

The effects of sulfur on the sorption of gold by organic matter under hydrothermal conditions: experimental study at 200–400°C and $P_{\text{tot}} = 1 \text{ kb}$

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It is known that noble metal deposits occur in black shales usually bearing sulfides and organic sulfur. For the Kupferschiefer deposit in Poland it was established that noble metals and other transition elements have been concentrated by a process of catalytic oxidation and desulfurization of organic matter (OM) [Kucha, *et al.*, 1999]. Numerous investigations focused on the gold adsorption onto sulfide mineral surfaces, and it was found that gold ions are reduced and adsorbed much more rapidly on pyrite (Py) and pyrrhotite than on quartz and iron oxides [Ran, *et al.*, 2002]. Although the adsorption of Au complexes on sulfides is quite well understood, there have been no experimental studies of gold sorption on OM in sulfur bearing systems under hydrothermal conditions. The main purpose of the present work is to estimate the effects of sulfur on the sorption capacity of asphaltene (As) with respect to gold in the hydrothermal temperature range between 200 and 400°C and at a fluid pressure of $P_{\text{fl}} = 1 \text{ kb}$.

The investigated system was chosen to be as simple as possible and can be described as having four major components: water, As, gold, and sulfur. The As (C 75.13, O 18.10, H 6.54 mass %, traces of N and S) extracted from the brown coal of Pavlovskoe deposit, (Primorye, Russia) was used as model organic matter. The hydrothermal experiments were carried out in externally heated autoclaves made of Ti–Ni alloy. The pressure was maintained by adding appropriate amounts of doubly distilled water, in accordance with the P – V – T relations for water. The measured amounts of water along with 50 mg of dry As were placed into gold ampoules (OD = 10, L = 100 mm), which also served as the source of gold by dissolution under the run conditions. To evaluate the effects of sulfur on the sorption of gold, three systems had been studied: C–O–H–Au, C–S–O–H–Au, and C–S–Fe–O–H–Au. In the first series of experiments, 10 mg of native sulfur (S_2) were used as the source of S, while in the second series 30 mg of Py (FeS_2) were used for this purpose. Native S was placed in the same ampoule together with As. Powdered pyrite was included in a separate ampoule (10×0.1×50 mm) which was placed inside the larger one, containing the As. Preliminary runs had shown that native S was completely dissolved under the experimental conditions, whereas about 80% of Py was retained in the solid run products.

Although at room temperature the sorption equilibrium can be reached within 3–5 days, the duration of our runs varied from 30 to 14 days at 200 and 400°C, respectively. This allowed us to make sure that equilibrium Au concentration was attained. After each run, the autoclaves were quenched with cold water 3–5 minutes. The quenched solutions (QS) were filtered through thin paper filters. Further fractionation of the organic matter precipitated on the filter included its heating at 50°C with an alcohol-benzene (1:2) mixture for 12–20 hrs. Subsequent filtration was used to separate an organic soluble fraction (SF) from the solid residue (SR)-kerogen. Then hydrocarbons of both fractions were subjected to oxidation and thermal destruction by concentrated inorganic acids until moist salts were formed. Gold was concentrated from these salts by alkylamine, and then analyzed by electrothermal atomization and AAS method with Shimadzu AA-6800. The integral experimental error of the entire process is estimated to be about 20%. The X-ray analysis of initial As, as well as the resulting kerogen, has verified the absence of any mineral impurities. IR-Fourier-spectra of the SF and SR were collected by a Nicolet 6700 spectrophotometer.

The concentration of Au was separately measured in: the QS, SF and SR for the C–O–H–Au, C–S–O–H–Au, and C–S–Fe–O–H–Au systems at 200, 300 and 400°C. These data are represented in Fig. 1 where a dependence of Au content on temperature is shown for all studied fractions of these three systems. There are some visible differences in the temperature dependence of Au content in the different fractions. The lowest Au concentration was measured in QS of the sulfur free (C–O–H–Au) system. The highest Au content was

obtained in the runs with native S which was entirely dissolved according to X-ray data. In this system the solubility maximum was observed at 300°C. In the C–S–Fe–O–H–Au system where S-speciation was caused by incongruent Py dissolution, the total Au concentration grows with increasing temperature up to 400°C.

