

## THE INTERACTION OF DISSOLVED PLATINUM WITH FULVIC ACID AND SIMPLE ORGANIC ACID ANALOGUES IN AQUEOUS SOLUTIONS

SCOTT A. WOOD

*Department of Geological Sciences and the Mineral Exploration Research Institute, McGill University,  
3450 University Street, Montreal, Quebec H3A 2A7*

### ABSTRACT

A preliminary investigation of the nature of the interaction of  $Pt^{2+}$  with natural fulvic acid in aqueous solution was performed at room temperature. The interaction of  $Pt^{2+}$  with synthetic organic acid analogues (phthalic, salicylic and thiosalicylic acids) containing binding sites similar to those on fulvic acid also was studied. Aqueous solutions of  $K_2PtCl_4$  were mixed with either distilled water or solutions of fulvic, phthalic, salicylic or thiosalicylic acids, and the concentration of Pt in solution was monitored as a function of pH. Aqueous solutions of both fulvic and phthalic acids are capable of maintaining a higher proportion of Pt in a hydromorphically transportable form than distilled water at acidic and perhaps also basic pH. Solid thiosalicylic acid shows a strong affinity for Pt; because its solubility in acidic to neutral solutions is relatively low, it very efficiently removes Pt from solution. Salicylic acid solutions were no more capable of maintaining Pt in a hydromorphically transportable form than pure water. It is still somewhat uncertain whether the ability of fulvic and phthalic acid solutions to transport Pt is due to formation of a soluble Pt-organic complex, formation of an organic-acid-stabilized colloidal suspension, or kinetic inhibition of Pt precipitation. The formation of a colloid seems most likely. In the absence of organic ligands, anomalous concentrations of Pt persist in aqueous solution at near-neutral pH; these are too high to represent equilibrium of Pt metal with aqueous Pt-chloro complexes, probably owing to either the metastable persistence of Pt chloride complexes outside their field of thermodynamic stability, the formation of colloids or the presence of additional dissolved species, such as hydroxy complexes.

**Keywords:** fulvic acid, platinum, complexes, colloids, natural organic acid.

### SOMMAIRE

Cette étude préliminaire porte sur l'interaction du  $Pt^{2+}$  avec l'acide fulvique naturelle en solution aqueuse à température ambiante, ainsi qu'avec les acides synthétiques analogues (phthalique, salicylique et thiosalicylique), dont les sites de liaisons sont semblables à ceux de l'acide fulvique. Des solutions aqueuses de  $K_2PtCl_4$  ont été mélangées avec soit de l'eau distillée, soit des solutions d'acides fulvique, phthalique, salicylique ou thiosalicylique; la concentration du Pt en solution a été mesurée en fonction du pH. Les solutions aqueuses des acides fulvique et phthalique peuvent retenir une plus grande proportion de Pt dans une forme hydromorphiquement transportable que l'eau distillée en milieux acides, et peut-être même basiques. L'acide

thiosalicylique cristallin fait preuve d'une forte affinité pour le Pt; parce que sa solubilité dans les solutions acides et neutres est relativement faible, cet acide peut extraire le Pt d'une solution de façon très efficace. Les solutions d'acide salicylique n'ont pas plus de succès à maintenir le Pt dans une forme hydromorphiquement transportable que l'eau. L'aptitude qu'ont les solutions d'acides fulvique et phthalique s'effectuer le transport du Pt pourrait être due à un complexe organique soluble, une suspension colloïdale stabilisée par un acide organique, ou une inhibition cinétique de la précipitation du Pt. La formation d'un colloïde paraît probable. En l'absence de ligands organiques, des concentrations anormales de Pt peuvent persister en solution aqueuse à un pH près de la neutralité; ces concentrations seraient trop élevées pour représenter l'équilibre entre le Pt métallique et un complexe aqueux chloruré, et résulteraient soit de la persistance métastable de tels complexes hors de leur champ de stabilité thermodynamique, soit la formation de colloïdes, soit la présence d'espèces dissoutes additionnelles, par exemple des complexes hydroxylés.

(Traduit par la Rédaction)

**Mots-clés:** acide fulvique, platine, complexes, colloïdes, acide organique naturel.

### INTRODUCTION

Much evidence is now available concerning the relative mobility of Pt in the surface weathering environment. For example, Fuchs & Rose (1974) and Riese & Arp (1986) documented the redistribution of Pt and Pd in the soil profile above rocks of the Stillwater Complex, Montana. Ottemann & Augustithis (1967), Travis *et al.* (1976) and Bowles (1986) concluded that Pt and Pd were chemically redistributed during laterite formation in Ethiopia, Australia and Sierra Leone, respectively. Finally, Cousins & Kinloch (1976) argued that dissolution and reprecipitation are responsible for the formation of Pt-Pd nuggets in alluvial deposits of these metals.

