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The role of humic acid in the transport of gold

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Abstract—Experimental data are presented to show that humic acid can dissolve, complex and transport Au. As much as 330 ng Au/ml (ppb) were taken into solution from 0.07 to 0.15 mm Au particles by 500 µg/ml (ppm) solutions of humic acid during a 50 day period. Au was mobilised in electrophoresis experiments in the presence of humic acid, whereas Au alone remains immobile. The formation of a complex between Au and humic acid was indicated by the results of polarographic, solvent extraction and X-ray diffraction investigations.

It is apparent that the formation of a humic acid complex of Au may be important in the mobilisation of element at the Earth's surface.

INTRODUCTION

THE MIGRATION of Au in the weathering cycle has been the subject of many investigations. Conflicting views and experimental evidence have been advanced favouring both inorganic and organic processes for the solution and transport of Au. STOKES (1906) and others studied the solution of Au by inorganic solvents such as $\text{Fe}_2(\text{SO}_4)_3$, which may occur in nature, and found that substantial solution occurred only in the presence of Cl^- . KRAUSKOPF (1951, 1967) presented experimental evidence and thermodynamic data for the dissolution of Au as AuCl_4^- . LAKIN *et al.* (1974) have suggested that HCN resulting from hydrolysis of naturally occurring cyanoglycosides, which are present in many plants, could be responsible for the mobility of Au in soils.

JULIEN (1879) made a generalised proposal that humic acid was active in the precipitation of Au in alluvial deposits. FREISE (1931) drew attention to the fact that some of the Au of Brazilian alluvial deposits was extremely fine-grained and of high purity, in contrast with detrital Au which contained Cu. The high purity Au often carried a brown to black coating which was found to be Fe humate. This 'black gold', as it has been named by prospectors, occurs in many alluvial Au deposits and has been observed by the writer from the Lisle and Jane River Au deposits in Tasmania. ONG and SWANSON (1969) have noted the occurrence of carbonaceous matter with Au in sedimentary rocks from several regions including the Witwatersrand in South Africa and the Thuringian shales in Germany. It is possible that such carbonaceous matter originated as a humate.

FREISE (1931) also presented experimental evidence for the solubility of Au in humic acid and BAKER

(1973) confirmed this. The theoretical plausibility of the formation of a humic acid complex of Au was established by SHCHERBINA (1956). Contrary views have been expressed by FETZER (1934, 1946) and ONG and SWANSON (1969). The latter investigators proposed that Au is transported as a colloid, in a system in which humic acid acts as a reductor and as a protective colloid. KRAUSKOPF (1974) accepted this model but also suggested that Au is mobilised as AuCl_4^- .

Modern reviews of the transportation of Au, such as that by KRAUSKOPF (1974), do not mention any evidence of the potential of humic acid to form a complex with Au. Such omissions have prompted a further and more thorough examination of the interaction of Au with humic acid, involving solution, electrophoresis, polarographic, solvent extraction and X-ray diffraction investigations.

EXPERIMENTAL STUDIES

Au solubility studies

It is important in solubility studies to use experimental conditions that are compatible with natural environments. The weathering of rock under moist conditions takes place at an irregular interface between soil and rock where the constituents of soil water react with solid mineral surfaces. The amount of humic substances in soil water is not well known. FOTIYEV (1971) gives a value of 300 µg/ml (ppm) of soluble humic substances in marsh water and, as soil water could be expected to exceed this, a concentration of 500 µg/ml (ppm) would appear reasonable for experimental studies. Simulation of slow movement of humic acid over Au particles was attempted by placing the reactants in horizontal tubes which were rotated at 100 rph.

With this experimental arrangement 2 g of Au having a particle size range of 0.07 to 0.15 mm were placed in each of three test tubes, and allowed to react with 20 ml of distilled H_2O , and 500 µg/ml (ppm) solutions of humic acid preparations THA-1* and THA-4 for a period of 50 days. The initial pH and Eh values of the humic acid solutions were 3.7 and +340 mV for THA-1 and 3.4 and +330 mV for THA-4. These values are compatible with those of natural solutions between rain water and bog waters, as given by GARRELS (1960), and are probably representative of many soil waters.

* Formerly HA-1 and HA-4 of BAKER (1973). The T has been included to specify Tasmanian samples. For all experiments, solutions were aqueous preparations with concentrations expressed on a w/v basis.

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Table 1.