It appears that the Au content in the SF does not strongly depend on either temperature or the system composition. All noted discrepancies of log mAu values are within the estimated experimental uncertainties. Thus, the effect of S on Au sorption by the SF is very minute. Gold content in the kerogen exceeds its content in the SF under similar experimental conditions. The largest difference between the two values of log mAu reaches at 400°C. It is noteworthy, that in the presence of dissolved S species, the sorption capacity of kerogen increases, especially in the runs with the Py-bearing system at 400°C (fig. 1). According to X-ray data, under these conditions Py transforms to pyrrhotite that must also be accompanied by changes of both the activity of sulfur and the redox potential of the system.

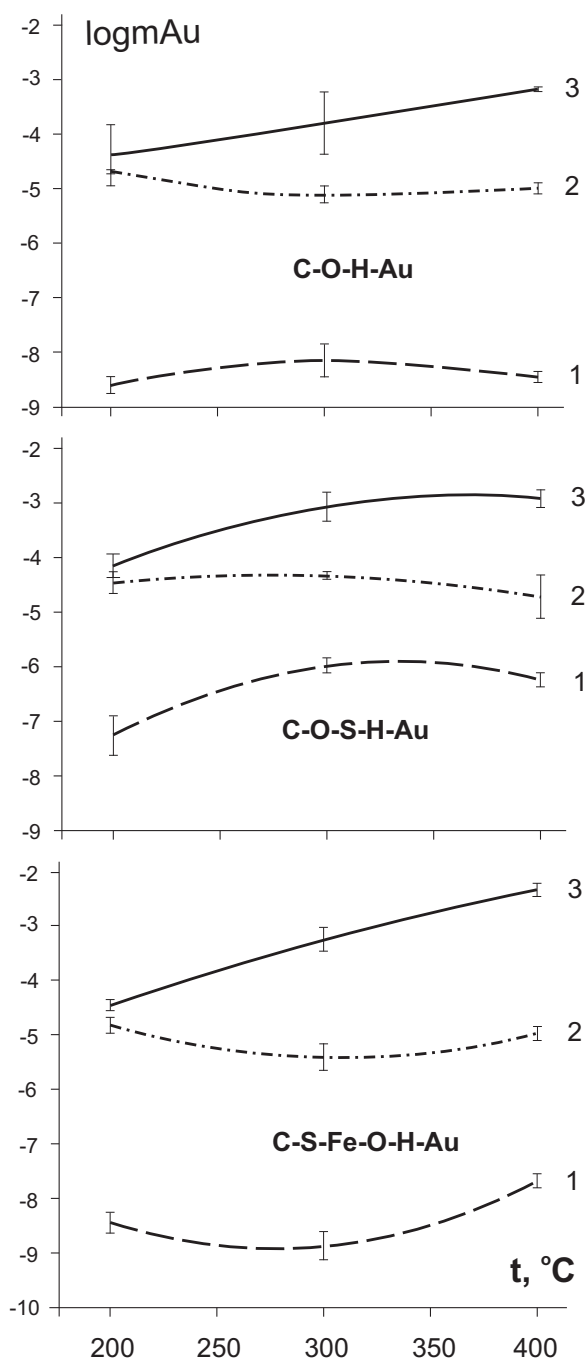


Fig. 1. Temperature dependence of the measured gold concentration in the quenched aqueous solutions (1), soluble organic fractions (2), and the kerogen (3) at $P_{fl} = 1$ kb. Error indicates the statistical uncertainty for Au content measured in 4 runs for each test series. Curves are a guide to the eye.

In addition to the analysis of organic fractions, the Au content of Py was also measured after the runs at 300 and 400°C. The starting Py had contained Au at about 0.99×10^{-4} mass %. With increasing temperature, the amount of Au in Py increases to 1.88×10^{-4} mass % at 300°C and to 3.34×10^{-4} mass % at 400°C. For better comparison with the Au content in Py, we have recalculated the Au content in kerogen, presented in Fig. 1 as log mAu, into mass%. Thus, the kerogen coexisting with Py contains about 1.17×10^{-2} % Au at 300, and 0.09 % at 400°C. Therefore, we can conclude that Au sorption by OM substantially exceeds the same on Py, contrary to some expectations.