An obvious obstacle to the study of the mobility of Pt in the weathering environment is the lack of knowledge of the form in which Pt is transported in aqueous media. Platinum may be transported in true solution as some form of complex. The ability of various inorganic ligands to transport Pt has been qualitatively assessed using available thermodynamic data (Fuchs & Rose 1974, Bowles 1986, Mountain & Wood 1988, Plimer & Williams 1988, Wood *et al.*

1990). Transport of Pt in surficial waters as the  $(\text{PtCl}_4)^{2-}$  complex has been suggested by Bowles (1986), but this can occur only under relatively oxidizing and acidic conditions (Mountain & Wood 1988, Plimer & Williams 1988). Transport by means of complexes with natural organic ligands has been proposed as an alternative (Cousins & Vermaak 1976, Cousins & Kinloch 1976, Dissanayake & Kritsotakis 1984, Bowles 1986).

The most widespread forms of dissolved organic matter in the surficial environment are humic and fulvic acids (Schnitzer & Khan 1972, 1978). Humic and fulvic acids are natural organic polymers with molecular weights ranging from several hundreds to tens of thousands of grams/molecule. These compounds contain a wide variety of functional groups, but the predominant ones are carboxylic, phenolic and ketonic groups. The compositions of fulvic and humic acids are quite variable and depend to a large extent on their source. Fulvic acid tends to have a lower molecular weight and a higher content of oxygen than humic acid. Also, fulvic acid is soluble over a much wider range of pH than humic acid, which is insoluble under acidic conditions. General reviews of the chemistry of humic and fulvic acids may be found in Schnitzer & Khan (1972, 1978) and more recent reports by Ephraim & Marinsky (1986), Ephraim *et al.* (1986), Marinsky & Ephraim (1986), Hatcher *et al.* (1989), and references therein.

There have been no experimental studies of the interaction of the platinum-group elements (*PGE*) with humic and fulvic acids, in spite of their potential relevance to *PGE* transport in natural waters. Humic and fulvic acids are known to bind cations such as  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  under natural conditions (Gamble *et al.* 1970, Gardiner 1974, Buffle 1980, Gamble *et al.* 1980, Schnitzer & Kerndorff 1981, Bizri *et al.* 1984, Olson & Shuman 1985, Turner *et al.* 1986). Experimental work also has shown that humic and fulvic acids are capable of transporting Au under natural conditions (Ong &

Swanson 1969, Fisher *et al.* 1974, Baker 1978, Fedoseyeva *et al.* 1986, Andrade *et al.* 1988). However, the form of transport is still in dispute. The data of Fisher *et al.* (1974) and Baker (1978) suggest the formation of a true complex between Au and natural organic acids, whereas Ong & Swanson (1969) and Andrade *et al.* (1988) have argued that the function of the organic acid is to reduce dissolved  $\text{Au}^{3+}$  or  $\text{Au}^+$  (initially present as complex ions) to Au metal and to maintain Au in solution as a stable colloid. Vlassopoulos *et al.* (1990) present evidence that simple organic analogues of various functional groups on fulvic and humic acids can dissolve and transport Au, just as (by extension) the more complicated natural organic acids. Thus, the cations  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Au}^+$  all appear to exhibit some type of interaction with natural organic acids. They are also all soft cations in the sense of Pearson (1963), as is  $\text{Pt}^{2+}$ . Therefore, one would expect  $\text{Pt}^{2+}$  also to interact with natural organic matter. It is, therefore, surprising that there are no previous experimental investigations of the interaction of  $\text{Pt}^{2+}$  and natural organic acids. The preliminary study reported here represents an initial attempt to rectify this situation.

#### EXPERIMENTAL

The interaction of aqueous solutions of  $\text{K}_2\text{PtCl}_4$  with pure water and aqueous organic acid solutions as a function of pH at room temperature was investigated. The simple organic acids employed (salicylic, thiosalicylic and phthalic acids) were chosen because they contain some of the same types of sites as those in fulvic acid molecules; metals are thought to bind to these sites (Schnitzer & Khan 1972, 1978). The structures of these analogues are illustrated in Figure 1.