Run No.	H ₂ O/CO ₂	0.05% THA-1	0.05% THA-4
1	8	200	300
2	11	170	360
3	10	210	320
Av.	10	190	330

At the completion of the 50 day reaction period the solutions were filtered through Whatman No. 42 paper and analysed by an atomic absorption carbon cup technique (AACC) which allowed a precision of about ± 10 ng Au/ml (ppb). The results, given in Table 1 show average yields of 10, 190 and 330 ng Au/ml (ppb) for distilled H₂O, THA-1 and THA-4 respectively, which indicates considerable mobilisation of Au in the presence of humic acid. There was no significant change in the pH and Eh values of the humic acid solutions as a result of their reaction with Au.

Electrophoresis

Electrophoresis has been used extensively to study complexes of humic acid with metals (e.g. MANSKAYA and DROZDOVA, 1968). To apply the technique in this study it was necessary to impregnate the electrophoresis membranes with a confined spot of Au. This was achieved by applying, in succession, 5 μ l drops of solutions of 1% SnCl₂ and 1 mg Au/ml as HAuCl₄ (5 μ g Au) at equivalent points of four 100 \times 20 mm membrane strips. After excess reagents were leached away by leaving the membranes in a large volume of distilled H₂O for 24 hr there remained spots of precipitated Au. Blank membranes were treated in the same manner, with the omission of the HAuCl₄ application. Before use, the membranes were soaked in a borate buffer of 0.02 M Na₂B₄O₇ adjusted to pH 8.6 with H₃BO₃. A 1% THA-1 solution (pH 3.2) was applied as a 5 μ l drop (50 μ g THA-1) on the cathodic side of the Au spot on two of the membranes and in an equivalent position on the two blanks. An electrophoresis cell was set up with the borate buffer and the membranes carrying Au, THA-1 and Au with THA-1 were subjected to electrophoresis at a potential of 300 V for 15 min. The runs were made in duplicate. One set of membranes was used for analytical purposes whilst the other was kept as a record of the electrophoretograms which are illustrated in Fig. 1.

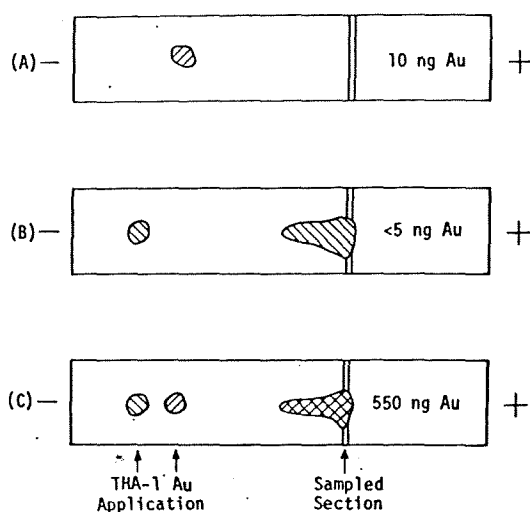


Fig. 1. Electrophoretograms of (A) Au, (B) THA-1 and (C) Au with THA-1 including Au contents of sample membrane sections.

The comparative Au contents of the humic acid fronts and the equivalent site for the Au run were determined by AACC analysis of 1 mm sections of the membranes. The analyses reveal that the front on the Au with THA-1 membrane contains 550 ng Au, which is far in excess of the 10 ng Au in the equivalent position of the Au membrane. A small amount of Au (<5 ng), which is near the detection limit, was found in the blank membrane and this is believed to be a contaminant acquired during the leaching of excess reagents from the membranes. The high content of Au in the sample from the membrane carrying Au with THA-1 suggests that Au has been mobilised as a complex with humic acid.

Polarography

Polarographic analysis can be applied to the study of complexation of metals. Changes in the state of a metal from ionic to complexed or from one complex to another, will generally be reflected in a polarogram by a change in the position of the half-wave potential for a particular reduction, and in the value of the diffusion current associated with this event. The application of polarographic procedures requires the use of supporting electrolytes of high ionic concentration. For studies with humic acid, electrolytes must be selected that will not cause precipitation. In the case of the polarographic study of the reduction of Au(III) this was achieved by the use of 1 M NaOH.

A study was made of the reduction of 10 μ g Au(III)/ml in 1 M NaOH in the absence and presence of 50 mg THA-1. Polarograms were recorded using pulsed DC polarography. The Au(OH)₄⁻ complex was stable in NaOH for several hours but eventually the formation of colloidal Au was indicated by the appearance of a red-blue colour in the solution. For this reason polarograms were recorded as soon as the solutions had been prepared and flushed with N₂ and again after a period of 24 hr. The resulting polarograms are shown in Fig. 2.

