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THE AQUEOUS GEOCHEMISTRY OF PLATINUM, PALLADIUM AND GOLD: RECENT EXPERIMENTAL CONSTRAINTS AND A RE-EVALUATION OF THEORETICAL PREDICTIONS

SCOTT A. WOOD[1], BRUCE W. MOUNTAIN AND PUJING PAN[2]
Department of Geological Sciences, McGill University, 3450 University Street, Montreal, Quebec H3A 2A7

ABSTRACT

Re-evaluation of theoretical calculations reaffirms that, at temperatures up to 300°C, significant solubility (>10 ppb) of Pt and Pd as chloride complexes is restricted to highly oxidizing and acidic conditions. This conclusion is supported by recently reported experimental solubility measurements. Experiments on the solubility of Pt and Pd in sodium hydroxide solutions at 25°C confirm that a change in species from $Pd(OH)_2^0$ to $Pd(OH)_3^-$ occurs at a pH of approximately 12, but apparently no such change in speciation occurs for Pt. The measured log β_2 for $Pt(OH)_2^0$ agrees very well with the previously predicted value, whereas predicted stability-constants for $Pt(OH)_3^-$ and $Pt(OH)_4^{2-}$ should be considered only as provisional estimates. Hydroxide complexation is unlikely to contribute to the hydrothermal transport of Pt and Pd in most geological environments. Nevertheless, Pt, Pd and Au hydroxide complexes may be the dominant inorganic species of these metals in oxidized surficial waters such as seawater, lake water, and river water. Ammonia complexes are predicted to contribute substantially to the solubility of Pd and Au, but probably not Pt, at temperatures near 300°C, with a maximum in solubility at the N_2–NH_3–NH_4^+ triple point. The solubilities of Pt, Pd and Au as ammonia complexes decrease very rapidly with decreasing temperature, owing to the shift of the N_2–NH_3–NH_4^+ triple point to successively lower fugacities of oxygen and higher pH. Preliminary results of an experimental investigation of the solubility of Pt, Pd and Au in hydrothermal bisulfide solutions from 200° to 500°C yield between 2 and 300 ppm Au, between 4 and 800 ppb Pt, and between 1 and 600 ppb Pd at 0.3–2.2 molal ΣS, $5.91 < pH < 9.43$ and oxygen fugacities near the sulfate–sulfide boundary. These solubilities are several orders of magnitude lower than those predicted theoretically, but do suggest that low ppb quantities of Pt and Pd metals can be transported as bisulfide complexes in geologically reasonable solutions. The solubility of Au under the same conditions is 1–3 orders of magnitude higher than that of Pt and Pd, placing severe constraints on models of formation of hydrothermal PGE deposits. Thiosulfate and polysulfide may form complexes with Au, Pt and Pd in relatively low-temperature environments where sulfide is being oxidized. The potential of these ligands to transport Pt and Pd is largely untested, but the importance of thiosulfate to gold transport has been demonstrated theoretically, experimentally and from field data. Natural organic acids (fulvic and humic acids) may increase the precious-metal-transporting capabilities of low-temperature waters. For Pt, it appears that the most important function of these acids may be to stabilize colloids. However, for Pd, stable dissolved complexes are formed with fulvic, acetic, phthalic, salicylic and oxalic acids. Bonding of Pt, Pd and Au with various atoms in complex organic acids exhibits the following order of strength: $-S > -N > -O$.

Keywords: platinum, palladium, gold, solubility, complexes, chloride, bisulfide, ammonia, thiosulfate, organic acids, hydroxide, thermodynamic data, predictions, experiments.

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[1] Present address: Department of Geology and Geological Engineering, University of Idaho, Moscow, Idaho 83843, U.S.A.

[2] Present address: Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X5.

SOMMAIRE

Nous avons ré-évalué les constantes de stabilité des complexes chlorurés de Pt et de Pd jusqu'à une température de 300°C. Cette ré-évaluation confirme qu'à ces températures, une solubilité importante (>10 ppb; parties par milliard) du Pt et du Pd sous forme de chlorure n'est possible que dans les solutions fortement acides et oxydantes. Cette conclusion est étayée par les résultats des expériences récentes portant sur la solubilité en présence de chlorure. En présence d'hydroxyde de sodium à 25°C, il y a un changement d'espèces, de $Pd(OH)_2^0$ à $Pd(OH)_3^-$, à un pH d'environ 12, mais un tel changement ne se produit pas dans le cas du Pt. La valeur de log β_2 mesurée pour $Pt(OH)_2^0$ concorde avec celle prédite théoriquement, mais les constantes de stabilité estimées antérieurement pour $Pt(OH)_3^-$ et $Pt(OH)_4^{2-}$ doivent être considérées provisoires. Il est peu probable que les complexes hydroxylés contribuent d'une façon importante au transfert hydrothermal de ces métaux dans la plupart des milieux naturels. Néanmoins, il est très probable que les complexes hydroxylés de Pt, Pd et Au sont les espèces inorganiques prédominantes de ces métaux dans les eaux de surface oxygénées, comme l'eau de mer, l'eau des lacs et des rivières. Les complexes avec l'ammoniaque semblent contribuer d'une façon importante à la solubilité thermodynamique du palladium et de l'or, mais probablement pas du platine, aux températures près de 300°C, avec un maximum de solubilité au point de coexistence de N_2, NH_3 et NH_4^+. Les solubilités de Pt, Pd et Au diminuent fortement avec une chute de température, à cause du déplacement du point de coexistence de N_2, NH_3 et NH_4^+ vers des fugacités d'oxygène de plus en plus faibles et des valeurs de pH de plus en plus élevées. Les résultats préliminaires des expériences sur la solubilité de Pt, Pd et Au dans les solutions hydrothermales sulfurées de 200° à 500°C donnent entre 2 et 300 ppm d'Au, entre 4 et 800 ppb de Pt, et entre 1 et 600 ppb Pd à une molalité ΣS entre 0.3 et 2.2, à un pH entre 5.91 et 9.43, et aux fugacités d'oxygène près de la limite entre H_2S ou HS^- et SO_4^{2-}. Ces solubilités sont plus faibles (de plusieurs ordres de grandeur) que celles qui sont prédites par la théorie, mais elles font penser que de faibles quantités (quelques ppb) de Pt et de Pd pourraient être transportées sous forme de bisulfures dans une solution géologiquement réaliste. La solubilité de Au dans les mêmes conditions est de plusieurs ordres de grandeur plus élevée que celles du Pt et du Pd. Ceci limite sévèrement les modèles de formation des gisements hydrothermaux des éléments du groupe du platine. Le thiosulfure et le polysulfure peuvent former des complexes avec Au, Pt et Pd dans des milieux de faible température où les sulfures sont oxydés. Le transfert du Pt et du Pd par ces ligands n'a pas encore été mis en evidence, mais nous démontrons l'importance du thiosulfure au transfert de l'or par expériences, théorie et études de terrain. Les acides organiques naturels, comme les acides fulvique et humique, peuvent augmenter, à de faibles températures, la capacité des eaux de transporter les métaux précieux. Dans le cas du Pt, il semble que le rôle le plus important de ces acides pourrait se situer dans la stabilisation de colloïdes. Dans le cas du Pd, des complexes sont possibles avec les acides fulvique, acétique, phthalique, salicylique et oxalique. La force des liaisons chimiques entre Pt, Pd et Au d'une part, et les divers atomes des acides organiques complexes, suit l'ordre: –S > –N > –O.

Mots-clés: platine, palladium, or, solubilité, complexes, chlorure, sulfure, ammoniaque, thiosulfure, acides organiques, hydroxyde, données thermodynamiques, prédictions, expériences.

INTRODUCTION

In spite of considerable geological and geochemical evidence that aqueous fluids may be capable of transporting and redistributing platinum and palladium (Kinloch 1982, Schiffries 1982, Stumpfl & Rucklidge 1982, Dissanayake & Kritsotakis 1984, Volborth & Housley 1984, Ballhaus & Stumpfl 1985, 1986, Boudreau & McCallum 1985, 1986, Boudreau *et al.* 1986a, b, Bowles 1986, Riese & Arp 1986, Rowell & Edgar 1986, Watkinson *et al.* 1986, Schiffries & Skinner 1987, Taufen & Marchetto 1989, Beaudoin *et al.* 1990, Tanguay *et al.* 1990, Prichard & Lord 1990, Harney & Merkle 1990, Barnes & Giovenazzo 1990, Wood & Vlassopoulos 1990, Cook & Wood 1990, Gottfried *et al.* 1990, Orberger *et al.* 1990, Ohnenstetter *et al.* 1991), few direct experimental data [see Kovalenko *et al.* (1981, 1985) and Orlova *et al.* (1987) for the hydrothermal experimental data available prior to 1988] have been available to test this hypothesis. In a series of previous publications (Mountain & Wood 1986, Wood 1987, Mountain & Wood 1988a, b, Plimer & Williams 1988, Jaireth 1988, Wood *et al.* 1989), theoretical thermodynamic calculations have been presented on the solubility, transport and deposition of Pt and Pd in aqueous solutions. These theoretical calculations have stimulated or influenced additional theoretical and field studies (Wilde *et al.* 1989, Crocket 1990, Nyman *et al.* 1990, Sassani & Shock 1990, McKibben *et al.* 1990, Eliopoulos & Economou-Eliopoulos 1991, Mogessie *et al.* 1991, Schmidt *et al.* in press), as well as a variety of recent experimental studies of the problem (Gorbachov *et al.* 1989, Wood 1990, 1991, Pan & Wood 1990, Hsu *et al.* 1991, Gammons & Bloom 1990, Tait *et al.* 1991). This paper describes some recent theoretical and experimental contributions to the question of the mobility of Pt and Pd in aqueous fluids. In addition, we briefly describe some recent related work on the solubility and transport of Au (for a more complete summary of aqueous Au geochemistry, see Seward 1984a, 1989, 1991). Our goal is to compare our updated theoretical predictions with the results of experimental investigations, and to apply the combined theoretical and experimental results to a discussion of several field studies that have appeared since 1988. Although experimental studies are ultimately required to determine the thermodynamic data for the dissolution and complexation reactions involved in the hydrothermal transport of Au, Pt and Pd, we consider it worthwhile to re-examine theoretical predictions in light of new experimental data. An experimentally validated theoretical model can be used as a framework for interpolation and extrapolation of the small body of experimental data likely to become available in the near future. Furthermore, a sound basis in theory helps provide a deeper understanding of the physicochemical processes occurring both in experiments and in nature.

Mountain & Wood (1988a, b) demonstrated that the predominant oxidation state for both Pt and Pd under geological conditions is the 2+ state, whereas Seward (1984a) identified the 1+ state to be most important for Au. These metals require extremely stable complexes in order to attain parts-per-billion levels in natural aqueous solutions. The theoretical studies mentioned above have identified the following ligands to be of possible importance in the complexation of Pt^{2+}, Pd^{2+} and Au^{+} in appropriate geological environments: chloride, hydroxide, bisulfide, thiosulfate, polysulfide, ammonia and natural organic acids. As pointed out by Mountain & Wood (1988a) and Seward (1984a), the "hard" ligands CO_3^{2-}, HCO_3^-, SO_4^{2-} and PO_4^{3-} form only very weak complexes, if at all, with the "soft" Au^+, Pt^{2+} and Pd^{2+} ions, and they are therefore not considered further in this paper.

ROLE OF CHLORIDE

Mountain & Wood (1986, 1988a), Jaireth (1988) and Wood *et al.* (1989) made the first attempts to theoretically calculate the stability constants of the chloride complexes of Pt and Pd in low-temperature hydrothermal solutions (≤300°C). The conclusion of all these studies was that significant transport of Pt and Pd by chloride complexes is restricted to relatively oxidizing and acidic environments, such as would exist during the formation of Kupferschiefer-type sediment-hosted deposits. Jaireth (1988), and later Wilde *et al.* (1989), also demonstrated that conditions appropriate for the transport of Pt and Pd as chloride complexes may be attained during the formation of unconformity-type uranium deposits. However, at magmatic temperatures (≥400°C), chloride complexes could become increasingly more important (Wood 1987, Mountain & Wood 1988a, Sassani & Shock 1990). The experimental data of Orlova *et al.* (1987) and Hsu *et al.* (1991) may indicate that Pt and Pd are soluble in chloride solutions at temperatures near and higher than 300°C, although critical variables such as pH and oxygen fugacity were not explicity controlled in these experiments, and it is probable that the solubilities measured are not solely due to chloride complexation (*cf.* Wood & Mountain 1991).

Recently, several reports of well-constrained experimental determinations of Pt and Pd speciation and solubility in hydrothermal chloride solutions at temperatures from 25° to 300°C have appeared in the literature (*e.g.*, Kovalenko *et al.* 1985, Gammons & Bloom 1990, Tait *et al.* 1991). It is of obvious interest to compare the results of these experiments to the most recent theoretical predictions of the thermodynamics of chloride complexation. Below, we first report the details of our latest improvements to the estimates of Mountain & Wood (1988a). We then compare these estimates to the experimental studies mentioned above and apply them to a discussion of Pt and Pd speciation in the Salton Sea geothermal system.

Re-evaluation of the thermodynamics of chloride complexes of Pt and Pd

The available stability-constants at 25°C and 1 bar for both Pt and Pd chloride complexes vary over several orders of magnitude. Because there are significant differences in the initial 25°C thermodynamic data-sets used in the various theoretical prediction models (Mountain & Wood 1988a, Jaireth 1988, Sassani & Shock 1990), a detailed critical assessment of these data is provided below.

The cumulative stability constants from the literature for Pd chloride complexes are compared as a function of ionic strength in Figure 1. Most measurements have been conducted at 1.0 M ionic strength (I), and the values for log β_4 at this ionic strength vary from 9.72 to 12.24. Similar ranges also are encountered for the other stability constants ($\beta 1$ – $\beta 3$). However, it is evident that the stability constants measured at I = 1.0 M by Shchukarev *et al.* (1961), Biryukov & Shlenskaya (1964), Fasman *et al.* (1965), Gel'fman & Kiseleva (1969), Elding (1972) and Victori *et al.* (1975) are generally within a log unit of one another. Unfortunately, the results of many early studies (*e.g.*, Droll *et al.* 1957 and Biryukov & Shlenskaya 1964) suffer from two problems. The first of these centers around the method used to prepare solutions containing the Pd^{2+} ion. Formerly, most investigators prepared these solutions by dissolution of solid Pd hydroxide into perchloric acid solutions; this procedure may yield polynuclear products of hydrolysis or colloidal species (Rasmussen & Jorgensen 1968, Elding 1972) in addition to Pd^{2+}, and cause significant error in the measurement of β_1 in particular. The second problem involves the difficulty in making accurate spectrophotometric measurements on the Pd chloride system in the visible region of the spectrum (approximately 400 nm), which was the common practice in early spectrophotometric work on Pd (*e.g.*, Droll *et al.* 1957). All Pd chloride species have maximum absorption in this region, and the extinction coefficients for the various species are all relatively small (Burger 1964, Rittner *et al.* 1970), thus making precise determination of stability constants very difficult. More accurate measurements can be made in the ultraviolet region (*e.g.*, Elding 1972). The study of Elding (1972) is the only one that 1) does not suffer from either of these problems, 2) presents estimates of all four Pd-chloride stability constants, and 3) is in relatively good agreement (within ±1 log unit) with the bulk of other independent studies. Therefore, Elding's (1972) values are taken to be the best available at 25°C and are used in this paper as the basis for the prediction of stability constants at higher temperature.

