

Low temperature Au-humic acid interaction experiments: implication for Au transport in surface conditions

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Experiments were conducted at 25°C in aqueous solutions with variable concentrations of Au and humic acid (HA) in order to characterize the formation of Au-HA complexes, reduced colloidal Au⁰, and the effect of photo-redox activity. The literature concerning the interaction of gold and humic substances at low temperature is not extensive and, in many cases, contradictory. For many years, it has been suggested that Au transport in ore systems is mostly achieved through inorganic complexation, however, low temperature experiments indicate that Au solubility is enhanced in the presence of humic and fulvic acids suggesting the existence metal-organic complexes (Baker, 1978; Vlassopoulos *et al.* 1990). Other studies suggest that the role of humic substances is to reduce Au(III) species rather than forming gold-organic complexes (Ong and Swanson, 1969; Machesky *et al.*, 1992). None of these studies explored the photo-redox effect on the system Au(III) – humic acid, however the photo-redox effect have been considered for other elements in nature (Hoigné, 1996).

Experimental methodology

A pure (99.99%) gold wire and humic acid obtained from Fluka[®] Chemical Corporation were used in the experiments. The humic acid (HA) solution was prepared by dissolving the powder in distilled-deionized water. The solution with a pH = 6.7 was filtered through a 0.45 µm Millipore filter. The Au solution was prepared by dissolving 1mm of gold wire in aqua regia and then diluted, and the pH adjusted to a value of 5.85 by adding NaOH. A paired set of solutions with a Au/DOC ratio up to 20 (Au=µmol/L, DOC=mg/L) were prepared, one set of solutions were stored in total darkness and the other set were left outdoor in order to permit direct sunlight exposure. Both sets of solutions were left to equilibrate with the atmospheric CO₂ at 25°C and the pH was measured daily for a period of 10 days. Paired solutions stored under dark and sunlight

conditions were filtered through a Centricon-10[®] (molecular weight (MW) = 10000) membrane cut off filters. These solutions were analysed for dissolved Au using inductive-coupled plasma mass spectrometry (ICP-MS) before and after filtration.

Experimental results and discussion

The addition of Au (III) in the form of chloro-hydroxo complex to the HA solution induce a significant decrease of the pH, from pH = 6.7 to a steady-state value of pH = 5.4 at ~4–5 µmol of Au/mg of DOC. This steady-state value represents the maximum HA uptake capacity for Au needed to form the metal-organic complex. A reddish colour developed with a maximum wavelength absorbance at 530.4 nm determined by photocolourimetry. The absorbance is proportional to the Au/DOC ratio. After 6 days, only those solutions with Au/DOC > 4 and exposed to sunlight showed the formation of a gold-purple colloid and a purple film was deposited

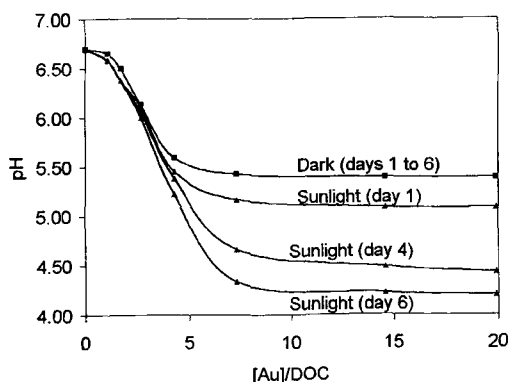


FIG. 1. pH vs [Au]/DOC ratio during six days. The solutions stored in dark conditions have the same pH of the first day. In the sunlight exposed samples the increase of H⁺ activity is concomitant with Au⁰ formation.

on the container walls, in these sunlight exposed solutions the proton activity is enhanced up to pH=4.2; about 1.3 pH units lower than those stored under dark conditions (Fig. 1). This is interpreted as an excess of Au(III) that did not react with HA to form the organic complex which is reduced to Au⁰ gold-purple colloid with sunlight exposure.