The fulvic acid employed was supplied by Dr. C.H. Langford of Concordia University, Montreal, and was extracted from Prince Edward Island soil (Armada Bh horizon). This particular fulvic acid and the nature of its binding sites have been extensively characterized (Gamble 1970, 1972, Schnitzer & Khan 1972), and all batches are uniform with respect to elemental analyses and behavior during base titration (C.H. Langford, pers. comm. 1988). Phthalic and salicylic acid were A.C.S. certified grade, supplied by Fisher Scientific. Thiosalicylic acid and  $\text{K}_2\text{PtCl}_4$  were both 98% pure, supplied by Aldrich Chemical Company. All reagents were used as received without further purification.

The procedure followed was similar to that employed by Schnitzer & Kerndorff (1981) in their study of the interaction of fulvic acid with solutions containing Fe, Al, Cr, Pb, Cu, Hg, Zn, Ni, Co, Cd and Mn. Two series of solutions were prepared containing respectively 43 and 250 ppm Pt (as  $\text{K}_2\text{PtCl}_4$ )

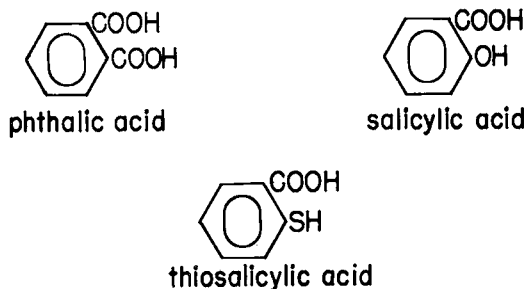


FIG. 1. Structural formulas for the three synthetic organic acid analogues of fulvic acid used in this study. The hexagons with the oval in the middle represent benzene rings.

in doubly distilled water, as well as in 0.5 g/L fulvic, 0.5 g/L phthalic, 0.5 g/L salicylic and 0.5 g/L thiosalicylic acid solutions (a concentration of 0.5 g/liter of each of these acids is below the solubility limit except for thiosalicylic acid in the acidic pH range: Windholz *et al.* 1976). The doubly distilled, deionized water used to make all solutions was thoroughly degassed (to remove dissolved  $\text{CO}_2$  and  $\text{O}_2$  gas) by subjecting it to a vacuum for several minutes until bubbling ceased. Each of the solutions was made in duplicate or triplicate 1-liter batches and generally had initial values of pH between 1 and 2. These solutions were transferred to opaque (to preclude possible photosensitive reactions) polyethylene bottles of 1-liter capacity and were stored at room temperature under an  $\text{N}_2$  atmosphere to exclude  $\text{CO}_2$  and  $\text{O}_2$  gas during the experiment.

After an equilibration period of two to three days, the bottles were transferred to a glove box containing an  $\text{N}_2$  atmosphere. Solution pH was measured (all pH measurements were made with a combination glass-saturated calomel electrode calibrated against at least two pH standards, NBS standards at pH values of 4.0, 7.0 and 9.2, and  $\text{NaOH} + \text{KCl}$  at a pH value of 12.45) and approximately 10 mL of the solution were withdrawn and syringe-filtered through 0.1 or 0.45  $\mu\text{m}$  Durapore (composition: polyvinylidene difluoride) filters, supplied by Millipore. Some of the samples also were centrifuged at 14,000 rpm and only the supernatant retained. The filtration and centrifugation steps were taken to attempt to minimize carry-over of solid particulate matter into the aliquots of solution sampled. The pH of the solution remaining in the polyethylene bottle was then