In Fig. 2A the polarographic reduction of Au(III) is seen to occur with a half-wave potential of -0.53 V (vs SCE) and a diffusion current of 8.2 μ A. The residual current in this case is near zero. Reduction in the presence of THA-1 is shown in Fig. 2B which reveals that for this system the half-wave potential has moved to -0.75 V and the diffusion current has decreased to 3.6 μ A. There is a small residual current due to the electrolytic properties of the humic acid. This change in wave characteristics is clear evidence of the complexation of Au by humic acid. The large shift of the half-wave potential of -0.22 V in the presence of THA-1 indicates that the stability constant of the humic acid complex of Au is much greater than that of Au(OH)₄⁻. Figure 2C shows the results of repeating the polarographic reduction of Au(III) in NaOH after 24 hr. The half-wave potential remains at -0.53 V although the presence of colloidal Au has caused a sharp increase in the residual current. Since the concentration of Au(III) has been decreased by the formation of colloidal Au, the diffusion current has fallen to 3.2 μ A. The polarogram of Au(III) in NaOH with THA-1, repeated after 24 hr, was found to be identical with Fig. 2B. Thus in the presence of THA-1 a complex with Au has formed which remains stable and prevents the formation of colloidal Au.

Solvent extraction

SHCHERBINA (1956) suggested that the humic acid complex of Au is stronger than AuCl₄⁻ and possibly of similar strength to Au(SCN)₄⁻. This was investigated by examining the extraction of 10 μ g Au/ml as AuCl₄⁻ and Au(SCN)₄⁻ into amyl methyl ketone in the absence and presence of 50 mg THA-1. In the absence of THA-1, 90% of the AuCl₄⁻ and 85% of the Au(SCN)₄⁻ were extracted in 2 min. With THA-1 present the extraction of AuCl₄⁻ decreased to 30% whereas that of Au(SCN)₄⁻ remained at 85%. The lower extraction of AuCl₄⁻ could be due to the

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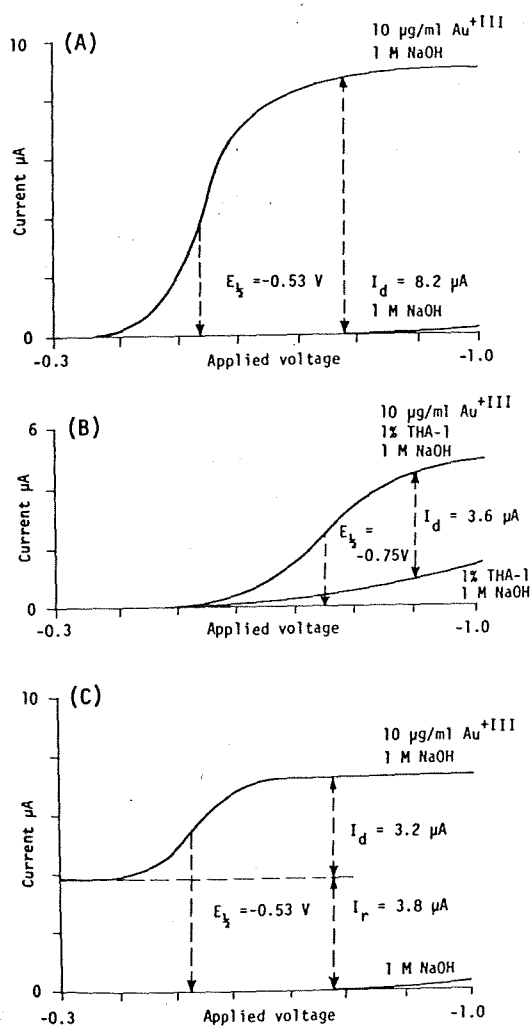


Fig. 2. Polarograms of Au(III) in 1 M NaOH. (A) Au(III) within 15 min of preparation. (B) Au(III) with THA-1 both within 15 min of, and 24 hr after, preparation. (C) Au(III) 24 hr after preparation. $E_{1/2}$ = half-wave potential; I_d = diffusion current; I_r = residual current.

displacement of Cl^- by humic acid to yield a stronger non-extractable complex with Au. Alternatively since the oxidation potential of humic acid is less positive than that of AuCl_4^- , reduction to Au would also cause a decrease in the extraction. In the case of $\text{Au}(\text{SCN})_4^-$, the fact that humic acid has no effect on the extraction is an indication that the complex of Au with humic acid has a stability of the same order as that with thiocyanate.

X-ray diffraction

In an association of Au with humic acid the metal may exist as a dispersed colloidal phase or as some form of complex. Provided that the association contains sufficient Au to be detected by X-ray diffraction it should be possible to distinguish between these two possibilities. It was found that when 1 mg of colloidal dispersed Au was dried in the presence of 100 mg of humic acid, the Au(III) planes yielded a sharp diffraction peak. The results of the solution experiment however, indicate that under conditions approaching those in nature, the time required to produce such high contents of Au in humic acid would be extremely long.