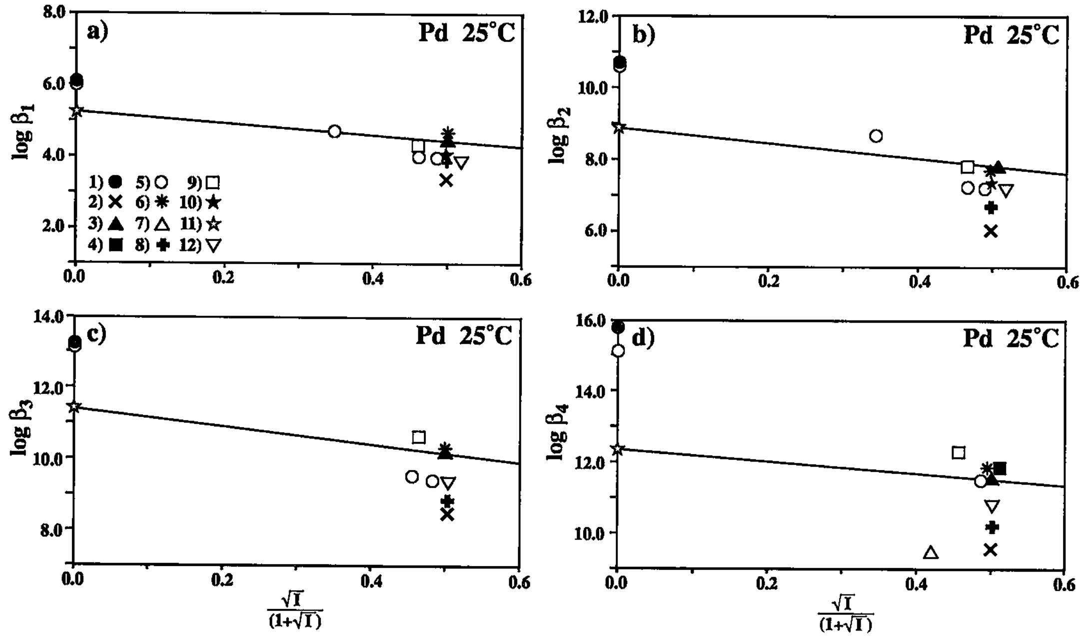

FIG. 1. Plots of a) log β_1; b) log β_2; c) log β_3; d) log β_4 *versus* $I^{1/2}/(1 + I^{1/2})$ at 25°C for Pd chloride complexes using data from the literature (I = ionic strength). Data sources: 1) Droll *et al.* (1957); 2) Rittner *et al.* (1970); 3) Elding (1972); 4) Fasman *et al.* (1965); 5) Biryukov & Shlenskaya (1964); 6) Gel'fman & Kiseleva (1969); 7) Hancock *et al.* (1977); 8) Burger (1964); 9) Shchukarev *et al.* (1961); 10) Shlenskaya & Birukov (1966); 11) Extrapolation of data of Elding (1972) to infinite dilution using an extended Debye–Hückel equation; 12) Victori *et al.* (1975). The solid straight line in each case has no significance other than to connect the data of Elding (1972) as measured at I = 1.0 molar and as extrapolated to zero ionic strength. In some cases, symbols have been slightly offset along the *x* axis for clarity. Note that in all four cases, but particularly for log β_4, the stability constants of Droll *et al.* (1957), and those of Biryukov & Shlenskaya (1964) at lower ionic strengths, appear to be too high compared with any reasonable extrapolation (extended Debye–Hückel) to zero ionic strength of the bulk of the other constants.

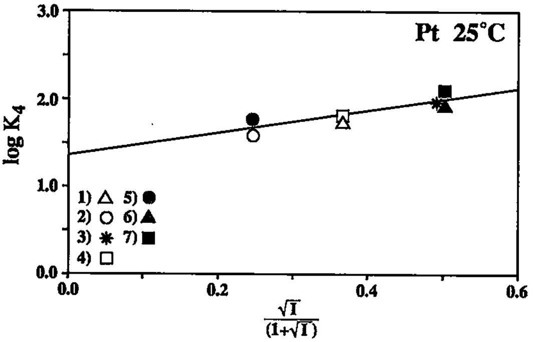

FIG. 2. Plot of log K_4 *versus* $I^{1/2}/(1 + I^{1/2})$ at 25°C for Pt chloride complexes using data from the literature. Data sources: 1) Grantham *et al.* (1955); 2) Nikolaeva *et al.* (1965); 3) Drougge *et al.* (1967); 4) Sanders & Martin (1961); 5) Grinberg & Shagisultanova (1960); 6) Elding (1966); 7) Elding (1978). Here the straight line is a least-squares fit to the data.

On the other hand, the stability constants of Droll *et al.* (1957), chosen by Sassani & Shock (1990) as the basis for their predictions, and those of Biryukov & Shlenskaya (1964) at zero ionic strength, are clearly discrepant with respect to any reasonable extrapolation of the other measured values to infinite dilution and are probably in error (*i.e.*, too high) owing to the experimental problems described above. Note that Victori *et al.* (1975) presented several convincing arguments, in addition to those given above, that also indicate that the stability constants of Droll *et al.* (1957) are erroneously high. The choice of Elding's (1972) stability constants over those of Droll *et al.* (1957) is further supported by recent Raman and absorption spectroscopic studies by Tait *et al.* (1991).

The situation for the stability constants of the Pt chloride complexes is less straightforward. Only Elding (1978) and Mestre *et al.* (1982) gave complete sets of stability constants for all four Pt^{2+} chloride complexes. Most studies have yielded stepwise (*K*) rather than cumulative (β) stability-constants owing to difficulties

TABLE 1. RECOMMENDED STABILITY CONSTANTS FOR Pt AND Pd CHLORIDE COMPLEXES AT 25°C, CORRECTED TO ZERO IONIC STRENGTH

Ion	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	Source
Pt^{2+}	5.73	10.07	13.04	14.78	a
Pd^{2+}	5.23	8.86	11.36	12.33	b
	(5.08)	(8.88)	(11.30)	(12.18)	c

Data sources: a) Elding (1978); b) Elding (1972); c) Kragten (1980)

Note: The values listed from Elding (1972, 1978) were corrected from an ionic strength of 1.0 Molar to infinite dilution as described in the text. The values listed for Pd from Kragten (1980) are listed for comparison only. Kragten's original values referred to infinite dilution and were obtained by an independent regression of all reliable data available to him at the time.

inherent in producing the aqueous Pt^{2+} ion. There is relatively good agreement among K_4 values measured by a variety of investigators (Fig. 2), but there are few measured values of K_1, K_2 and K_3. The cumulative stability-constants of Elding (1978) have been chosen as the best available at 25°C, because these are consistent with those of Elding (1972) for Pd chlorides as indicated by linear free-energy relationships (Hancock *et al.* 1977, Mountain & Wood 1988a) and because Elding's values are based on extensive research on the Pt^{2+} chloride system (Elding 1966, 1970a, b, c, 1976, 1978, Elding & Leden 1966, Drougge *et al.* 1967). Furthermore, Elding (1976) provided the only report of the preparation of the aqueous Pt^{2+} ion of which we are aware; accurate measurement of β_1 ($=K_1$) depends on the ability to prepare and isolate this ion.

The log β values of Elding (1972) and Elding (1978) for Pd and Pt chloride complexes, respectively, were corrected to zero ionic strength using an extended Debye–Hückel equation (Henley *et al.* 1984) with å = 6.0 for Pd^{2+}, Pt^{2+} and their complexes (note that the stability constants calculated at infinite dilution are quite insensitive to the actual å parameters chosen for Pd and Pt). Elding listed his stability constants as applying to ionic strengths of 0.5 to 1.0 molal. We assumed an ionic strength of 1.0 molal to correct the activity coefficients. This should introduce little uncertainty into the calculations because activity coefficients are a relatively weak function of ionic strength between 0.5 and 1.0 molal at 25°C (see data summarized in Wood *et al.* 1984). These corrected values of log β are given in Table 1. Note that Kragten (1980) also carried out a critical assessment of available stability-constants for Pd chloride complexes. His method differs from ours in that he regressed stepwise stability-constants as a function of ionic strength, using what he considered to be the more reliable data from the literature. Cumulative stability-constants for Pd chloride complexes deduced from Kragten's (1980) equations (6–9) are given in Table 1 for comparison with those adopted in the present study. It is evident that both sets of data are in excellent agreement, *i.e.*, within 0.2 log units.

TABLE 2. LITERATURE VALUES FOR ENTHALPIES OF Pd AND Pt CHLORIDE COMPLEX FORMATION.

Complexation step	ΔH, (cal/mole)	I (moles/L)	Method	Source
Palladium				
0 - 1	-3030	1.0	calorimetry	a
1 - 2	-2590	"	"	"
2 - 3	-2560	"	"	"
3 - 4	-3410	"	"	"
3 - 4	-2800	1.0	d(log K)/dT	b
3 - 4	-2800	2.0	d(log K)/dT	c
0 - 4	-5500	0.1	calorimetry	d
0 - 1	-8000	0.44	d(log K)/dT	e
1 - 2	-9000	"	"	"
2 - 3	-8000	"	"	"
3 - 4	-8000	"	"	"
Platinum				
3 - 4	-5100	0.318	d(log K)/dT	f
3 - 4	-5350	0.1	d(log K)/dT	g
3 - 4	-4400	1.0	d(log K)/dT	h

Note: the numerals 0, 1, 2, 3, and 4 denote M^{2+}, MCl^+, $MCl_2(aq)$, MCl_3^-, and MCl_4^{2-}, respectively, where M represents either Pd or Pt.

Data sources: a) Ryhl (1972); b) Shlenskaya & Biryukov (1966); c) Levanda (1968); d) Izatt et al. (1967a); e) Droll et al. (1957); f) Grantham et al. (1955); g) Nikolaeva et al. (1965); h) Drougge et al. (1967).

In order to extrapolate stability constants from 25°C to higher temperatures, enthalpies and entropies of complexation are required. The data available for enthalpies of formation of the Pd chloride complexes are summarized in Table 2. Estimates of the enthalpy of the reaction:

$$PdCl_3^- + Cl^- = PdCl_4^{2-} \tag{1}$$

given by Shlenskaya & Biryukov (1966), Levanda (1968) and Ryhl (1972) are in relatively good agreement in spite of differences in ionic strength, suggesting that the enthalpies are relatively independent of the latter. Droll *et al.* (1957) assigned a relatively large estimated error (±2000 cal/mole) to their values, and these are clearly in disagreement with the other measurements. The calorimetrically derived enthalpy for the formation of $PdCl_4^{2-}$ from Pd^{2+} of Izatt *et al.* (1967a) is much lower than would be expected based on the other data in Table 2, and therefore we believe it also to be in error. We submit that the best available values for the enthalpies of formation of chloride complexes with Pd^{2+} are given by Ryhl (1972). These values were derived calorimetrically (such values are generally believed to be more accurate than those derived from the temperature dependence of equilibrium constants) and are internally consistent with the log β values of Elding (1972). In their theoretical calculations, Sassani & Shock (1990) chose to estimate the enthalpies of chloride complexation for Pd in spite of the availability of apparently reliable experimentally measured values.

In the case of the Pt chloride complexes, only the enthalpy of the fourth stepwise complexation step has been reported. This enthalpy has been determined in at least three studies (Grantham *et al.* 1955, Nikolaeva *et al.* 1965, Drougge *et al.* 1967), and all three measurements are in reasonable agreement (Table 2). Apparently there have been no attempts to determine enthalpies of Pt chloride complexation calorimetrically.