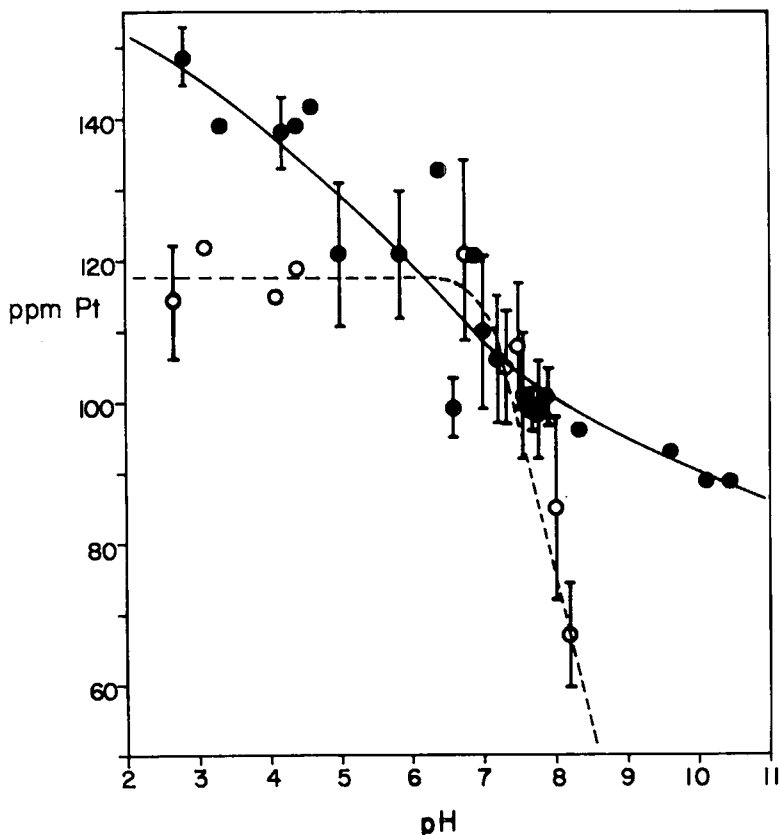


FIG. 2. Concentration of Pt (in ppm) versus pH for solutions initially containing 250 ppm Pt as  $\text{K}_2\text{PtCl}_4$  in pure water (open circles) and 0.5 g/liter fulvic acid (closed circles). Solid and dashed curves represent visual fits to the fulvic acid and pure water data, respectively, to emphasize trends. Fluid samples depicted were passed through a 0.45  $\mu\text{m}$  filter and centrifuged before analysis. Error bars represent one standard deviation in Pt concentration where two or more measurements occur at nearly the same pH. Where there are no error bars, there were no replicate measurements at that particular pH.

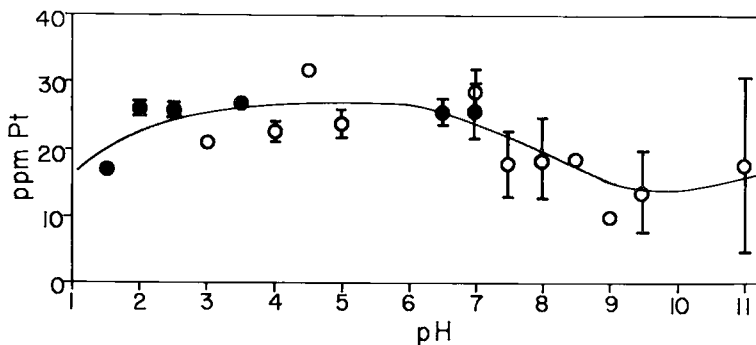


FIG. 3. Concentration of Pt (in ppm) versus pH for solutions initially containing 43 ppm Pt as  $K_2PtCl_4$  in distilled water. Solutions represented by filled symbols were passed through  $0.45 \mu m$  filters, and those represented by the open symbols were passed through  $0.1 \mu m$  filters. Centrifugation was not used in this series of experiments. The curve represents a visual fit to the data and will be shown on subsequent diagrams for purposes of comparison.

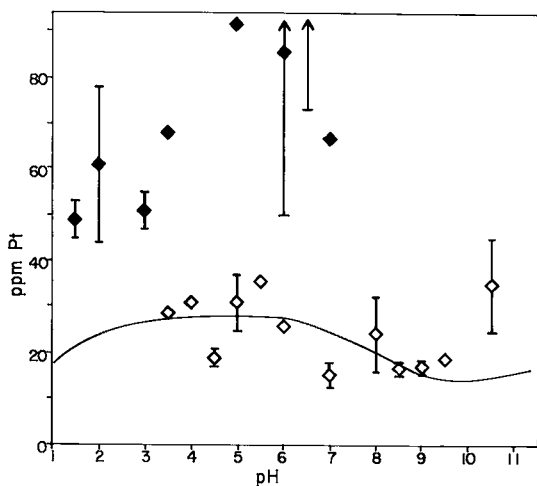


FIG. 4. Concentration of Pt (in ppm) versus pH for solutions initially containing 43 ppm Pt as  $K_2PtCl_4$  and 0.5 g/L fulvic acid. Open diamonds represent solutions passed through a  $0.1 \mu m$  filter, and solid diamonds represent solutions passed through a  $0.45 \mu m$  filter before analysis. See caption to Figure 2 for significance of error bars. The solid curve from Figure 3 also is shown for comparison. Arrows at the end of some error bars indicate Pt concentrations higher than 90 ppm.