A concentrated association of Au with humic acid was produced by mixing 2 mg Au as HAuCl_4 with 20 ml of

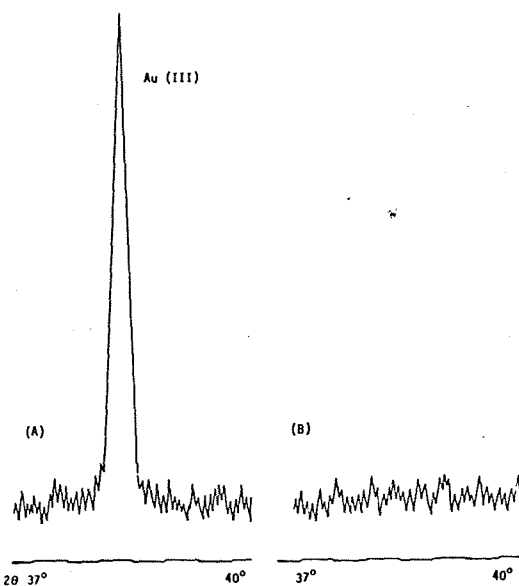


Fig. 3. X-ray diffraction results for (A) 1 mg colloidal Au in physical admixture with 100 mg THA-1 and (B) 1 mg Au as HAuCl_4 reacted 24 hr with 10 ml 1% THA-1 in presence of KMnO_4 .

1% THA-1. The solution was adjusted to $\text{pH} = 5$ with NH_4OH and 10 mg of KMnO_4 were added to ensure the dissolution of the Au. After shaking for 24 hr the humic acid was precipitated by the addition of $\text{Al}_2(\text{SO}_4)_3$, separated by centrifuging and dried. The Au content of the residual solution was less than 0.1 µg/ml (ppm) whereas analysis of the dried humic acid revealed an Au content of 0.9%.

The Au humate and the colloidal dispersion of 1 mg Au in 100 mg THA-1 were examined by X-ray diffraction. The resulting diffractograms are illustrated in Fig. 3. It is apparent from the strength of the diffraction by the (111) planes that the metal is present only in the physical mixture with THA-1. The reaction of Au with the humic acid solution produced an amorphous complex of Au.

DISCUSSION

The possible means of Au transport in the weathering cycle include ionic, colloidal and organic complexation. The low content of Au in river water, stated by FISCHER (1966) to be 0.002 ng/ml (ppb), prevents direct assessment of these possibilities. Ionic and colloidal transport require that Au enters the hydrosphere largely as AuCl_4^- . KRAUSKOPF (1967) has shown that AuCl_4^- can be produced during weathering of an Au-bearing ore body. The conditions necessary for this to occur are that both H^+ and Cl^- are present, with one of these in relatively high concentration and in addition an oxidising agent such as MnO_2 , must also be present. As KRAUSKOPF (1967) points out, such conditions occur rarely and result only locally in appreciable transport of Au.

ONG and SWANSON (1969) have calculated the theoretical concentration of Au in river water from mean composition values (LIVINGSTONE, 1963) and equilibrium constant data for the various possible ionic Au species (MARTELL and SILLEN, 1964). The

maximum value obtained of $10^{-10.5}$ M (0.006 ppb) is compatible with the concentration given by FISCHER (1966). At pH 4 the dominant species was found to be AuCl_2^- whereas at pH 9 it was AuO_2^- . This presents a problem at the lower pH since, as BAES and MESMER (1976) indicate, Au(III) produces more stable complexes than Au(I) and, in the presence of the latter valence state, disproportionation reactions of the type: $3\text{AuX}_2^- \rightleftharpoons \text{AuX}_4^- + 2\text{Au}^0 + 2\text{X}^-$ will occur. If the stable species is AuCl_4^- , then the theoretically possible concentration of 10^{-17} M, as calculated by ONG and SWANSON (1969) indicates that the observed concentration cannot be explained in terms of this ion. BAES and MESMER (1976) have also noted the existence of the neutral complexes AuCl_3 , $\text{Au}(\text{OH})_3$, $\text{Au}(\text{OH})\text{Cl}_2$ and $\text{Au}(\text{OH})_2\text{Cl}$ which, with solubilities of the order of $10^{-5.5}$ M (0.6 ppm), would more than adequately solve the concentration problem. However since AuCl_3 is stable only at pH < 2 and also, for the reaction: $\text{Au}(\text{OH})_3 + 3\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Au}^0 + 3\text{H}_2\text{O}$, $\Delta G = -5.8 \times 10^5$ joule/mole (-140 kcal/mole), it is unlikely that these species would occur under natural conditions. The formation of the very stable $\text{Au}(\text{CN})_2^-$ ion by the action of cyanoglycosides could explain the Au uptake by plants but, as LAKIN *et al.* (1974) comment, $\text{Au}(\text{CN})_2^-$ would have limited mobility due to the rapid hydrolysis and enzymic destruction of the CN^- ion in nature. Thus the mobility of Au in the weathering cycle does not appear to be adequately explained in terms of inorganic complexes of Au.