TABLE 3. ESTIMATED CUMULATIVE STABILITY CONSTANTS (LOG ß) FOR Pt AND Pd CHLORIDE COMPLEXES AT ELEVATED TEMPERATURE

t(°C)	$PtCl^+$	$PtCl_2^\circ$	$PtCl_3^-$	$PtCl_4^{2-}$	$PdCl^+$	$PdCl_2^\circ$	$PdCl_3^-$	$PdCl_4^{2-}$
50	5.4	9.5	12.3	14.0	5.1	8.6	10.9	11.7
100	5.0	8.6	11.2	12.7	5.0	8.2	10.3	10.8
150	4.9	8.1	10.5	12.0	5.1	8.1	10.0	10.3
200	5.0	8.2	10.4	11.9	5.4	8.4	10.2	10.3
250	5.3	8.5	10.6	12.0	5.9	9.0	10.7	10.6
300	5.7	9.3	11.3	12.6	6.5	9.9	11.5	11.3

Entropies for Pd chloride complexation were derived using the relationships

$$\Delta G^\circ = -RT \ln K \qquad (2)$$

and

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

as well as the corrected values of log β in Table 1 and the ΔH values given by Ryhl (1972). The isocoulombic method (Lindsay 1980, Cobble *et al.* 1982, Ruaya 1988) was employed to extrapolate log β to higher temperatures. Isocoulombic reactions, *i.e.*, reactions having equal numbers of charges of the same magnitude and sign on both sides of the equation, have relatively small changes in heat capacity and can be extrapolated up to approximately 300°C using a simple plot of log K *versus* 1/T. In this study, the cumulative complexation reactions were made isocoulombic by adding the appropriate reaction (and the corresponding enthalpies and entropies) below:

$$Pb^{2+} + Cl^- = PbCl^+ \qquad (4)$$

$$Pb^{2+} + 2Cl^- = PbCl_2^0 \qquad (5)$$

The summed reactions were then extrapolated to higher

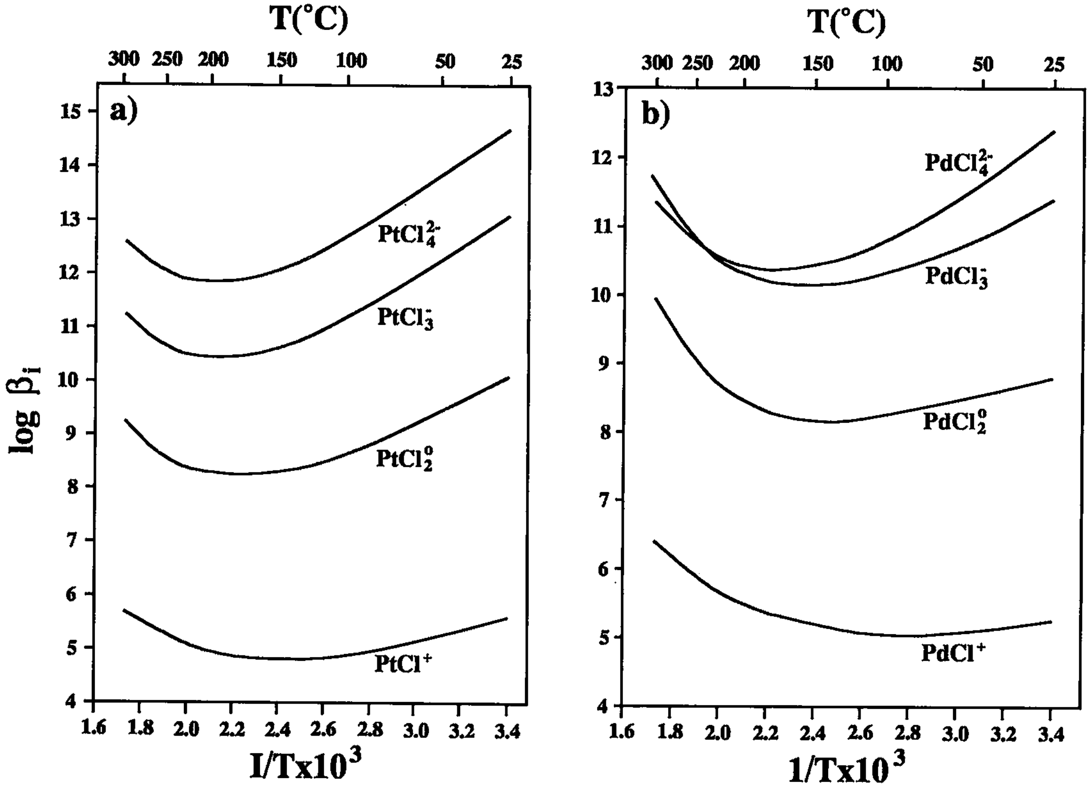

FIG. 3. Log β *versus* 1/T for chloride complexes of a) Pt^{2+} and b) Pd^{2+}. Note the minimum in log β values between 100 and 200°C. The shapes of these curves are consistent with an interaction between the metal ions Pt^{2+} and Pd^{2+} and the ligand Cl^-, which is of the "soft–soft" or predominantly covalent type at low temperature (exothermic reaction) and which becomes increasingly "hard" or ionic at higher temperatures (endothermic reaction).

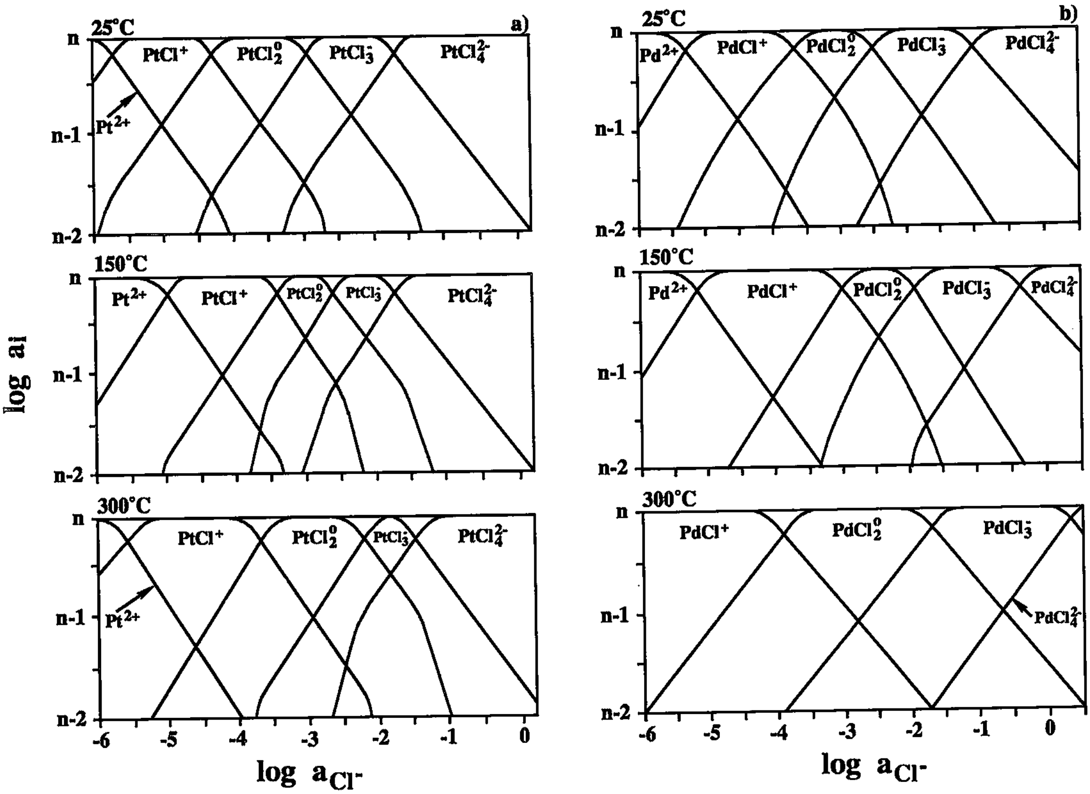

FIG. 4. Distribution of chloride complexes of a) Pt^{2+} and b) Pd^{2+} as a function of the activity of free chloride at 25, 150 and 300°C. The diagrams are generalized for total metal concentrations of 10^{-n} molal, where n is any positive integer. Note that at geologically reasonable activities of chloride (*i.e.*, $a_{Cl^-} > 10^{-1}$ m), the predominant species of Pt is predicted to be $PtCl_4^{2-}$ at all temperatures, whereas in the case of Pd, $PdCl_3^-$ is predicted to predominate at 300°C. As discussed in the text, this difference may be an artifact of the need to estimate entropies for Pt chloride complexation. The Pd speciation scheme is considered the more reliable, although both Pt and Pd speciation schemes are consistent with recent experimental measurements cited in the text.

temperatures assuming $\Delta C_{p,r} = 0$. The Pd complexation reactions were recovered at each temperature by subtracting log K for either reaction (4) or (5), as required. Thermodynamic data for reactions (4–5) were taken from Seward (1984b) and Ruaya (1988). Seward (1984b) gave an estimated error of less than 0.1 log unit for the values of log K for equations (4–5). Note that the above procedure differs from that used by Mountain & Wood (1988a) in that, in the latter work, appropriate multiples of the dissociation reaction of water

$$H_2O = H^+ + OH^- \qquad (6)$$

were added to the Pd chloride complexation reactions in order to make them nearly isocoulombic. The use of equations (4) and (5) instead of (6) is expected to yield heat capacities of reaction that are a closer approximation to zero because the former involves a divalent metal ion that is "soft" in the sense of Pearson (1963) and hence provides a better match with the Pd^{2+} ion (Ruaya 1988) than the H^+ ion for cancelling out the effects of heat capacity. On the other hand, the thermodynamics of Pb chloride complexation have not been as thoroughly studied as those of the dissociation of water, a fact that may introduce a somewhat greater uncertainty in the estimated thermodynamic data for Pd chloride complexes. However, the agreement between the estimated stability-constants and available experimental data at elevated temperatures (see below) lends credibility to the procedure.

Because of the lack of ΔH data for the complexation of chloride with Pt^{2+}, we employ the ΔS values estimated by Ruaya (1988) and the log β values in Table 1 to calculate ΔH *via* equations (2) and (3) [note that the stability constants for Pt chloride complexes at 25°C quoted by Ruaya (1988) appear to be incorrect, and as a result, so are his calculated values of ΔH]. The values of ΔH and ΔS so obtained were then used to extrapolate log β for Pt (Table 1) to elevated temperatures using the isocoulombic procedure already described for Pd.

The calculated log β values for Pt and Pd chloride complexes are given as a function of temperature in Table 3 and Figure 3. Note that the stability constants first decrease with increasing temperature, pass through a minimum near 150–200°C, and then increase with further increases in temperature. This is the expected behavior for complexation of a "soft" metal ion with an "intermediate" ligand (Ahrland 1968, Nancollas 1970). In the case of Pt, Mountain & Wood (1988a) used the data of Elding (1978) at 25°C and of Mestre *et al.* (1982) at 60°C to perform isocoulombic extrapolations. However, considering the magnitude of the enthalpies given in Table 2, log β_4 of Mestre *et al.* (1982) appears to be too low relative to that of Elding (1978). Thus, the values of log β_4 (and perhaps also β_3) estimated by Mountain & Wood (1988a) initially decrease too sharply with temperature (compare their Fig. 4 with our Fig. 3).

The distribution of Pt^{2+} and Pd^{2+} among the various chloride complexes is depicted as a function of free chloride activity in Figure 4 at three different temperatures. For Pt, the fields of predominance of the $PtCl_2^0$ and $PtCl_3^-$ complexes initially decrease in size relative to those of the other complexes as temperature increases. However, by 300°C, the $PtCl_2^0$ complex appears to become important again at the expense of $PtCl_3^-$. The situation is somewhat different for Pd where, at first, the predominance fields for $PdCl^+$ and $PdCl_3^-$ grow at the expense of the other species as temperature increases. However, by 300°C, the stability field of $PdCl_2^0$ has again increased in size, and the only species of geological importance remaining are $PdCl^+$, $PdCl_2^0$ and $PdCl_3^-$. The slightly different behavior of Pt and Pd could be an artifact of the need to estimate the entropies and enthalpies of complexation for Pt. Because the predictions for Pd chloride complexes are based on experimentally (calorimetric) derived ΔH values, we consider them to be more reliable. Furthermore, the positions of the calculated boundaries among $PdCl_2^0$, $PdCl_3^-$ and $PdCl_4^{2-}$ are in relatively good agreement (within ±0.2 log units) with those directly measured by Tait *et al.* (1991) up to 90°C using spectroscopic techniques. These boundaries are considerably different from those calculated by Sassani & Shock (1990), which is a result of their use of the data of Droll *et al.* (1957) as input for their predictions. It is also worth mentioning that the stepwise stability-constants K_3 and K_4 for Pt chloride complexes predicted in this study at 150°C (2.38 and 1.51, respectively) are in good agreement with those experimentally measured in 1 M H_2SO_4 solutions at 152.5°C by Kovalenko *et al.* (1985) (2.21 and 1.62, respectively), in spite of the fact that the entropies and enthalpies for stepwise complexation of Pt had to be estimated. Although the two sets of stepwise stability-constants refer to different ionic strengths, the dependence on ionic strength is expected to be small (*cf.* Fig. 2), because both stepwise complexation reactions are isocoulombic or nearly so.

TABLE 4. ESTIMATED LOG K VALUES FOR THE DISSOLUTION OF Pt AND Pd AT ELEVATED TEMPERATURE: $M(s) + 2H^+ + 1/2O_2 = M^{2+} + H_2O$

t(°C)	log K (Pd)	log K (Pt)
25	10.6	-0.2
50	9.1	-0.9
100	6.8	-1.9
150	5.0	-2.7
200	3.5	-3.4
250	2.3	-3.9
300	1.3	-4.4

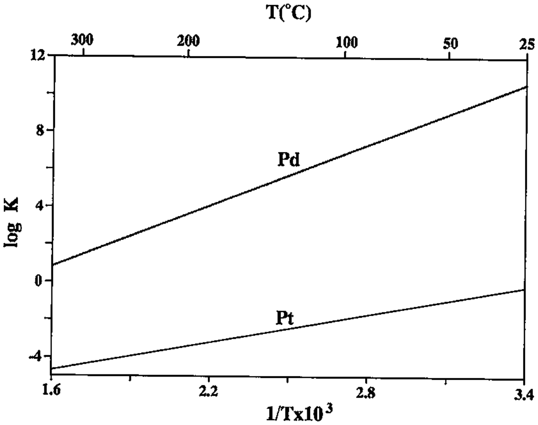

FIG. 5. Log *K versus* 1/T for the oxidative dissolution reactions of Pt and Pd from 25 to 300°C. These data were estimated using the modified Helgeson – Kirkham – Flowers equation of state for aqueous ions (Tanger & Helgeson 1988, Shock & Helgeson 1988) to calculate the free energy of Pt^{2+} and Pd^{2+} at elevated temperatures and the free energy data for water as a function of temperature tabulated by Helgeson & Kirkham (1974). Note that log *K* for both reactions decreases with temperature.