increased slightly (usually between 0.2 and 0.8 pH units) by addition of a small amount of concentrated NaOH solution. The bottles were then stored for an additional two- to three-day period of equilibration. This entire process was repeated until solution pH reached 10–11, at which point the experiment was terminated. The filtered and centrifuged samples of solution were acidified with HCl when the sample solution pH was 7 or less and made basic with ammo-

niun hydroxide when the pH exceeded 7, in order to preserve Pt in solution until analysis.

Fluid samples were then analyzed by air-acetylene flame atomic absorption spectrometry using a Perkin Elmer 5100 AA unit. The method of standard additions was employed because the presence of some of the aqueous organic acids in solution noticeably depressed the sensitivity of flame atomic absorption for Pt. Analyses of blank organic acid solutions gave Pt concentrations below the detection limit for flame AA, *i.e.*, approximately 1 ppm.

In the case of the solutions initially containing 250 ppm in Pt, Eh measurements also were made at each sampling using a Pt electrode as an indicator and the saturated calomel electrode (SCE) as a reference. This Eh cell was periodically calibrated against a standard solution of 0.05 M potassium ferricyanide and 0.1 M potassium ferrocyanide (+196 mV versus SCE). The Eh measurements gave values ranging from approximately 400 mV at pH = 2 to 50 mV at pH = 10. Generally the fulvic acid solutions were up to 20 mV more reducing than the fulvic-acid-free solutions at a given pH.

## RESULTS AND DISCUSSION

The results of the interaction study for the 250 ppm Pt solution in pure water and in fulvic acid solution as a function of pH are plotted in Figure 2. These experiments were carried out in triplicate, and the results of all three replicates are plotted. The solution samples in this set of experiments were both centrifuged and filtered through  $0.45 \mu m$  filters before analysis in an attempt to remove particulates or colloidal material. Some of the scatter in the data, as depicted by the error bars, may be due to slight differences in Eh from sample to sample. The data depicted in Figure 2 clearly demonstrate that the con-

centration of Pt remaining in solution is higher in the fulvic acid solutions than in the pure water solutions in the pH ranges 2–6 and 8–11. However, in the near-neutral region, *i.e.*, pH 6–8, the concentrations of dissolved Pt are similar. Thus, fulvic acid is apparently more effective in maintaining Pt in a hydromorphically transportable form than doubly distilled water under both acidic and basic conditions.

Although the results for the solutions originally containing 43 ppm Pt are similar, the data are more scattered at this lower concentration of Pt (Figs. 3, 4). Much of the scatter in these data is due to a change in filter size during the experiment. In those experiments using fulvic acid or doubly distilled water and denoted by open symbols, the solution samples were filtered through 0.1  $\mu\text{m}$  filters, whereas in those experiments denoted by closed symbols, samples were filtered through 0.45  $\mu\text{m}$  filters. None of the solution samples was centrifuged in this experiment. The Pt analyses of solution samples from the experiments using doubly distilled water (Fig. 3) were unaffected by the pore size of the filters used, but the fulvic acid solutions filtered through the 0.45  $\mu\text{m}$  filter clearly have greater concentrations of Pt than those filtered through the 0.1  $\mu\text{m}$  filter (Fig. 4). This finding suggests that Pt species in the fulvic acid solutions have a relatively large size. In addition, many of the samples from fulvic acid solutions that were filtered through the larger-pore filter yielded analyzed Pt contents higher than the original 43 ppm Pt. The reason for this is currently unknown, but it may be related to the redissolution of the fine-grained solid Pt that had precipitated earlier or inhomogeneous sampling of fine-grained suspended material. One reviewer of this manuscript suggested the possibility that the filter membrane employed may act as a short chromatographic column, giving rise to a "chromatographic" peak in Pt concentration. No matter what the source of the "extra" Pt, the phenomenon was observed only in fulvic and phthalic (*vide infra*) acid solutions. This fact attests to the superior ability of fulvic and phthalic acids to maintain Pt in a hydromorphically transportable form.