The measured Au contents in the QS and organic fractions at 200–400°C testify to the high degree of metal extraction by OM from hydrothermal solutions. It was shown before, that the sorption due to metal-organic complexation is assumed to be the predominant mechanism of metal concentration in carbon bearing rocks [Varshal, *et al.*, 1996; Plyusnina, *et al.*, 2000]. The sorption of Au by hydrocarbons depends on their composition and molecular structure. For these reasons we used IR-spectroscopy to determine the functional groups present in the organic fractions.

In the present study, the aliphatic groups in the IR-spectra of starting As are well recognized by absorbance band at 1216–1272, 1375–1460, 2852–2923 cm^{-1} exceeding the number and intensity of spectral bands for the aromatic groups (Fig. 2). After the experiments at 200–400°C, the aromatization of aliphatic matter in the SF and in SR is obvious as can be determined by the well resolved absorbance bands at 720–880 cm^{-1} associated with benzene ring vibrations. The IR-spectra of the SF demonstrate the increasing intensity of the bands due to aromatic groups at 1566, 650624 cm^{-1} with increasing temperature (tables 1, 2). Due to the low variations in Au concentration of all SF, we can conclude that sulfur does not form mixed C–S–Au species. The IR-spectra of the resulting kerogen are especially interesting due to some variations in Au contents noted in the systems bearing pyrite and elemental S. By the absence of absorbance bands for C=O vibrations at 950, and 1300 cm^{-1} , these spectra illustrate the higher degree of aromatic condensation in the S-bearing systems. The IR-spectra of kerogen reflect the predominance of aromatic ring condensed structures. Relatively high intensities of absorbance bands around 866–671 cm^{-1} may be related to the mono-bi-tri-substitution of aromatic structures. Possibly, gold is involved in these substitutions. At the same time, Au complexation with carboxyl and carbonyl groups is also possible [Varshal, *et al.*, 1996]. A very strong absorbance band at 417 cm^{-1} was present in the IR-spectrum of the kerogen derived from the 400°C run in the pyrite-bearing system. The highest Au content measured in this run supports the possibility of a C–S–Au bond.