In order to calculate solubilities of Pt and Pd metal as chloride complexes, it also is necessary to obtain log *K* at various temperatures for the reaction

$$M(s) + 2H^+(aq) + 1/2O_2(g) = M^{2+}(aq) + 2H_2O(l) \quad (7)$$

where *M* represents either Pt or Pd. Mountain & Wood (1988a) used thermodynamic data from Barner & Scheuerman (1978) to calculate the equilibrium constant

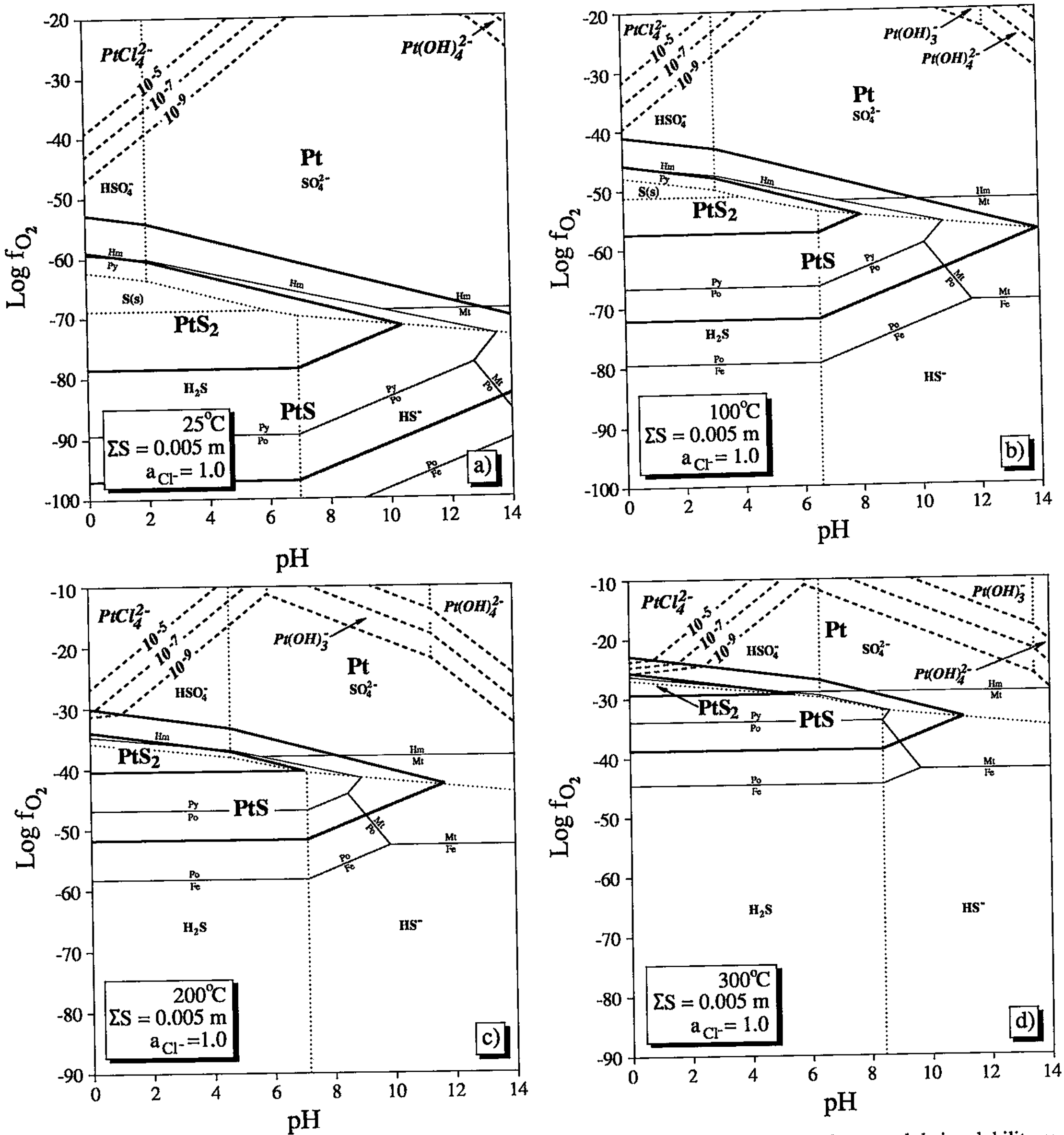

FIG. 6. Log $f(O_2)$ – pH diagrams for the system Pt–H–O–S–Cl showing the stability of various Pt phases and their solubility as chloride and hydroxide complexes. The stability fields of Fe minerals are shown for reference. The heavy and light solid lines separate fields of stability of solid Pt and Fe phases respectively. The thin dotted lines separate fields of predominance of aqueous S species at $\Sigma S = 0.005$ molal. The dashed lines represent activity contours (molal units) for the predominant chloride ($a_{Cl^-} = 1.0$ molal) and hydroxide complexes of Pt under the given conditions. a) 25°C, b) 100°C, c) 200°C, d) 300°C. Note that even at the highest temperature the Pt chloride solubility contours do not impinge significantly onto the pyrite stability field, *i.e.*, significant solubility of Pt as chloride complexes is restricted to acidic and oxidizing conditions in the upper left-hand corner of the diagram.

for reaction (7). The Gibbs free energies of aqueous Pt^{2+} and Pd^{2+} were calculated using entropies estimated from the relationship of Cobble (1953) and heat capacities estimated from the correspondence principle (Criss & Cobble 1964). Mountain & Wood (1988a) found log *K* for both these reactions to decrease strongly as a function of temperature. The correspondence principle applies strictly only to temperatures up to 200°C (Cobble *et al.* 1982, and see below), and as a result there could be significant error in the Mountain & Wood (1988a)

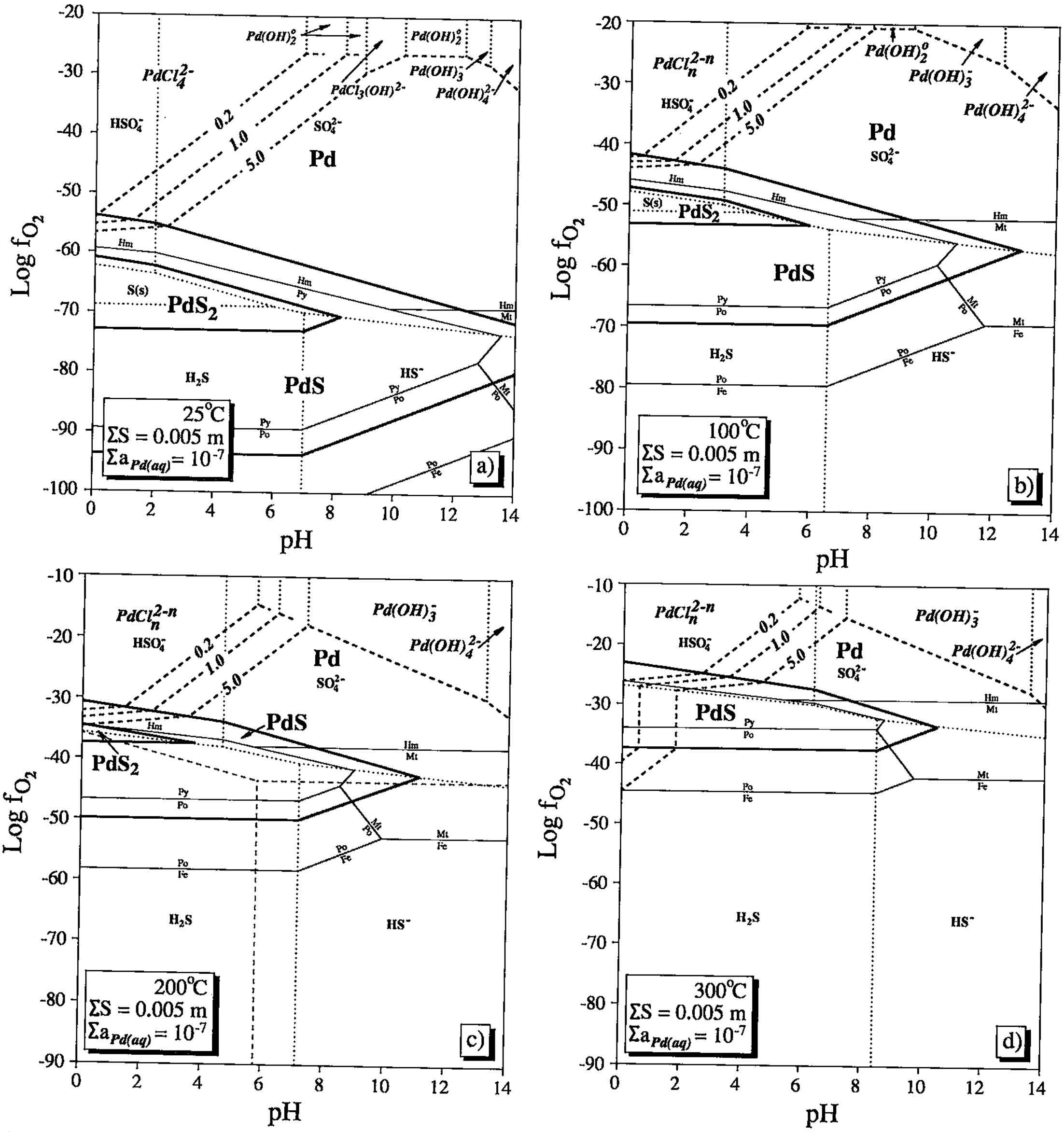

FIG. 7. Log $f(O_2)$ – pH diagrams for the system Pd–H–O–S–Cl showing the stability of various Pd phases and their solubility as chloride and hydroxide complexes. The stability fields of Fe minerals are shown for reference. The heavy and light solid lines separate fields of stability of solid Pd and Fe phases respectively. Note that for simplicity, other phases such as Pd_4S, Pd_3S and $Pd_{16}S_7$ known to exist in the Pd–S system (Taylor 1985) have not been included in these diagrams. The omission of these phases has little impact on the conclusions regarding Pd solubility and transport reported in the text. The thin dotted lines separate fields of predominance of aqueous S species at $\Sigma S = 0.005$ molal. The dashed lines represent the locations of the $\Sigma a_{Pd} = 10^{-7}$ molal contours for the predominant chloride and hydroxide complexes of Pd at three activities of chloride (0.2, 1.0 and 5.0 molal) and the following temperatures. a) 25°C, b) 100°C, c) 200°C, and d) 300°C. In b), c) and d) the Pd–chloride species, designated as $PdCl_n^{2-n}$, n varies depending upon conditions. At 100°–200°C and $a_{Cl^-} = 0.2$, and at 300°C and $a_{Cl^-} = 0.2$, 1.0, n is equal to 3. Under all other conditions n is equal to 4. Note that at 25°C, the mixed chloride–hydroxide complex of Pd has a predominance field on these diagrams only at $a_{Cl^-} = 5.0$ molal. Predominance fields for these complexes also may exist at the higher temperatures, but they are not included for lack of data.

estimated log K for reaction (7) at 300°C. Recent advances in theoretical aqueous geochemistry by Tanger & Helgeson (1988) and Shock & Helgeson (1988) have led to an equation of state based on the Born equation, which allows relatively accurate predictions of the free energy of simple aqueous ions at elevated temperatures and pressures. The free energies of Pt^{2+} and Pd^{2+} were calculated at saturated water vapor pressure and temperatures from 25 to 350°C using the data and equations contained in Shock & Helgeson (1988). These were combined with the free energy data for water given by Helgeson & Kirkham (1974) to calculate the log K values for reaction (7) up to 300°C. These values are tabulated in Table 4 and are illustrated as a function of temperature in Figure 5. The new log K estimates are very similar to those presented by Mountain & Wood (1988a) (compare Fig. 5 with their Fig. 1). The excellent agreement between the values of log K of reaction (7) calculated using these two independent methods supports the validity of the estimates of log K.

Figures 6 and 7 consist of log $f(O_2)$ – pH diagrams depicting the solubility of Pt and Pd as chloride complexes. At all temperatures, the solubilities of both Pt and Pd chloride complexes calculated in the present study are approximately equal to or slightly less than those predicted by Mountain & Wood (1988a), in spite of slight differences in the predicted speciation between the two models. Accurate experimental data on enthalpy and entropy will allow further improvement of the estimates of the stability of the Pt chloride complexes, but we believe that our estimated stability-constants for both Pt and Pd chloride complexes result in solubilities that are in error by no more than 1–2 log units at the highest temperature (300°C). This belief is supported by the agreement between our predictions and the experiments of Kovalenko *et al.* (1985) and Tait *et al.* (1991). The solubilities of Pt as $PtCl_4^{2-}$ calculated independently by Jaireth (1988) from 25° to 200°C using the Criss and Cobble correspondence principle agree quite closely (±1 to 2 log units) with our predicted solubilities over the same range. Furthermore, the recently measured solubilities of Gammons & Bloom (1990) are in excellent agreement with our estimates at 300°C. It is difficult to compare our theoretical estimates of Pd solubility in chloride solutions with those of Sassani & Shock (1990) because the latter authors give only predicted solubilities at 400°C and above. As noted previously, the details of Pd chloride speciation differ considerably between the two models, and the stability constants estimated by Sassani & Shock (1990) are one to two orders of magnitude greater than ours, but their model nevertheless yields conclusions with respect to the importance of chloride complexation of Pd at low temperature ($\leq$ 300°C) similar to ours.

It is thus important to emphasize that, according to three independent theoretical investigations (Jaireth 1988, Sassani & Shock 1990, and the present study) and recent well-constrained experimental measurements (Gammons & Bloom 1990, Tait *et al.* 1991), significant transport (*i.e.*, ppb quantities) of Pt and Pd as chloride complexes at temperatures less than or equal to 300°C is possible only in acidic, oxidizing and highly saline hydrothermal solutions. Our predictions and the experimental data of Gammons & Bloom (1990) suggest that even at salinities of 5.0 molal NaCl, much less than 1 ppb Pt or Pd can be transported as chloride complexes in the stability fields of pyrite or pyrrhotite (or at the sulfate–sulfide boundary) at a geologically reasonable pH. Nyman *et al.* (1990) have recently suggested that Pt and Pd were transported as chloride complexes during the formation of the New Rambler deposit in Wyoming, based on the identification of highly saline fluid inclusions in quartz. However, the hypogene PGE mineralization at New Rambler was probably coprecipitated with pyrrhotite and pyrite near 300°C (McCallum *et al.* 1976), which thus appears to preclude PGE transport as chloride complexes in spite of the presence of high-salinity fluids (although subsequent supergene transport as chloride complexes is not ruled out). Likewise, chloride complexes cannot be responsible for the accumulation of Pt and Pd measured by Crocket (1990) in seafloor massive sulfides, which were probably formed at conditions near the pyrite–pyrrhotite–magnetite triple point (*cf.* Bowers *et al.* 1985). Conditions sufficiently oxidizing and acidic to allow Pt and Pd transport as chloride complexes may occur during the formation of sediment-hosted stratiform copper deposits, unconformity-type uranium deposits and possibly the higher-temperature porphyry copper deposits. Under reducing conditions (pyrite to pyrrhotite stability field or sulfate–sulfide boundary) and at slightly acidic to basic pH, other types of complexes must be responsible for Pt and Pd transport. It should be noted that the experimental results of Orlova *et al.* (1987) and Hsu *et al.* (1991) would seem to contradict the above conclusions. However, these studies were not well constrained with respect to pH, oxygen fugacity, and activity of free chloride, and cannot be considered definitive (Wood & Mountain 1991).