At values of pH greater than 8, higher concentrations of Pt in fulvic acid solutions than in doubly distilled water would be expected if fulvic acid were to form a complex with Pt. Potentiometric titrations of the fulvic acid with NaOH solution show a very broad endpoint. Deprotonation of the fulvic acid employed begins at a pH of 2 or less but is more or less complete by a pH of 8 to 9. This finding is in accord with those of Gamble (1970, 1972) for the titration of a similar batch of fulvic acid. Thus, in basic solutions, Pt does not have to compete with the proton for binding sites. However, the increased concentration of Pt in acidic solutions is somewhat

harder to explain by complexation.

As mentioned above, another possible explanation for the observed behavior is that fulvic acid stabilizes a Pt colloid against coagulation by forming a protective coating on the individual particles of Pt, as has been suggested in the case of Au (see Frondel 1938, Ong & Swanson 1969). If this is the case, then fulvic acid apparently is not effective as a colloid protector in the near-neutral pH range. This may be related to the ability of the fulvic acid to maintain a charged double layer as a function of pH. Although it seems rather unlikely that a fulvic-acid-protected Pt colloid would be able to pass through either the 0.1 or 0.45  $\mu\text{m}$  filters used in sampling the fluid (0.45  $\mu\text{m}$  is usually taken as the arbitrary, operational cutoff between colloids and true solutions), the differing results obtained using the filters of two different pore-sizes provide some support for this hypothesis. Thus, at least some of the Pt in solution may be in colloidal form. However, it must be noted that the above interpretation is complicated at lower pH by the possibility of hydrogen-bonded sorption of humic - Pt particles onto the filter membranes and at higher pH by the possibility of sorption of the Pt chloro-complexes onto the filters.

In Figure 5, the results of the experiment using phthalic acid solutions are compared to those for doubly distilled water. A comparison of Figures 4 and 5 illustrates that the phthalic acid and fulvic acid experiments gave similar results: elevated Pt concentrations with respect to the pure water experiments at acidic pH in the cases where the 0.45  $\mu\text{m}$  filters were employed. On the other hand, there appears to be no difference between the solutions containing salicylic acid and doubly distilled water (Fig. 6).

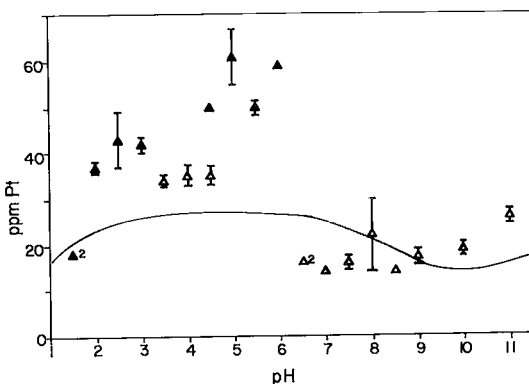


FIG. 5. Concentration of Pt (in ppm) versus pH for solutions initially containing 43 ppm Pt as  $\text{K}_2\text{PtCl}_4$  and 0.5 g/L in phthalic acid. Solid triangles: 0.45  $\mu\text{m}$  filters; open triangles: 0.1  $\mu\text{m}$  filters. Small numerals near triangles represent the number of replicate measurements in cases where one standard deviation is less than the size of the triangle. Solid curve from Figure 3 also is shown for comparison.

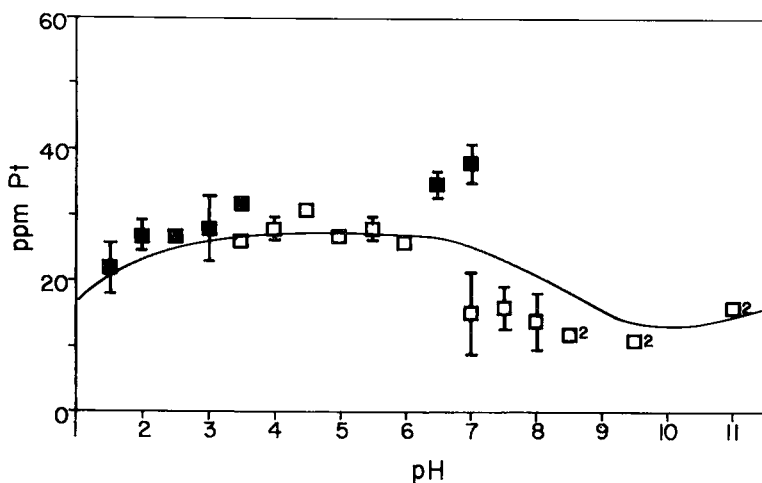


FIG. 6. Concentration of Pt (in ppm) versus pH for solutions initially containing 43 ppm Pt as  $K_2PtCl_4$  and 0.5 g/L in salicylic acid. Solid squares: 0.45  $\mu m$  filters; open squares: 0.1  $\mu m$  filters. See captions to Figures 2 and 5 for significance of error bars and numerals. Solid curve from Figure 3 also is shown for comparison.