There is no doubt that the molecular weight range of humic substances, estimated by DUBACH and MEHTA (1963) to be in the range of 2000–300,000, demands that a large proportion of such molecules are of colloidal size. Colloidal phenomena have been observed by ONG and SWANSON (1969) in experiments with Au and humic acid. These investigators found that AuCl_4^- was reduced to colloidal Au in the presence of humic acid which was also found to act as a protective colloid for the Au sol so formed. As a result of such observations a colloidal model of Au mobilisation in the weathering cycle was proposed. Although the reducing groups of humic acid are capable of producing colloidal Au from AuCl_4^- the problem of concentration of this ion remains. Also, given sufficient residence time in an environment with an excess of humic acid, it is likely that the complexing groups of this material will react with colloidal Au to produce a humic acid complex. For environments where organic activity is low, a colloidal model of transport is more satisfactory than one based on inorganic complexes.

The results of experiments reported above clearly indicate the complexation of Au by humic acid. The Au solubility in the presence of 500 $\mu\text{g}/\text{ml}$ (ppm) humic acid, which was up to 330 ng/ml (ppb), is far in excess of that found in river water (0.002 ppb). An organic complexation model could thus readily explain the observed Au solubility in the hydrosphere.

Although analytical restrictions made it necessary to carry out experimental work at higher concentrations than those in nature, the results are believed to be applicable to the mobilisation of Au. In the experiments the concentration of humic acid was kept well in excess of Au, as is the case in the natural environment. Whereas the content of humic substances in river water is highly variable, a value of only 5 $\mu\text{g}/\text{ml}$ (ppm) would be in excess of Au by the order of 10^6 . From a more general point of view, REUTER and PERDUE (1977) have shown that complexation of trace metals in river waters by humic substances can be significant even in the presence of high excesses of major cations.

The concept that Au cannot be complexed by humic acid derives from the fact that such complexation involves oxidation, and that humic acid has been generally considered a reducing agent. Although reducing conditions occur in areas of peat formation, such conditions are not necessarily due the presence of humic acid nor do they apply universally to interfaces between soil and rock. The Eh values of the 500 $\mu\text{g}/\text{ml}$ (500 ppm) humic acid preparations, which are of the order of +300 mV, indicate that these are not strongly reducing in character. Waters such as these, which contain atmospheric oxygen, would be relatively common in soil profiles where free drainage exists. SZILAGYI (1971) made a comprehensive study of the redox characteristics of suspensions of peat humic acid in H_2O and derived a value for E_0 of +0.7 V. SHCHERBINA (1956) has noted that the redox potential of complexes of Au decreases with their increasing stability. Thus for reactions of the type: $\text{AuX}_4^- + 3\text{e}^- \rightleftharpoons \text{Au}^0 + 4\text{X}^-$ where X is respectively Cl^- , Br^- and SCN^- the E_0 values are +1.00, -0.86 and +0.66 V. If the stability of the humic acid complex of Au is near that of $\text{Au}(\text{SCN})_2^-$, as suggested by SHCHERBINA (1956) and supported by the solvent extraction results, it is possible that oxidation of Au can occur under natural conditions.

DRAEGER and LAUER (1967) have noted that almost 70% of the Earth's land surface is covered by forest or grassland. The sulphide deposits carrying Au from which AuCl_4^- may be readily generated, occupy an insignificant proportion of this surface. It therefore seems plausible that a substantial amount of Au, which has its origin as a trace element in the lithosphere, is mobilised by some process other than the formation of AuCl_4^- . Humic acid, originating through microbial action in the products of degeneration of the extensive vegetation cover, appears well suited to such a role. Since it is present in soil water from the time of formation of the interface between soil and rock, it could generate a humic acid complex of Au by reaction with traces of the metal. Such a complex of Au is not subject to the problems of stability and solubility, characteristic of ionic or colloidal Au, and it could migrate readily in the hydrosphere.

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