Speciation of Pt and Pd in the Salton Sea brines

Recent measurements of the Pt and Pd content of the hypersaline Salton Sea brines yield values of <0.005 to 0.5 ppb and 0.02 to 2.0 ppb, respectively, at an inferred pH of 5.4 (muscovite + quartz + K-feldspar equilibrium) and log $f(O_2)$ of –30 (sulfate–sulfide boundary) at 300°C (McKibben *et al.* 1990). Because of the high salinities involved, these authors made the assumption that the chloride complexes $PtCl_4^{2-}$ and $PdCl_4^{2-}$ were the metal-transporting species, and attempted to constrain Pt and Pd solubilities as chloride complexes using their analytical data. Comparing their maximum measured Pt and Pd contents with the concentrations of $PtCl_4^{2-}$ and $PdCl_4^{2-}$ calculated from the estimated thermodynamic data given by Mountain & Wood (1988a), McKibben *et al.* (1990) concluded that these data underestimate the solubilities of Pt and Pd by up to 6 and 4 orders of magnitude, respectively. However, as demonstrated in the previous section, it now appears highly unlikely that the true solubilities of Pt and Pd as chloride complexes at 300°C are 4 to 6 orders of magnitude higher than the estimates of Mountain & Wood (1988a), especially in light of the experimental verification of the calculated solubilities (Gammons & Bloom 1990). Therefore, we strongly believe that alternative explanations must be sought for the Pt and Pd content measured in the Salton Sea.

The assumption of McKibben *et al.* (1990) that the species $PtCl_4^{2-}$ and $PdCl_4^{2-}$ are solely responsible for Pt and Pd contents in the Salton Sea is considered open to question; it is possible that complexes such as mixed chloride–hydroxide, mixed chloride–ammonia, organic or others, for which there are presently few or no thermodynamic data, may contribute substantially to the total measured solubility. Although mixed hydroxide–chloride complexes do not appear to be important at 25°C and 1 bar (Mountain & Wood 1988a, Tait *et al.* 1991), it is possible that they become more stable at higher temperatures and could be responsible for the observed Pt concentrations (the measured pH of the Salton Sea brines is approximately neutral at 300°C, so that mixed chloride–hydroxide complexes may be viable in spite of the high salinities involved).

Other species possibly responsible for the measured concentration of Pt and Pd in the Salton Sea include ammonia and bisulfide complexes. Both ammonia and bisulfide complexing may result in Pt and Pd solubilities at 300°C sufficiently high to explain the observed Pt and Pd concentrations (see below). McKibben *et al.* (1990) stated that neither bisulfide nor ammonia complexes can be responsible for the observed PGE concentrations because there is no apparent loss of these metals to down-hole scale upon flashing of the hydrothermal fluid, as is the case for Au (which clearly is transported as a bisulfide complex). However, this finding is not necessarily a valid argument against the involvement of volatile ligands such as ammonia or bisulfide. The point during boiling at which a metal, complexed by bisulfide or ammonia, precipitates depends on the stoichiometry of the precipitation reaction and the proximity of the fluid to saturation with respect to that metal prior to phase separation. The former factor is related to the nature of the mineral being precipitated and to the stoichiometry of the complex. If the degree of saturation with respect to possible Pt or Pd minerals is less than that of Au, or more likely, if the stoichiometries of the complexes are different, then it is possible for a solution to boil, destabilizing Au bisulfide or ammonia complexes and causing Au to precipitate, but leaving Pt and Pd complexes with these same types of ligands in solution. Only detailed modeling of the boiling process, employing well-established thermodynamic data, would lead to a definitive evaluation of this question. Finally, as McKibben *et al.* (1990) themselves pointed out, kinetic factors may play a key role in explaining their results. A considerable body of data in the literature suggests that reactions involving Pt and, to a lesser extent, Pd in aqueous solution are kinetically inhibited even at elevated temperatures (Grantham *et al.* 1955, Banerjea *et al.* 1957, Aprile & Martin 1962, Tucker *et al.* 1964, Nikolaeva *et al.* 1965, Langford & Gray 1966, Drougge *et al.* 1967, Kazakova & Ptitsyn 1967, Ginstrup & Leden 1967, Elding 1966, 1970a, b, c, 1978, Westland 1981, Elding & Gustafson 1971, Wu *et al.* 1990, Tait *et al.* 1991).

In summary, because of the inherent danger in assuming that metal contents in a complex natural fluid can be related to a specific complex, especially for metals such as Pt and Pd, for which very few experimental data obtained at high temperatures are available, the Salton Sea data cannot presently be used as a reliable constraint on the solubility of Pt and Pd as chloride complexes.

ROLE OF HYDROXIDE

The competition between hydroxide and chloride complexes of Pt and Pd at 25°C is illustrated in Figure 8. Stability constants for palladium hydroxide complexes used in the construction of this diagram come from Nabivanets & Kalabina (1970). These data are in relatively good agreement with those measured by Izatt *et al.* (1967b) for the first and second hydrolysis steps. Stability constants for Pt hydroxide complexes were estimated from linear free energy relationships (Wood *et al.* 1989) between Pt and Pd. It is apparent that the complexes $Pt(OH)_2^0$ and $Pd(OH)_2^0$ are the predominant hydroxide complexes over a wide range of pH at 25°C, and that hydroxide complexes can predominate over chloride complexes even at relatively low pH and high activities of chloride. Data for mixed hydroxide–chloride complexes come from Peshchevitskiy *et al.* (1962) and Kazakova & Ptitsyn (1967). It is evident (Fig. 8) that mixed chloride–hydroxide complexes with Pt and Pd have predominance fields at 25°C only at chloride activities greater than 10 and 1, respectively, and pH values greater than 10 and 9, respectively. Thus, these species are unlikely to be geologically important at low temperatures, a conclusion that has recently been reached for Pd on the basis of optical and Raman spectroscopic studies (Tait *et al.* 1991). Such species could, however, become important at higher temperatures.

In an attempt to corroborate some of the data used in constructing Figure 8, experiments have been conducted (Wood 1991) on the solubility of Pt and Pd metal in hydroxide solutions at 25°C. These studies indicate a change in predominant species from $Pd(OH)_2^0$ to $Pd(OH)_3^-$ at a pH near 12, which is in excellent agreement with the speciation illustrated in Figure 8b. Such a change in species also was expected for Pt, but was not observed. This suggests that the stability constants for $Pt(OH)_3^-$ and $Pt(OH)_4^{2-}$ estimated by Wood *et al.* (1989) may be in error and should be considered provisional at best. However, the experimental value of log β_2 given by Wood (1991) for the $Pt(OH)_2^0$ complex is in excellent agreement with the estimated value given by Wood *et al.* (1989). Further work on hydroxide complexing of Pt

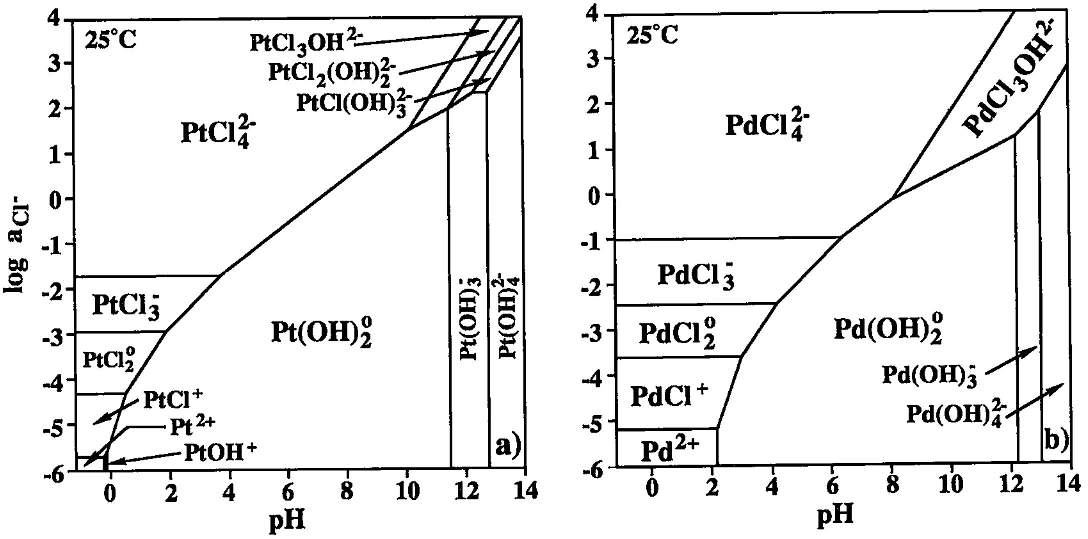

FIG. 8. Plot of log a_{Cl^-} *versus* pH for a) Pt and b) Pd at 25°C, showing the fields of predominance of the various chloride, hydroxide and mixed hydroxychloride complexes.

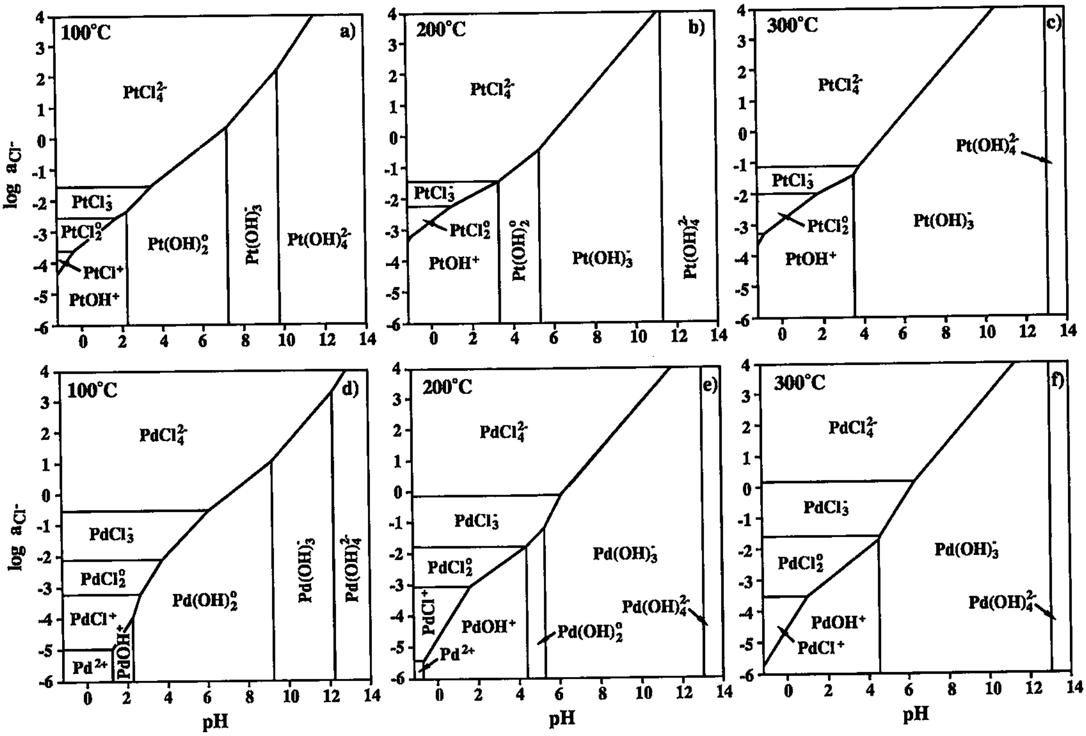

FIG. 9. Plot of log a_{Cl^-}–*versus* pH for Pt at a) 100°, b) 200°, and c) 300°C and for Pd at d) 100°, e) 200°, and f) 300°C, showing the fields of predominance of the various chloride and hydroxide complexes. Although mixed hydroxychloride complexes may well have predominance fields, they are not shown in these diagrams owing to a lack of data. Note the change in predominant hydroxide species under geologically realistic conditions of pH from the neutral $M(OH)_2^{\circ}$ to $M(OH)_3^-$ where *M* represents Pt or Pd.

and Pd at both 25°C and higher temperatures is in progress.

Stability constants for Pt and Pd hydroxide complexes were extrapolated to 300°C by Wood *et al.* (1989) (their Table 2) using a combination of the isocoulombic and correspondence principles. The latter authors also showed that $Pt(OH)_3^-$ and $Pd(OH)_3^-$ become increasingly important as temperature rises. Predominance diagrams for chloride *versus* hydroxide complexing at elevated temperatures are given in Figure 9. Note that these diagrams neglect the possibility of mixed chloride–hydroxide complexes at higher temperatures for lack of data.

Combining the hydroxide stability constants of Wood *et al.* (1989) with the equilibrium constants for reaction (7) estimated in this study, the solubility of Pt and Pd as hydroxide complexes can be calculated at temperatures up to 300°C. Solubility contours for hydroxide complexes are shown in Figures 6 and 7. The calculated solubilities are similar to those given by Wood *et al.* (1989), but considerably lower than those given by Mountain & Wood (1988a). Wood *et al.* (1989) concluded that hydroxide complexes of Pt and Pd are probably not important in most hydrothermal ore-forming solutions. However, hydrothermal transport of the PGE as hydroxide complexes may be possible during the serpentinization of ultramafic rocks. Fluids in equilibrium with ultramafic rocks during serpentinization can be quite basic. For example, fluids thought to be responsible for present-day serpentinization have a measured pH in the range 10–12 at low temperature (Barnes *et al.* 1967, 1972, Barnes & O'Neil 1969). Furthermore, Janecky & Seyfried (1986) have shown experimentally that under certain conditions, hydrothermal fluids with chemistries related to seawater can evolve toward high-temperature pH values up to 2 units more basic than neutral upon interaction with harzburgite or lherzolite. However, it is doubtful whether the highly oxidizing conditions necessary to transport Pt and Pd as hydroxide complexes are attained in such environments. On the other hand, reducing and alkaline serpentinizing fluids should be capable of PGE transport as bisulfide complexes (see below).

An environment in which hydroxide complexes are more likely to be responsible for Pt and Pd speciation is in surface waters such as lakes, rivers and surface seawater. Figure 10 shows an Eh–pH diagram for Pd at 25°C and 1 bar for a chloride activity equal to that of seawater. It is apparent that the expected predominant species in seawater at pH 8 and higher will be the hydroxide complex. This possibility also was raised by Tait *et al.* (1991). However, the hydroxide–chloride boundary occurs quite close to pH 8, and recent direct spectroscopic measurements by Kump & Byrne (1989) on Pd speciation in seawater lead to the conclusion that chloride complexes should predominate in seawater, with a lesser contribution from hydroxide complexes. Kump & Byrne (1989) did not state how long they waited for Pd to come to equilibrium with seawater, and the work of Tait *et al.* (1991) and Kazakova & Ptitsyn (1967) suggest that equilibrium during the hydrolysis of $PdCl_4^{2-}$ is not completely attained even after a few days. Thus, there is still some uncertainty as to the exact speciation of Pd in seawater. Nevertheless, it does appear that a significant fraction of Pd may be present as hydroxide complexes. Although the data are less complete for Pt, it appears that this metal is even more likely than Pd to be present in seawater mainly as a hydroxide complex (Wood 1991).