Finally, the results of the thiosalicylic acid experiment are illustrated in Figure 7. Owing to the low solubility of thiosalicylic acid in acidic aqueous solutions, most of the 0.5 g/L thiosalicylic acid added initially in these experiments did not dissolve and remained as a granular solid at the bottom of the polyethylene bottle. At acid values of pH, the Pt content of the thiosalicylic acid solutions is below the detection limit (1 ppm) for flame atomic absorption. Apparently, solid thiosalicylic acid has a strong affinity for  $Pt^{2+}$ , and Pt was readily adsorbed onto the solid acid (this is consistent with the recently demonstrated tendency of the similar metal ion  $Pd^{2+}$  to be strongly adsorbed onto and reduced by sulfide mineral surfaces: Hyland & Bancroft 1990). As the solution pH was increased, both the Pt content and the thiosalicylate content of the sample solutions increased. Vlassopoulos *et al.* (1990) have demonstrated that the solubility of Au is greatly increased at basic pH in the presence of dissolved thiosalicylate. There are currently too few data to say whether this is also the case for Pt. However, given the similarities in the geochemical behavior of Au and Pt (Mountain & Wood 1988), it is expected that thiosalicylate should be capable of forming strong complexes with  $Pt^{2+}$ .

It is important to realize that the Pt concentrations measured, even in the doubly distilled water experiments, probably do not represent equilibrium solubilities of Pt as the  $(PtCl_4)^{2-}$  complex. At the values of Eh and chloride concentrations (chloride coming from the  $K_2PtCl_4$  initially added) of the doubly distilled water experiments, the concentration of  $(PtCl_4)^{2-}$  in equilibrium with Pt metal should be on

the order of  $10^{-20}$  ppm instead of the measured tens of ppm (according to an  $E_0$  for the reaction  $(PtCl_4)^{2-} + 2e^- = Pt + 4Cl^-$  of 0.73; Lopis & Colom 1976). Of course, at the low concentrations of chloride (approximately  $10^{-3}$  molal) used in these experiments, the  $(PtCl_2)^0$  and  $(PtCl_3)^-$  complexes are predominant (see Fig. 3 in Mountain & Wood 1988), but inclusion of these complexes increases the calculated solubility of Pt by at most 2 or 3 orders of magnitude. It is well known that the kinetics of aqueous reactions involving Pt can be extremely sluggish (Langford & Gray 1966, Westland 1981). Therefore, Pt may be metastably maintained in solution as a chloride complex. Another possibility is that there may exist other, as yet unidentified aqueous species, such as hydroxide complexes (Mountain & Wood 1988), which allow higher solubilities to be maintained in the experiments using doubly distilled water. It is unlikely that these elevated concentrations of Pt in distilled water are due to colloid formation because the same concentration is measured consistently at a given pH no matter what size of filter is used. In addition, the salicylic acid solutions have more or less the same concentrations of Pt as the distilled water solutions at a given pH.

Thus, the results of the present study suggest that both fulvic and phthalic acid are effective in maintaining Pt in a hydromorphically transportable form over a wide range of pH. Salicylic acid apparently has little effect, whereas thiosalicylic acid shows a strong affinity for Pt, at least in the solid form. The results also indicate that anomalous amounts of Pt, which were originally introduced as  $(PtCl_4)^{2-}$ , remain in solution even at very low chlorinities and

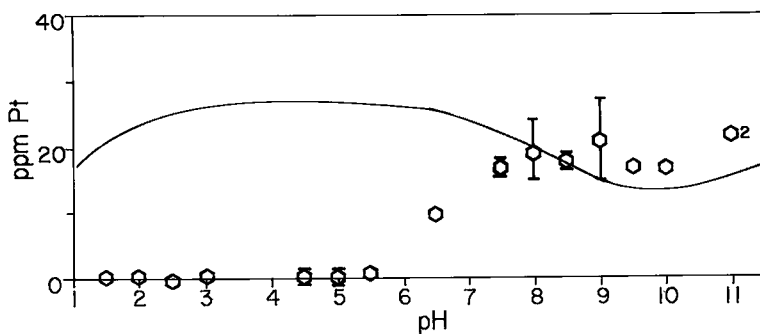


FIG. 7. Concentration of Pt (in ppm) versus pH for thiosalicylic acid solutions initially containing 43 ppm in Pt as  $K_2PtCl_4$ . Note that approximately 0.5 g of thiosalicylic acid was added to 1000 mL of water to prepare the latter solutions, but at an acidic pH only a small portion of the thiosalicylic acid dissolved, leaving a solid residue that efficiently fixed Pt from solution. Curve from Figure 3 also is shown for comparison.

relatively high pH, where the chloride complexes are no longer predominant.