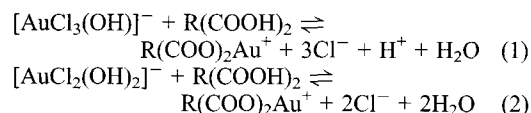
After six days, solutions stored under dark and sunlight conditions were filtered through a membrane (Centricon-10[®]) cut off filters. The Au concentrations analysed before and after filtration, are shown in table 1. Using a complexation capacity of 5 micro Mol of Au/mg of DOC, it is possible to estimate the mass of Au transformed from AuCl_xOH_y⁻ complex (where X + Y = 4) to a Au-humic complex. Assuming that the Au in solution that managed to pass through the filter is AuCl_xOH_y⁻, then the total Au concentration is given by,

$$[Au]_{TOTAL} = [AuCl_xOH_y]^- + [Au-Humic] + [Au^0] \quad (1)$$

THROUGH FILTER + RETAINED BY THE FILTER

The results listed in Table 1 show the calculated AuCl_xOH_y⁻ concentration values that remained in solution and the measured values for both dark and sunlight conditions after filtration. These values indicate that in the experiments exposed to sunlight there is a considerable amount of Au⁰ colloid retained in the filter. The Au complexed with DOC is [Au]_{COMPLEXED BY DOC} = 5 × [DOC], and the excess of AuCl_xOH_y⁻ complex that do not react with DOC is reduced to Au⁰ only under sunlight exposure. Mass transfer calculations showed that the membrane filters used in this study can retain about 95% of the HA macromolecules as well as all the reduced Au⁰ colloid. The rate of this reductive process on the formation of the Au⁰ colloid, is proportional to the intensity and time of light exposure and to the humic concentration in the solution.

Humic acids contain many functional groups that could be involved in the metal binding process. For sake of simplicity, a carboxylic is chosen as the *a priori* functional group that is mainly responsible for the formation of the Au-organic complex. Assuming a bidentate bonding with a carboxylic, two possible reactions can be drawn:

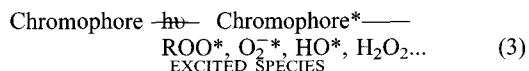


According to these experimental results, reaction (1) is the most likely to occur because it involves the release of hydrogen ions which is compatible with the pH decrease observed. In the case of the samples

TABLE 1. Measured concentration of Au (micro Mol/L) and DOC (mg/L), [Au] before (BF) and after filtration in dark (AFD) and sunlight (AFS) conditions. Computed concentration using equation 1 and assuming that the gold retained by the filter is only Au-humic complex: (A) Au complexed with DOC, (B) Au as AuCl_x(OH)_y, and (C) DOC not complexing gold

DOC Total	(BF)	Au/DOC	(A)	(B)	(C)	(AFD)	(AFS)
2.5	74.2	29.7	12.5	61.7	0.0	58.00	21.30
3.7	74.2	19.9	18.6	55.6	0.0	52.70	16.30
5.1	74.2	14.6	25.5	48.8	0.0	43.00	0.27
10.2	74.2	7.3	50.9	23.3	0.0	18.80	0.10
27.2	74.2	2.7	74.2	0.0	12.3	0.50	0.03
50.9	74.2	1.46	74.2	0.0	36.1	0.62	0.02
70.0	74.2	1.06	74.2	0.0	55.2	0.52	0.01

exposed to the sunlight, where the excess of Au-chloro-hydroxo not complexed with humic acid is reduced to colloidal Au⁰, could be involved the chromophores present in dissolved organic matter. The excitation of a chromophore by sunlight produce a reactive species with a very short life (Hoigne, 1996), that can react as a reductant for Au(III):



Future work will involve the characterization of organic functional groups in HA (extracted from tropical soils) involving Au-organic complexation. These preliminary results show that Au-HU complexation can play a significant role in the transport of Au at surface conditions. Moreover, the observed photo-redox effect on pH is not negligible and may render some constrains on the Au-HU speciation and the formation of Au⁰ colloid. Formation of a colloid consequently adds to a significant effect in Au transport, particularly in tropical hydrodynamic surficial systems where the presence of organic matter is ubiquitous.

References

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