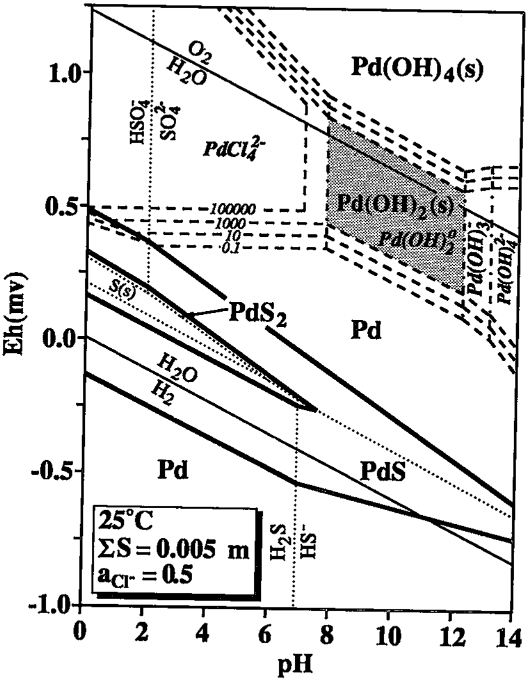

FIG. 10. Eh *versus* pH diagrams for the system Pd–O–H–Cl–S at 25°C, 1 bar, $\Sigma S = 5 \times 10^{-3}$ molal, and $a_{Cl^-} = 0.5$, showing the stability and solubility of phases. Bisulfide complexes have been omitted for clarity, but these would occur in the lower half of the diagram near the H_2S–HS^-–SO_4^{2-} triple point. Light solid lines denote the limits of stability of water with respect to oxidation and reduction. The heavy solid lines separate fields of stability of solid Pd phases, and the dotted lines separate fields of predominance of dissolved aqueous S species. The dot–dashed lines represent boundaries between fields of predominance of dissolved Pd species, and the dashed lines are solubility contours labeled in ng/L (ppb). In the shaded field, the solubility of $Pd(OH)_2(s)$ is constant at 1000 ng/L, and the predominant dissolved species is the $Pd(OH)_2^0$ (aq) complex. Note that in surface seawater (pH=8), the hydroxide complexes of Pd are predicted to be slightly predominant over the chloride complexes.

In the case of fresh surface waters, where chloride concentrations are generally less than 100 ppm, hydroxide complexes should dominate the inorganic speciation to even more acidic pH values. Wood & Vlassopoulos (1990) have measured Pt and Pd contents in lake and groundwaters adjacent to two Cu–Ni–Pt–Pd prospects in the Grenville Province of Quebec. They showed that in some cases, the measured Pd contents (0.1 to 0.4 ppb) are in close agreement with the solubility of Pd calculated assuming hydroxide complexing at the measured Eh and pH of the waters. In other cases, however, the measured Pd contents were found to exceed those attributable to hydroxide complexes. In these cases, it was postulated that organic complexes may be responsible for the measured Pt and Pd contents.

Recent determinations of the solubility of gold in hydroxide solutions (Vlassopoulos & Wood 1990) indicate that a hydroxide complex, AuOH°, should also dominate the inorganic speciation of Au in oxidized seawater and freshwater. Thus, in the surficial environment it is most likely that the dominant inorganic species for all three precious metals (Pt, Pd and Au) are the neutral hydroxide complexes.

ROLE OF AMMONIA

Stability constants for Pt and Pd ammonia complexes were estimated to 300°C by Wood *et al.* (1989) using the data at 25°C of Rasmussen & Jorgenson (1968) and Grinberg & Gel'fman (1961) and a combination of the isocoulombic and correspondence principles. A similar procedure, starting with the 25°C data of Skibsted & Bjerrum (1974), was employed in the present study to extrapolate the stability constants for Au ammonia complexes up to 300°C (Table 5). These data were combined with log *K* values (Tables 4 and 6) calculated using the equation of state of Tanger & Helgeson (1988) for reactions (7) and (8)

$$Au + H^+ + 1/4O_2 = Au^+ + 1/2H_2O(l) \qquad (8)$$

to calculate the solubilities of Pt, Pd and Au as ammonia complexes. The results of these calculations are shown in Figures 11, 12 and 13. The predominant complexes at the activities of ammonia chosen (and in fact at all geologically reasonable activities of ammonia) are $Pt(NH_3)_4^{2+}$, $Pd(NH_3)_4^{2+}$ and $Au(NH_3)_2^+$. The newly calculated solubilities of Pt and Pd as ammonia complexes at 300°C are approximately the same as those obtained by Wood *et al.* (1989) (note that Pt solubilities as ammonia complexes were incorrectly plotted in Fig. 7a of Wood *et al.* 1989), with Pd being several orders of magnitude more soluble than Pt. These calculations indicate an excellent potential for the transport of Pd as ammonia complexes at elevated temperatures (Fig. 13), but this possibility appears less likely for Pt [in qualitative agreement with the calculations by Jaireth (1988) who only dealt with Pt]. The calculated solubilities also are quite high for Au at 300°C (Fig. 11). Note that the maximum in solubility for all three metals occurs at the NH_3–NH_4^+–N_2 triple point (Wood *et al.* 1989). Because this triple point moves toward lower pH and higher oxygen fugacity with temperature, the solubility of the metals as ammonia complexes increases dramatically with temperature, even though the stability constants themselves are not strong functions of temperature in the case of Pt and Pd, and decrease with temperature in the case of Au. The diagrams (Figs. 11–13) were calculated assuming that the kinetics of the oxidation of ammonia to nitrogen are rapid even at low temperature. As discussed by Wood *et al.* (1989), ammonia may persist metastably outside of its field of thermodynamic stability, which would increase its importance as a potential ligand for Pt, Pd and Au. However, Lechler & Hsu (1990) have recently presented evidence that Pt and, to a lesser extent, Pd, catalyze the oxidation of ammonia in the surficial environment. In any event, the results of the calculations presented in this section clearly indicate the importance of experimental and field studies of the viability of ammonia as a ligand for these metals.

TABLE 5. CUMULATIVE STABILITY CONSTANTS FOR THE $Au(NH_3)_2^+$ COMPLEX

t(°C)	log β_2
25	26.5
50	25.7
100	24.4
200	22.5
300	21.0

TABLE 6. LOG K FOR THE REACTION: $Au + H^+ + 1/4O_2 = Au^+ + 1/2H_2O(l)$ AT ELEVATED TEMPERATURE

t(°C)	log K
25	-7.8
50	-7.1
100	-5.8
200	-4.1
300	-3.0

Another intriguing possibility for Pt, Pd and Au transport is mixed chloride–ammonia complexation. Figure 14 is a log $a(NH_3)$ *versus* log $a(Cl^-)$ diagram at 25°C depicting the fields of predominance of chloride, ammonia and mixed complexes of palladium (stability data for mixed chloride–ammonia complexes with Pd come from Reinhardt *et al.* 1967). Mixed chloride–ammonia complexes of Pt also are known to exist at 25°C (Aprile & Martin 1962, Tucker *et al.* 1964). Figure 14 illustrates that important fields exist for a variety of mixed chloride–ammonia complexes of Pd and that these fields occur in geologically reasonable ranges of activity. We have not attempted to extrapolate the stability constants of the mixed complexes to elevated

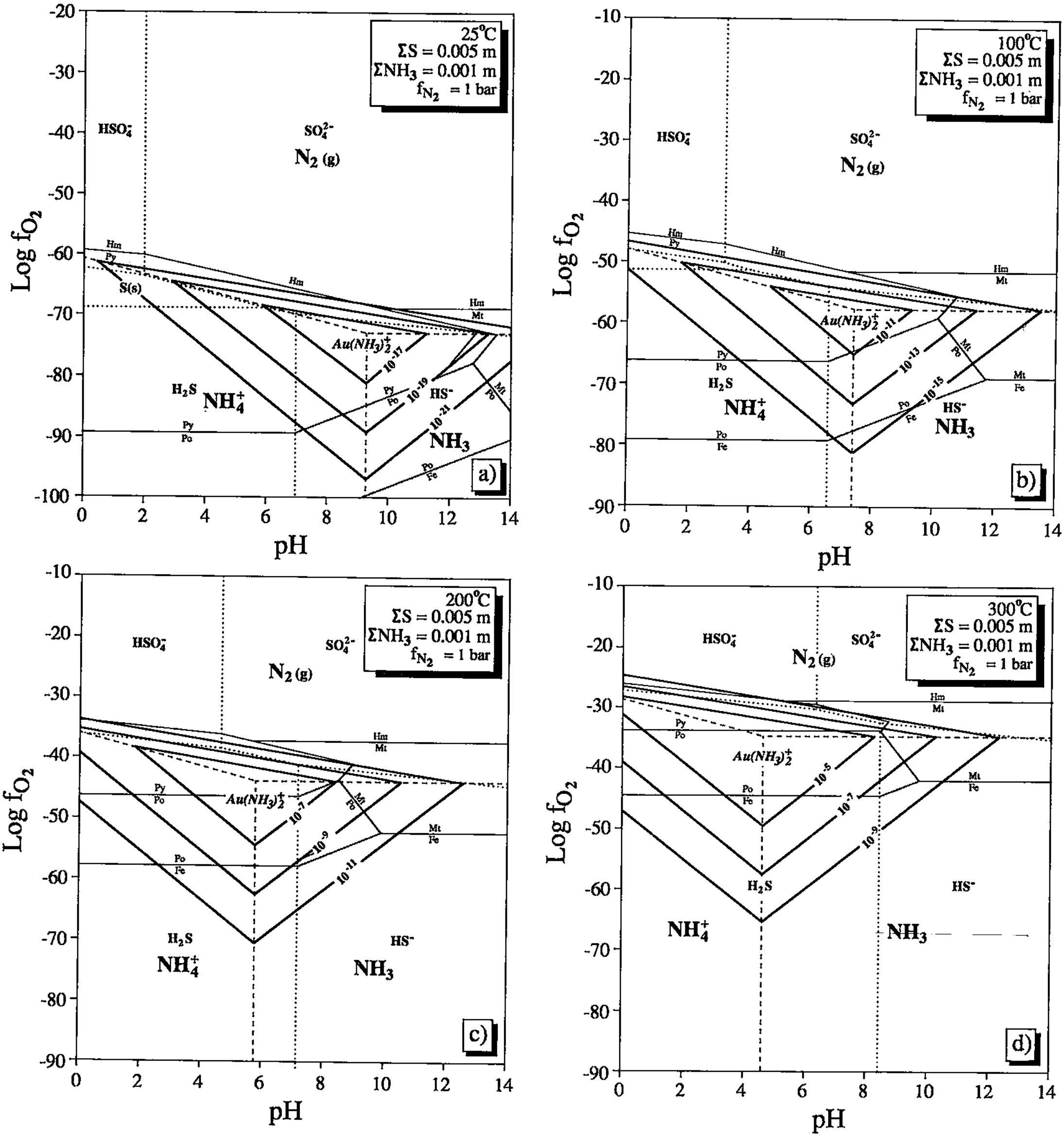

FIG. 11. Log $f(O_2)$ – pH diagrams for the system Au–H–O–N–S showing the solubility of Au as ammonia complexes. Bisulfide complexes have been omitted for clarity; these would occupy more or less the same region of the diagram as the ammonia complexes. Light solid lines separate fields of stability of solid Fe phases. The dotted and dashed lines separate fields of predominance of aqueous S species at $\Sigma S = 0.005$ molal, and aqueous N species at $\Sigma NH_3 = 0.001$ molal and $f(N_2) = 1$ bar, respectively. The heavy solid lines represent activity contours (log molal units) for the $Au(NH_3)_2^+$ complex at the following temperatures. a) 25°, b) 100°, c) 200°, and d) 300°C. Note the dramatic increase in solubility predicted as temperature increases.

temperatures, but there is no reason to believe that they will not persist.

It should be noted that Jaireth (1988) carried out theoretical calculations of the solubility of Pt as ammonia and mixed ammonia–chloride solutions using the correspondence principle. His calculated Pt solubilities as ammonia complexes are in more or less close agreement with ours at 25°–100°C, but we have calculated a somewhat steeper temperature-dependence above 100°C. Although Jaireth (1988) did not calculate solubilities at 300°C, his calculations at 200°C also suggest that ammonia and mixed–ammonia complexes are probably not important in the transport of Pt in hydrothermal solutions.