Platinum is most likely to be released to solution initially as  $(PtCl_4)^{2-}$  or a similar chloride complex during the oxidation of PGE-bearing sulfide orebodies. Surficial waters and groundwaters draining from such bodies will be highly oxidizing and quite acidic owing to the oxidation of sulfide minerals; Pt chloride complexes may be stable under such conditions if sufficient chloride is present (Bowles 1986, Mountain & Wood 1988, Plimer & Williams 1988). However, as these acidic waters drain into lakes, rivers and groundwaters, they will tend to become less acidic and perhaps also more reduced. According to available thermodynamic data, the Pt chloro complexes should therefore become unstable. However, the results of the experiments described in this report seem to suggest that the Pt would not drop out of solution immediately, but may be either a) maintained in solution metastably, b) transformed into a different dissolved form (e.g., a hydroxide complex), or c) transported further as a colloid. If fulvic or other natural organic acids are present, more Pt may be maintained in transportable form over a wide range of pH, most likely as an organic-matter-protected colloid.

It should be noted that the Pt concentrations employed in this study are clearly higher by several orders of magnitude than those likely to be encountered in natural waters. It is possible that the mechanisms responsible for keeping ppm quantities of Pt in a hydromorphically transportable form do not apply at near to sub-ppb levels. It is well known, for example, that ppm quantities of trace metals like Pt and Au can be kept in solution for long periods of time without significant loss, but that sub-ppb levels commonly are lost to the container by adsorption (Chao *et al.* 1968). However, it is clear that a

definitive statement on the effect of fulvic acid on Pt transport will require the application of additional techniques, such as infrared (IR), nuclear magnetic resonance (NMR) and ultraviolet-visible (UV-VIS) spectroscopy to the problem. These techniques require the use of high concentrations (relative to those found in nature) of both fulvic acid and Pt. The preliminary experiments described here were conducted with such high concentrations in order that they may be directly compared with subsequent experiments using spectroscopic techniques. Once the nature of the fulvic acid - Pt interactions described in this paper are more clearly defined using spectroscopy, then additional experiments may be carried out to measure the concentration of Pt at ppb to sub-ppb levels as a function of pH both in fulvic acid solutions and distilled water, in order to determine if the same interactions between fulvic acid and Pt are pertinent at low concentrations of Pt. Such experiments will, of course, require more sensitive analytical techniques, such as graphite-furnace atomic absorption spectrophotometry or inductively coupled plasma - mass spectrometry.

#### CONCLUSIONS

Evidence has been presented to suggest that natural dissolved organic acids such as fulvic acid may play an important role in maintaining Pt in a transportable form in aqueous solution. Although it is still somewhat unclear whether the interaction of Pt with fulvic acid involves true complexation, kinetic inhibition of precipitation, or stabilization of colloidal suspensions, the latter appears most likely. Colloidal stabilization is supported by the dependence of measured concentrations of Pt on the pore size of the filter and the indifference of Pt to fulvic acid in the near-neutral (6-8) range of pH, which is

difficult to explain in terms of complex formation. It is probable that the concentration of Pt remaining in solutions filtered through the 0.1  $\mu\text{m}$  filters represents Pt in true solution (although perhaps metastably so), whereas the increase in Pt that results from filtration through 0.45  $\mu\text{m}$  filters represents colloidal transport.

More work clearly is required to elucidate further the nature of the interaction of the PGE with fulvic and humic acids. Experiments on the dissolution of elemental Pt and Pd by fulvic acid and synthetic analogues are in progress. The higher solubility and more rapid reaction kinetics of Pd may alleviate some of the problems in interpretation encountered in the present study of Pt. Finally, other techniques such as NMR, IR and UV-VIS spectroscopy and polarography are being investigated for their potential to discriminate between the possibilities of complexation and colloid formation.

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