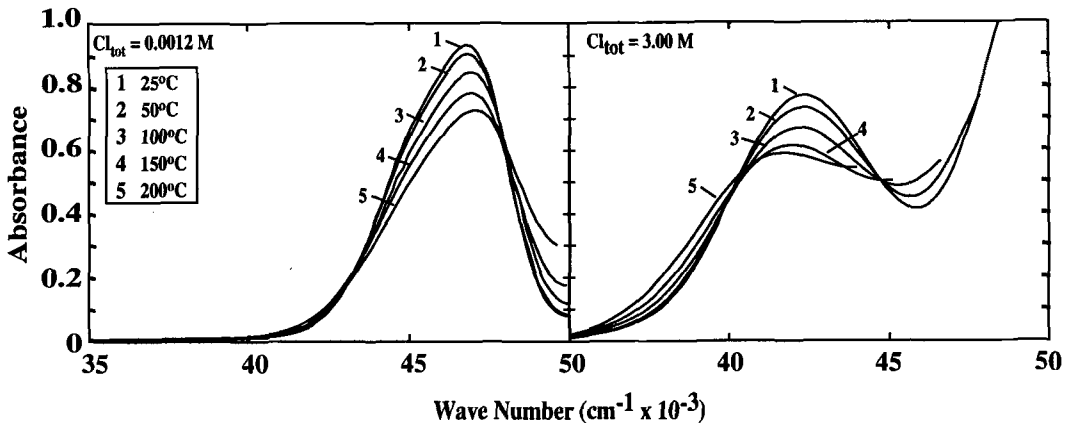


FIG. 1. Background corrected spectra of chloride solutions containing  $2 \times 10^{-4}$  mol  $dm^{-3}$  thallium.

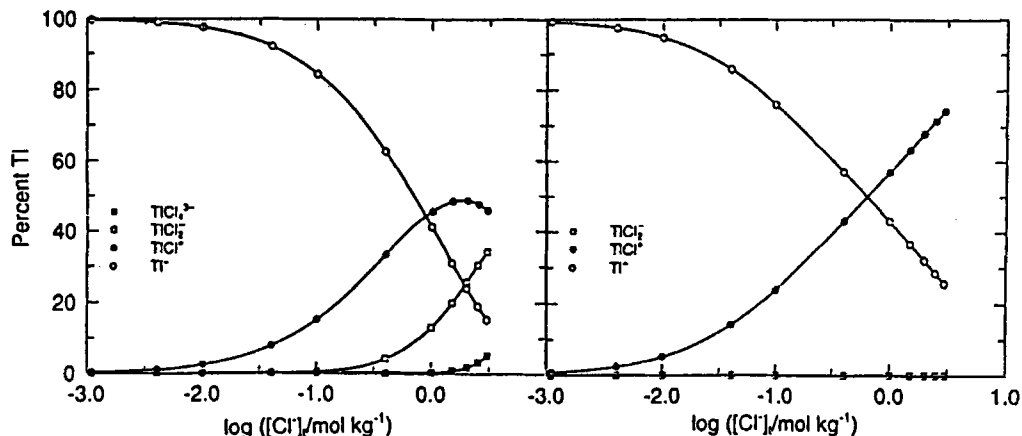


FIG. 2. The percentage distribution of thallium (I) chloride complexes as a function of total chloride concentration,  $Cl_{tot}$ , at saturated vapour pressure.

TABLE 1. Equilibrium cumulative formation constants,  $\log \beta_{mn}$  (molal) for thallium (I) chloride complexes up to 200°C

	25°C	50°C	100°C
$\log \beta_1$	+0.491	+0.511	+0.450
$\log \beta_2$	+0.003	-0.120	-0.388
$\log \beta_4$	-1.419		
	150°C	200°C	
$\log \beta_1$	+0.671	+0.890	
$\log \beta_2$	-0.445		

ion activity coefficients as specified.  $\epsilon_{mn}$  are the molar absorptivity of the chloridothallium (I) complexes and  $l$  is the path length (= 0.962 cm).

Values for  $\beta_{mn}$  obtained from these experiments are given in Table 1. The scheme of species which best-fitted the data at 25°C contained  $Tl^+$ ,  $TlCl^0$ ,  $TlCl_2^-$  and with less certainty,  $TlCl_4^{3-}$ .

This is in agreement with the recent species distribution reported by Read and Aldridge (1992).

With increasing temperature to 200°C, all the thallium is present as the free aquated  $Tl^+$  ion and the uncharged  $TlCl^0$ , as shown in Figure 2. This

tendency towards simple molecular species of low to neutral charge with increasing temperature has also been noted for the formation of chloride complexes of other metals.

### Discussion

In ore-forming hydrothermal fluids at  $T \geq 200^\circ C$ , the dominant Tl (I) chloride complex will be the neutral  $TlCl^0$ . Deep fluids in Ohaaki-Broadlands geothermal system (New Zealand) contain approximately  $10 \mu g kg^{-1}$  of thallium. Preliminary calculations indicate that 20 to 30% of the total thallium in solution may be accounted for in terms of  $TlCl^0$ , thus suggesting that hydrosulphide complexes of thallium (I) such as  $TlHS^0$  and  $Tl_2HS^+$  may also be important in hydrothermal thallium transport.

### References

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