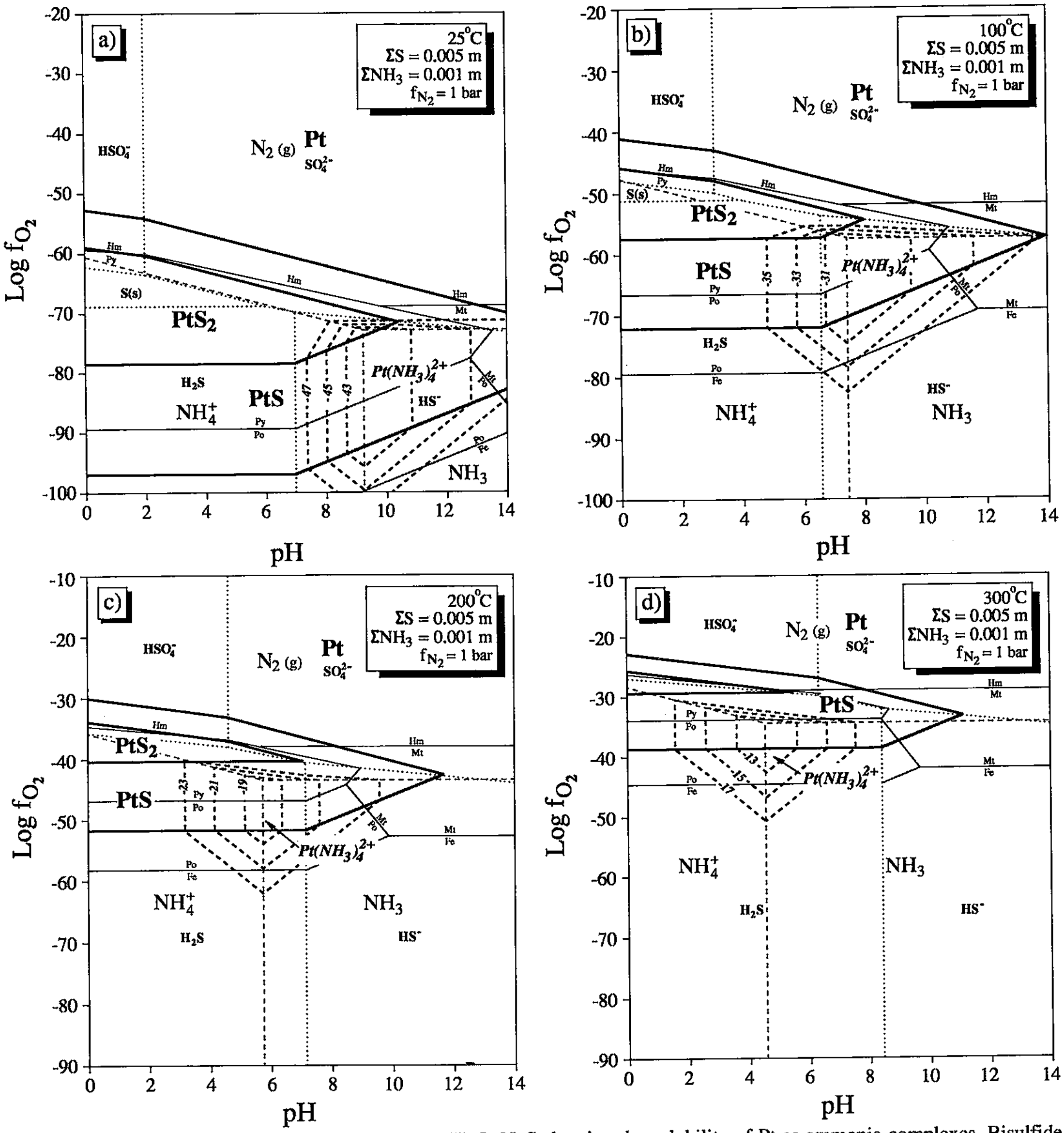

FIG. 12. Log $f(O_2)$ – pH diagrams for the system Pt–H–O–N–S showing the solubility of Pt as ammonia complexes. Bisulfide complexes have been omitted for clarity; these would occupy more or less the same region of the diagram as the ammonia complexes. Light solid lines separate fields of stability of solid Fe phases. The dotted and light dashed lines separate fields of predominance of aqueous S species at $\Sigma S = 0.005$ molal, and aqueous N species at $\Sigma NH_3 = 0.001$ molal and $f(N_2) = 1$ bar, respectively. The heavy dashed lines represent activity contours (log molal units) for the $Pt(NH_3)_4^{2+}$ complex at the following temperatures. a) 25°, b) 100°, c) 200°, and d) 300°C. Note the dramatic increase in solubility predicted as temperature increases.

Role of Bisulfide

Experimental studies

Mountain & Wood (1988a) first suggested that bisulfide complexes might play an important role in the aqueous transport of Pt and Pd, in analogy with Au. Thermodynamic data estimated by Mountain & Wood (1988a) and Wood *et al.* (1989) suggest that significant (>10 ppb) solubilities of Pt and Pd as bisulfide complexes could be attained in hydrothermal solutions at 300°C at log $f(O_2)$–pH–ΣS conditions near the pyrite –

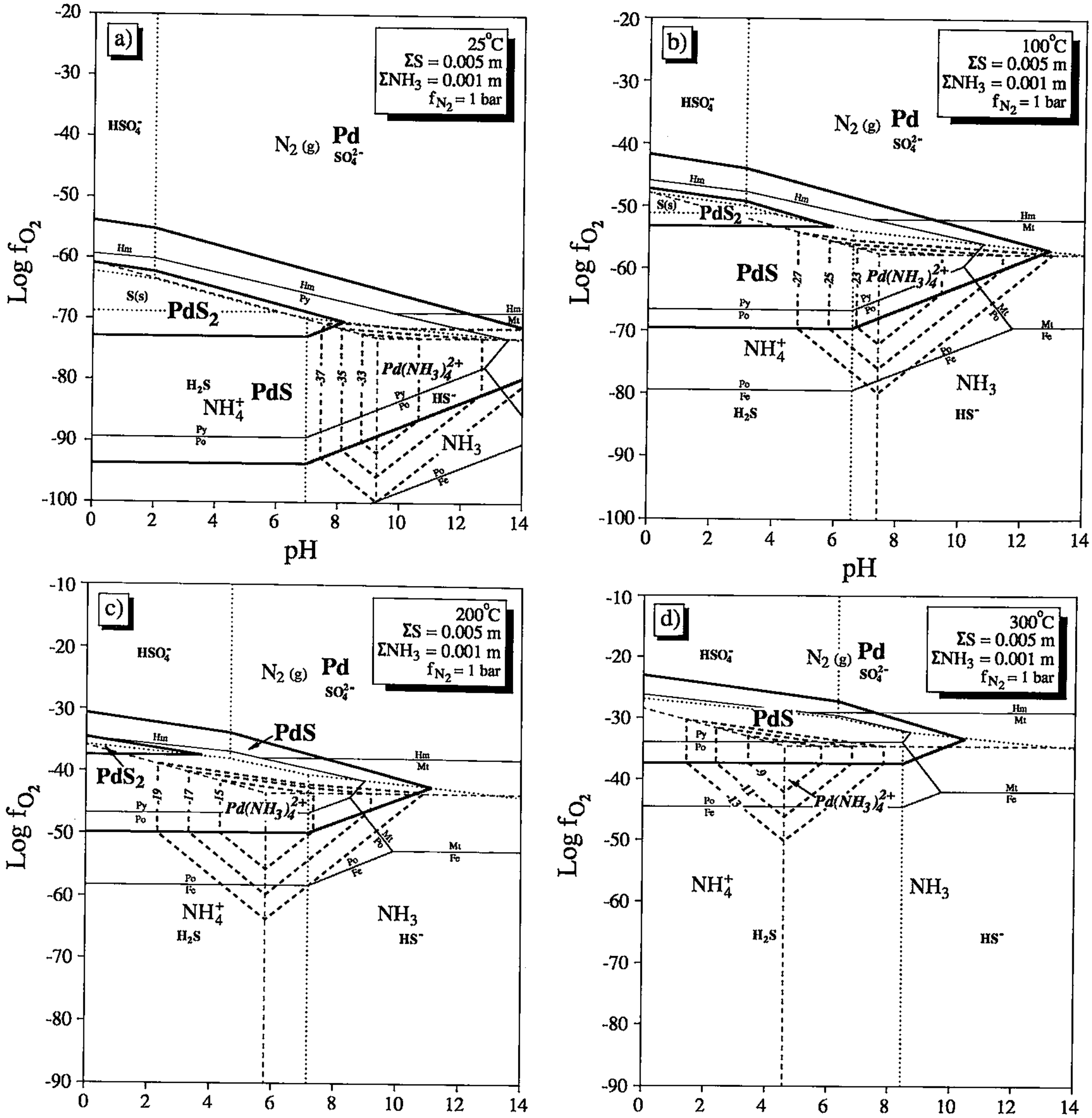

FIG. 13. Log $f(O_2)$ – pH diagrams for the system Pd–H–O–N–S showing the solubility of Pd as ammonia complexes. Bisulfide complexes have been omitted for clarity; these would occupy more or less the same region of the diagram as the ammonia complexes. Light solid lines separate fields of stability of solid Fe phases. The dotted and light dashed lines separate fields of predominance of aqueous S species at $\Sigma S = 0.005$ molal, and aqueous N species at $\Sigma NH_3 = 0.001$ molal and $f(N_2) = 1$ bar, respectively. The heavy dashed lines represent activity contours (log molal units) for the $Pd(NH_3)_4^{2+}$ complex at the following temperatures. a) 25°, b) 100°, c) 200°, and d) 300°C. Note the dramatic increase in solubility predicted as temperature increases.

pyrrhotite – magnetite triple point. These calculations provided the stimulus for experimental determinations of solubility, which are currently in progress. Preliminary results of these studies are reported here (complete details of individual experiments to date are available from the senior author in the form of unpublished reports). More detailed description and discussion of the results will be published elsewhere.

The experiments consisted of equilibrating PtS_2 or PtS, PdS and Au powder with solutions containing H_2S,

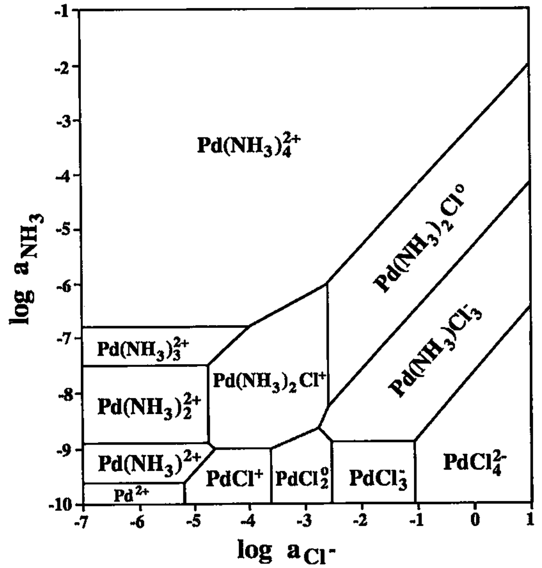

FIG. 14. Plot of log a_{NH_3} *versus* log a_{Cl^-} for Pd at 25°C, illustrating the fields of predominance of the various ammonia, chloride and mixed chloride–ammonia complexes. It is evident that there is a significant region where mixed chloride–ammonia complexes predominate. This region occurs at low a_{NH_3} but relatively high a_{Cl^-}.

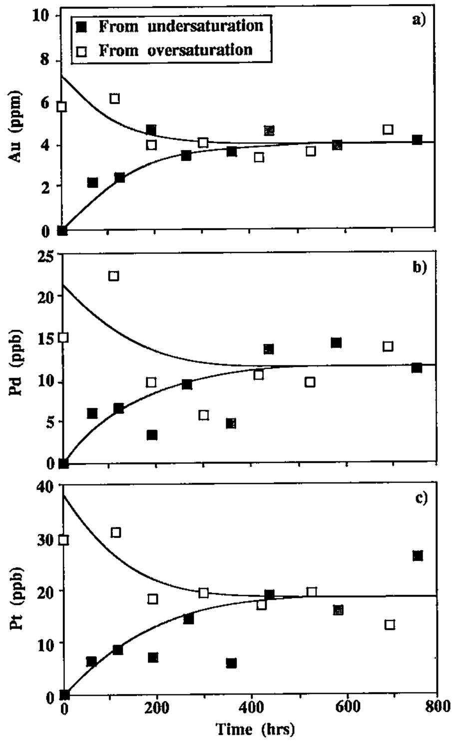

FIG. 15. Plots of a) Au, b) Pd, and c) Pt concentrations in hydrothermal bisulfide solutions at 200°C as a function of time. The experiments consisted of allowing Au metal, PtS_2 and PdS to react with a solution containing H_2S, HS^- and SO_4^{2-} (as a pH and oxygen fugacity buffer). Supersaturation was induced by holding the experiment at 300°C for 2 weeks and then lowering the temperature to 200°C. The approach from undersaturation started essentially at 25°C. The total dissolved sulfide in these runs was nominally 0.5 molal, and the pH at temperature was approximately 8. Note that equilibrium appears to have been attained after 400 hours for all metals, with the solubilities in the order Au > Pt > Pd.

NaHS and Na_2SO_4 at 200–500°C in a gold-lined, titanium autoclave. The coexistence of H_2S, HS^- and SO_4^{2-} allowed the calculation and control of both pH and $f(O_2)$. Calculated pH at elevated temperature ranged from 5.91 to 9.43, and total sulfur was varied from 0.3 to 2.2 molal (approximately 35 separate experiments have been carried out so far). A magnetic stirrer agitated the reaction mixture during the run. Solutions were sampled at temperature through a titanium sampling tube fitted with a 0.5-μm titanium frit on the high-temperature end. Upon each sampling, several aliquots of the fluid were analyzed by Zeeman graphite-furnace atomic absorption spectrophotometry for Pt and Pd, and by flame atomic absorption spectrophotometry for Au after oxidation of sulfide by addition of H_2O_2 and coprecipitation of the precious metals with tellurium (Fryer & Kerrich 1978) to reduce matrix effects. The analytical precision for all metal was about ±10%, and the limits of detection were 0.5, 1, and 5 ppb, respectively, for Au, Pd and Pt. A second aliquot was analyzed for sulfide by iodometric titration, and a third aliquot was analyzed for total sulfur by oxidizing sulfide to sulfate, precipitating the sulfate with barium acetate, and then weighing the resultant $BaSO_4$. Equilibrium was generally attained within 400 hours, as evidenced by approach from undersaturation (increasing temperature) and oversaturation (decreasing temperature) (Fig. 15). Solid phases were analyzed optically and by X-ray diffraction and SEM energy-dispersion analysis both before and after each run. No change in the number or composition of the phases was detected during any of the runs.

At present, the solubility data are insufficient to allow inferences to be made with confidence as to the Pt and Pd species present. However, the data do permit some preliminary conclusions. In all runs to date, the concentrations of the precious metals follow the order Au >> Pt > Pd, except in some low total sulfur runs, where Pd ≥ Pt. Evaluation of the significance of the relative order of Pt and Pd solubilities is complicated by the fact that two different types of starting solids, PtS_2 *versus* PdS, were employed in some runs. Nevertheless, the observed order Pt > Pd in most runs, including those where the platinum sulfide was PtS, is in agreement with that predicted theoretically by Wood *et al.* (1989). The ranges in metal concentrations observed are Au (2–300 ppm), Pt (4–800 ppb) and Pd (1–600 ppb). Our measured solubilities of Pt and Pd in hydrothermal bisulfide solutions appear to be of the same order of magnitude as the results of another independent study in progress (Gammons, pers. comm., 1991), but a detailed comparison of the two studies is not yet possible. The solubilities measured above 350°C are generally much lower than those below 350°C, a finding consistent with the predictions of the behavior of bisulfide complexes in general outlined by Crerar & Barnes (1976). The solubilities of Pt and Pd in these bisulfide solutions appear to maximize near neutral pH, as has long been known to be the case for Au (Seward 1973), and as predicted by Mountain & Wood (1988a).

In order to check the validity of our solubility measurements, we can compare our results for Au with the recent work of Shenberger & Barnes (1989). Assuming that the species $Au(HS)_2^-$ is predominant under the present experimental conditions (see, for example, Seward 1973, Shenberger & Barnes 1989), we can calculate the equilibrium constant for the reaction

$$Au + H_2S(aq) + HS^- = Au(HS)_2^- + 1/2H_2(g) \qquad (9)$$

from our data. The values of log K so derived are compared to those of Shenberger & Barnes (1989) in Table 7. Evidently, the agreement between the two data sets is remarkable, a finding that lends credence to our experimental solubility values for Pt and Pd as well.