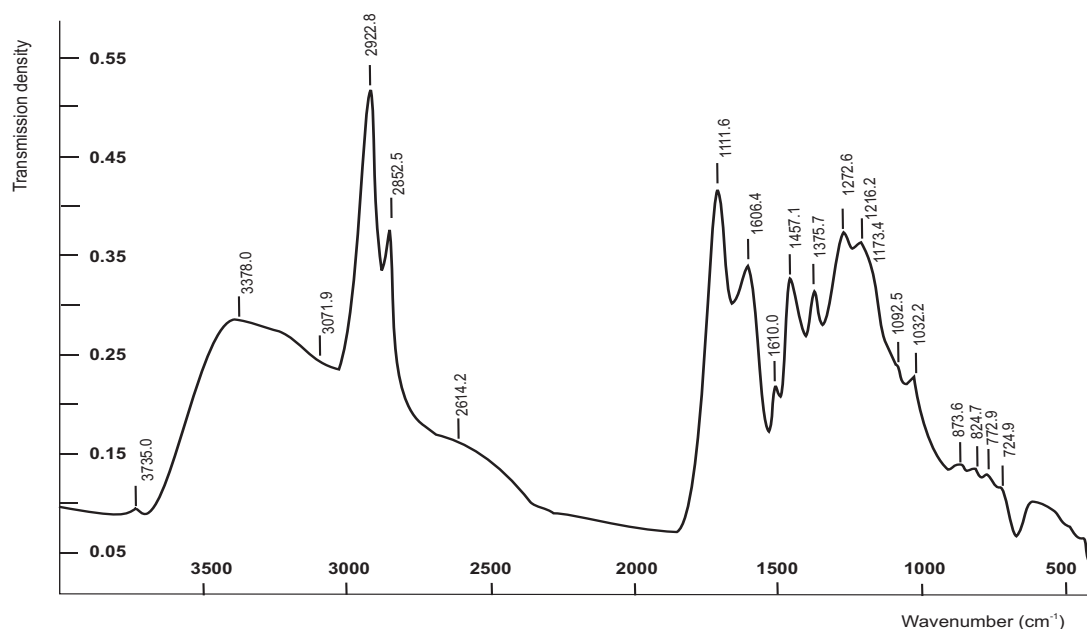


Fig. 2. The Fourier IR spectrum of the starting asphaltene

Present experimental results point to some differences in gold sorption on organic matter for the systems: C–O–H–Au, C–S–O–H–Au, and C–S–Fe–O–H–Au. The observed variations may be related to differences in the pyrite and S dissolution mechanisms. In agreement with thermodynamic data, Au was most likely transported as a bisulfide complex. The stability of $\text{Au}(\text{HS})_2$ complexes is redox sensitive, and a change in the oxidation state of Au-transporting fluid can lead to Au precipitation. Variation of S activity in solution can result in destabilization of $\text{Au}(\text{HS})_2$ complexes and, consequently, in metal precipitation. Under

oxidizing conditions of subsequent metamorphic-metasomatic processes Au-organic complexes disproportionate and metallic gold precipitates from fluids in form of finely dispersed elemental particles included into sulfide, quartz, graphite and so on.

Table 1. Spectral bands of IR absorbance (cm^{-1}) by the soluble organic fractions as a function of system compositions at 200°C

System compositions			Functional groups
C-O-H-Au	C-S-O-H-Au	C-S-Fe-O-H-Au	
624 vw*	621 w	628 vw	C-H, C-C Ar
721	721	721	C-C Ar
762 w	759 vw	-	C-C Ar
811 vw	794 w	795 vw	C-C Ar
881 ww	875 ww	-	C-C Ar
924 w	924 w	926 vw	C-O-C
1040 w	1052	1049	C=O Ar, C-C Al
-	-	1090 ww	CHOH
1114 w	1114 w	-	C-C Al
1271	1271	1271	CH ₂ Al
1384 w	1385 w	1386 w	CH ₃ Al
1460	1457 w	1457 w	COOH, COO ⁻ , CH ₃
-	1464 w	1464 w	COO ⁻
1567 s	1568 s	1570 s	COO ⁻
1702 s	1705 s	1705 s	C=O
2852 s	2851 s	2851 s	CH ₂ , CH
2920 s	2920 s	2920 s	CH ₄
3407 s	3407 s	3407 s	OH, CH ₄

* for tables 1, 2: Ar – aromatic, Al – aliphatic; intensities: w – weak, vw – very weak, ww – weak wide, s – strong, vs – very strong, medium intensities are given without letter symbols

Table 2. Spectral bands of IR absorbance by the soluble organic fractions as a function of system compositions at 300°C

System compositions			Functional groups
C-O-H-Au	C-S-O-H-Au	C-S-Fe-O-H-Au	
651	652	652	C-C Ar
720 w	721 w	718 w	C-C Ar
-	749 w	749 w	C=C Ar
1019 w	1019 w	1019 w	C-O Al
1341 w	1344 w	1344 w	CHOH, CH ₂ OH
1409 s	1409 s	1410 s	C-O-H
1566 s	1568 s	1568 vs	COO ⁻
2368 vw	2360	2360	-CH ₂ -CH ₃ Al
2849	2850	2850	CH ₃ , CH ₂ , CH
2917	2918 s	2918	CH ₃ , CH ₄
3388	3383	3383	OH

The most important results of this study may be summarized as follows.

1. Hydrothermal treatment of asphaltenes in aqueous sulfur-bearing environment leads to accumulation of sulfur in the kerogen, whereas S-bearing functional groups were not identified in the IR-spectra of soluble organic fractions. As a result, any sensible variations of Au concentration in the soluble organic fractions were not found in the studied systems.

2. Dissolved sulfur species in hydrothermal fluids facilitate aromatization, condensation, and sorption activity of the kerogen.

3. The sulfides commonly present in organic-rich geologic environments, have stronger effects on the sorption capacity of kerogen than elemental sulfur.

4. It was experimentally determined that the sorption capacity of organic matter is more dependent on its molecular structure than on Au content in coexisting solutions.

5. Sulfides may serve as catalysts of organic matter condensation and metals sorption on it from hydrothermal solutions. It was shown, by the example of pyrite, that Au chemisorption by organic matter markedly exceeds Au sorption on sulfides under the same conditions.

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