Although no definitive statement as to the speciation of Pt and Pd in these experiments can yet be made, it appears that the predicted Pt and Pd solubilities as bisulfide complexes of Wood *et al.* (1989) are considerably overestimated. Because of the large magnitude of the stability constants involved, even small imperfections in the linear free energy relationships used to estimate the stability constants of Pt and Pd bisulfides at room temperature can lead to significant absolute errors in the estimated constants, especially when these are extrapolated to higher temperatures. Thus, because even the 25°C thermodynamic data for the bisulfide constants had to be estimated, it is not surprising that the agreement between theory and experiment is not good in this case.

TABLE 7. COMPARISON OF EXPERIMENTALLY MEASURED LOG K VALUES FOR THE REACTION: $Au + H_2S(aq) + HS^- = Au(HS)_2^- + 1/2H_2(g)$ AT ELEVATED TEMPERATURE

t(°C)	log K[1]	log K[2]
200	-1.89	-1.89±0.01(2)
300	-1.35	-1.37±0.16(4)

[1]Shenberger & Barnes (1989); [2]This study. Mean given with one standard deviation. Number of measurements in parentheses.

The complete significance of the experimentally measured solubilities to the capacity of the bisulfide ligand to transport Pt and Pd in nature can only be assessed once the nature of the solution species is known, because the relatively high concentrations of reduced sulfur in the experiments are not common in nature. However, the experiments described above do suggest that at least a few ppb of Pt and Pd may be transported in hydrothermal solution as bisulfide complexes at geologically more reasonable concentrations of total reduced sulfur (10^{-3} to 10^{-1} molal) at temperatures 200–350°C and at near neutral pH. These experimental results, combined with those of Gammons & Bloom (1990) for chloride solutions and our theoretical predictions for Pt and Pd chloride complexes, also clearly demonstrate that from 200 to 350°C under moderately to strongly reducing conditions, with a pH within 1–2 units of neutral, bisulfide complexes are far more likely to result in significant hydrothermal transport of Pt and Pd than chloride complexes. Such conditions prevail in the Salton Sea, during the formation of seafloor massive sulfides, the formation of deposits of the New Rambler type, and active serpentinization. On the other hand, the solubility of Au as a bisulfide complex is at least an order of magnitude (and as much as three orders of magntitude) higher than that of either Pt or Pd under the same conditions over the entire range of pH, total reduced sulfur and temperature studied here. This finding may place some important constraints on models of Pt and Pd mobilization, because in many cases in which hydrothermal transport of Pt and Pd as a bisulfide complex is suspected, Au also is concentrated to similar or higher levels, *e.g.*, the Salton Sea (McKibben *et al.* 1990), Rathbun Lake (Rowell & Edgar 1986), and New Rambler (McCallum *et al.* 1976). However, the converse does not appear to be true, inasmuch as Pt and Pd are not generally found to be especially enriched in most epithermal and mesothermal (Archean lode) gold deposits; this is consistent with a generally higher solubility of Au as the bisulfide. The findings of Crocket (1990), who demonstrated that, in seafloor hydrothermal mineralization from the Juan de Fuca and Mid-Atlantic ridges, Au is orders of magnitude more concentrated than Pd, are consistent with a fractionation of the two metals due to the higher solubility of Au relative to Pd as bisulfide complexes. Part of the explanation for varying ratios of Au, Pt and Pd in different environments may be related to relative concentrations of these metals at their source. Nevertheless, it is now apparent from experimental data that the relative solubilities of these metals also may play a key role.

TABLE 8. COMPARISON OF STABILITY CONSTANTS FOR THE $Au(HS)_2^-$ COMPLEX

t(°)	$\log \beta_2$[1]	$\log \beta_2$[2]	$\log \beta_2$[3]
25	30.1	----	----
100	----	----	24.2
200	21.0	21.1	19.8
250	20.0	19.5	18.7
300	18.9	----	17.5

[1]Derived from experimental data (Renders & Seward 1989, Shenberger & Barnes 1989). See text for details; [2]Derived experimentally by Seward (1973); [3]Theoretically estimated (this study). See text for details.

It has been suggested that the presence of Pt and Pd intermetallic compounds (bismuthinides, tellurides, arsenides) in preference to Pt and Pd sulfides is evidence against Pt and Pd transport as bisulfide complexes during the formation of hydrothermal PGE deposits such as New Rambler, Wyoming (C.G. Ballhaus, 1989, pers. comm. cited by Nyman *et al.* 1990). This is clearly not the case because, as was demonstrated by Mountain & Wood (1988a), the stabilities of such intermetallic solid compounds are far greater than those of the sulfides. Thus, even in the presence of a large excess of sulfide over Te, Bi or As, which would favor PGE transport as bisulfide complexes, the PGE minerals most likely to precipitate upon destabilization of these complexes would be the tellurides, bismuthinides, *etc.*, not the sulfides.

Theoretical extrapolation of stability constants for gold bisulfide complexes

It was of interest to test the method described above for the extrapolation of the stability constant for the gold–ammonia complex using gold bisulfide complexes as a test case. Using the data reported by Shenberger & Barnes (1989) and the equilibrium constants estimated for reaction (8) above, the stability constants of the $Au(HS)_2^-$ complex may be derived as a function of temperature. These are considered "experimental" values in this paper. Stability constants for this complex also were derived experimentally by Seward (1973). We obtained theoretical estimates by extrapolating the 25°C stability constant for $Au(HS)_2^-$ measured by Renders & Seward (1989), using the techniques described above for the extrapolation of the stability constants of the gold–ammonia complex (*i.e.*, a combination of the isocoulombic and correspondence principles). The experimental and theoretical values are compared in Table 8. The maximum deviation is only 1.4 log units at 300°C, with the theoretical value less than the experimental ones. Considering the accumulation of errors possible in deriving $\log \beta_2$ from the data of Shenberger & Barnes (1989) and Seward (1973), and the recent criticisms leveled against the correspondence principle (Hovey & Tremaine 1986, Hovey et al. 1988, 1989), the agreement is surprisingly good. In any event, this exercise gives an indication of the magnitude of the errors to be expected for the estimates of Au–ammonia complexes at elevated temperatures given in Table 5 (and perhaps also for all the thermodynamic data estimated in this paper using the same techniques, providing accurate stability constants at 25°C are available).

ROLES OF THIOSULFATE, SULFITE AND POLYSULFIDE

Plimer & Williams (1988) and Mountain & Wood (1988b) have discussed the possible importance of thiosulfate ($S_2O_3^{2-}$) as a ligand for Pt and Pd in the surficial environment. Webster (1986) did the same for Au and Ag. The transport of these metals by thiosulfate is complicated by the fact that this ligand does not have a predominance field in Eh–pH space. However, according to the data of Goldhaber (1983), it is quite likely that thiosulfate could exist in sufficient quantities during oxidation of sulfide orebodies to transport Au, Ag, Pt and Pd, at least on a local scale. Mountain & Wood (1988b) presented Eh–pH diagrams to show that significant Pt and Pd transport as thiosulfate complexes could occur in near-neutral to basic, mildly oxidizing solutions, a conclusion reached for Au by Webster (1986). The experimental results of Plyusnin *et al.* (1981) suggest that gold transport by thiosulfate can occur during sulfide oxidation even under acidic conditions. Benedetti & Boulègue (1991) have demonstrated a link between thiosulfate and gold contents of streams draining gold occurrences, and Stoffregen (1986) called upon transient Au thiosulfate complexation to explain gold mobility in the supergene zone at Summitville, Colorado. In a recent study, Machesky *et al.* (1991) have demonstrated that the complex $Au(S_2O_3)_2^{3-}$ is less strongly adsorbed onto goethite than is $AuCl_4^-$, which suggests that the former complex will result in greater mobility of Au in the presence of adsorbent phases such as Fe and Mn oxyhydroxides. The above findings have obvious implications for the use of geochemical surveys of surficial media in exploration for PGE and Au.

There currently are insufficient kinetic and thermodynamic data to evaluate the importance of thiosulfate, sulfite and polysulfide at elevated temperatures. However, the suggestion has been made that once formed, complexes of thiosulfate with Pt and Pd could be more resistant to thermal decomposition than thiosulfate alone, thus extending the importance of these ligands (Plimer & Williams 1988) to elevated temperatures and pressures. This hypothesis requires experimental testing.

As explained in Mountain & Wood (1988b), sulfite (SO_3^{2-}) is even less stable than thiosulfate, especially in the presence of other sulfur anions, and is therefore not likely to contribute significantly to the transport of Pt and Pd. On the other hand, polysulfide anions (S_x^{2-}) have been demonstrated to persist metastably to 240°C

(Giggenbach 1974). These anions can form during oxidation of sulfides or upon acidification of thiosulfate (Murowchick & Barnes 1986). Polysulfides, being soft ligands (in the sense of Pearson 1963), should form strong complexes with Pt, Pd and Au and could be responsible for some transport of these metals under hydrothermal conditions. Indeed, polysulfide is known to form very stable complexes with Cu^+, another soft metal ion, at 25°C (Shea & Helz 1988).

ROLE OF ORGANIC ACIDS

Although there is a considerable body of data on complexes of Pt and Pd with organic ligands, very little of this relates to organic ligands present in significant quantities in natural aqueous fluids. The most important aqueous organic ligands in natural waters are the humic and fulvic acids. These are highly polymerized species with a wide variety of possible metal-binding sites (Schnitzer & Khan 1978). In spite of the possible importance of these acids as ligands, very little is known about their ability to transport Au, Pt and Pd in aqueous fluids. Wood (1990) and Vlassopoulos *et al.* (1990) have carried out theoretical and experimental investigations of the interaction of Pt and Au, respectively, with fulvic acid and some simple organic acids in aqueous solutions at 25°C. It was shown that organic sulfur groups bind Au more strongly than organic nitrogen groups, which in turn bind more strongly than organic oxygen groups. Furthermore, aqueous solutions of thiosalicylic acid, which contains both a thiol (–SH) and a carboxyl (–COOH) group, are capable of dissolving up to hundreds of ppm of Au. It would thus appear that the aqueous organic geochemistry of Au, like its inorganic geochemistry, is dominated by a strong affinity for sulfur. In the case of Pt, a strong affinity for organic sulfur also was indicated (Wood 1990). Fulvic acid increases the ability of an aqueous fluid to transport Pt, but whether this is due to true complexation or formation of an organic-matter-protected colloid is still not clear. More detailed experiments on Pd, including solubility and Raman and UV-visible spectrophotometric studies (Wood *et al.* 1991), suggest that ligands such as acetate, oxalate, phthalate, salicylate, and fulvic acid can form complexes with Pd sufficiently stable to cause Pd mobility in the surficial environment.

Recently, Li & Byrne (1990) have measured the stability constant for a mixed chloride–amino acid (glycine) complex of Pd^{2+} at 25° in seawater. Their results suggest that at amino acid concentrations typical of seawater, such complexes could dominate Pd speciation in seawater. Although we agree that organic complexes may be very important, it is not clear at this point that amino acids are the most important organic compounds. Because of the great preference of Pt and Pd for S-groups, it is highly likely that even small amounts of S-bearing organic matter may be more important in seawater and other natural waters.

CONCLUSIONS

The main conclusions of this paper are as follows:

1) A critical re-examination of estimated thermodynamic data for Pt and Pd chloride complexes at elevated temperatures (up to 300°C) confirms that, at low temperatures, such complexes are restricted in importance to highly saline, oxidizing and acidic environments, such as would be attained during formation of sediment-hosted stratiform Kupferschiefer-type Cu, unconformity U and porphyry Cu–Mo–Au deposits. The solubilities of Pt and Pd as chloride complexes predicted in this study are in excellent agreement with the recent experimental data of Gammons & Bloom (1990).

2) The predominant Pd chloride complex at 300°C and at most geological salinities is considered to be $PdCl_3^-$, and not $PdCl_4^{2-}$ as previously predicted. Similar conclusions may apply to Pt as well, but lack of thermodynamic data precludes a more definitive statement at present.

3) Chloride complexation alone probably is not responsible for observed concentrations of Pt and Pd of up to 0.5 and 2.0 ppb, respectively, in the Salton Sea brines. Alternative explanations include complexes involving bisulfide, ammonia, mixed ammonia–chloride, mixed chloride–hydroxide, organic acids, *etc.*

4) Data for Pd hydroxide complexation at 25°C from the literature are in broad agreement with recently conducted experiments on the solubility of Pt and Pd in NaOH solutions. Previously estimated thermodynamic data for $Pt(OH)_2^0$ are, but for $Pt(OH)_3^-$ and $Pt(OH)_4^{2-}$ are not, consistent with the experimental results.

5) Hydroxide complexes of Pt and Pd alone are not likely to be important in the transport of Pt and Pd in most hydrothermal solutions, but they may be important in oxidized surficial waters such as lake and river water and seawater, as is the case for Au.

6) Mixed chloride–hydroxide complexes may be important at elevated temperatures, but apparently not at 25°C.

7) Significant solubilities (>10 ppb) of Au and Pd, but probably not Pt, are predicted to occur in solutions at the N_2–NH_3–NH_4^+ triple point at 300°C at geologically reasonable activities of ammonia. If equilibrium is maintained among the nitrogen-bearing species, then the solubility of these metals as ammonia complexes decreases dramatically with decreasing temperature.

8) Mixed chloride–ammonia complexes are worthy of experimental investigation.

9) Measured solubilities of Au, Pt and Pd in bisulfide solutions near the SO_4^{2-}–HS^-–H_2S triple point at 200–500°C range up to 300, 0.8 and 0.6 ppm, respectively, with solubilities generally following the order Au >> Pt > Pd. At higher temperatures, the solubility as bisulfide complexes falls off sharply owing to the expansion of the H_2S predominance region with respect to that of HS^-.

10) Our measured solubilities for Au in hydrothermal bisulfide solutions agree very well with those measured by Shenberger & Barnes (1989).

11) Stability constants for $Au(HS)_2^-$ estimated using a combination of the isocoulombic and correspondence principles agree to within 1.5 log units of those derived from experimental solubility data at 200° and 300°C.
12) Thiosulfate and polysulfide may be important in the transport of Au, Pt and Pd under certain conditions, particularly at low temperatures in the presence of sulfides undergoing weathering.
13) The preference of organic functional groups for binding Au and Pt mirrors the preference of inorganic ligands, *i.e.*, $-S > -N > -O$.
14) Fulvic acid can contribute to the transport of Pt and Pd in the surficial environment, most likely by either complexation or protection of colloidal particles.

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