EXPERIMENTAL STUDY OF GOLD AND PLATINUM GROUP ELEMENTS ACCUMULATION IN BLACK SHALES

G.M.Varshal, T.K.Velyukhanova, D.N.Chkhetia,Yu.V.Kholin*, T.V.Shumskaya, O.A.Tyutyunnik, A.V.Korochantsev, I.Ya.Koshcheeva, I.V.Bikov, A.Kh.Galuzinskaya

Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS

*Chemical Faculty, Kharkov State University, Svobody Sq.4, 310077 Kharkov, Ukraine

The carbonaceous matter of black shales is known as a result of diagenetic and metamorphic transformation of humic acid (HA), the latter being main components of organic matter of fluvial and marine sediments, soils and suspended matter in waters. In order to find out the mechanism of gold (III) and platinum group elements (PGE) accumulation in black shales as well as for the quantitative estimate of chemical bond strength of those metal ions with carbon- bearing matrix the number of physical chemical data are necessary. The data are as following: nature and protolytic parameters of HA oxygen-bearing functional groups, the data on HA sorption capacity in relation to noble metal ions. The objects selected for investigation are presented with HA isolated from peat and marine sediment samples of Peru oceanic shelf.

HA properties were studied by use of IR-spectrometry, potentiometric titration, CHNS-analysis and X-ray diffraction analysis.

It was shown that IR-spectra of HA from peat are very near to those from marine sediments. Very intensive 1605-1630 cm^{-1} absorption band is result of valent asymmetric oscillations of ionised carboxyl groups. The intensive 1700-1720 cm^{-1} absorption band is markedly revealed, being a result of valent asymmetric oscillations of nonionised carboxyl groups. 1040-1050 cm^{-1} absorption band characteristic of oxygroups is also registered. The presence of carboxyl and phenol oxygroups in HA structure provides the possibility of strong complex compound formation with noble and other metal ions.

The potentiometric titration of HA ashless preparations was accomplished by separate weight method by use of KOH aqueous solutions free of CO_2. Three distinct peaks are observed on the differential curves of peat HA potentiometric titration, whereas corresponding titration curve of marine sediment HA have only two peaks. Quantitative physical chemical analysis (QPCA) was applied for determination of HA functional group dissociation constants (pK_a) from potentiometric titration data [1]. For the treatment of potentiometric titration data the Langmuir transformed equation is used. The isotherm parameters in this procedure are calculated by the non-linear least square method by use of CLINP 1.0 program. It was established that in both cases carboxyl group pK_a values are varying in

substantionally broad range: HA of peat samples are characterised by 5-7 (mean value of pK_a=6.1), that of marine sediments are correspondingly 6-8 (mean value of pK_a=7.0). The distribution function of HA functional groups in relation to pK_a values is in accord with Gauss distribution low .

The contribution of aliphatic and aromatic components in HA structure was estimated by use of X-ray diffraction analysis applying the HA experimental diffractogram resolution on individual peaks [2]. The contribution of aliphatic and aromatic components in HA of peat samples is evaluated as 77.2% and 22.8% correspondingly. Those values in relation to HA of marine sediments were found as 66.0% and 34% correspondingly.

The sorption of Au(III), Pt(IV), Pd(II), Rh(III), Ru(IV) and Os(IV) ions in a form of their chloride complexes was studied by use of modelling experiments. The ashless HA preparations isolated from peat and marine sediments were used. It was found that equilibrium in PGE ions -HA system is attained in 2 hours-1 day time interval and that of Au(III)- HA system in 7 days. It was established that HA isolated from peat and marine sediments are characterised with very high and rather similar values of sorption capacity in relation to Au(III), Pd(II), and Rh(III) ions. The sorption capacity of peat HA is as following: Au 320 mg/g, Pd 100 mg/g, Rh 11 mg/g, Ru 16-19 mg/g, Os 23 mg/g. The similar value of marine sediment HA was found as following: Au 351 mg/g, Pd 110 mg/g, Rh 11.6 mg/g.

An interesting phenomenon was observed in Pt(IV) sorption. It was found that HA isolated from peat and marine sediments practically do not sorb Pt(IV) ions in contrast to other carbon bearing objects such as coal, carbonaceous particles of rocks and bitumen [2]. The adjustment of this phenomenon causes is important for the understanding of black shale noble metal ore deposit genetical peculiarities.

The treatment of gold and PGE ion sorption data by QPCA method allowed to estimate the chemical bond strength values of these metal ions with HA sorption centra.

It was demonstrated that the sorption of Au(III), Pd(II) and Rh(III) on peat and marine sediment HA is convincingly ascribe by Langmuir isotherm equation.

The isotherm parameter calculation by non-linear least square method was resulted in estimation of HA sorption center conventional affinity constants in relation to noble metal ions (table). Just those constants are considered as quantitative parameters of metal ion chemical bond strength in relation to HA functional groups.

Table

Conventional affinity constants of HA sorption centers in relation to Au(III) and PGE ions

Metal ion	lg β	
	HA of peat	HA of marine sediments
Au(III)	4.4	6.0
Pd(II)	4.7	5.0
Rh(III)	3.4	3.2
Ru(IV)	3.5	

The distribution function of HA sorption centra in respect of conventional affinity constant logarithms for every metal ions was carried out by use of CAS algorythm. It was found that this distribution is in accord with Gauss distribution low. The energetic inhomogeneity of HA functional groups in the sorption of ions shown in the Table is practically not exhibited.

The chemical bond strength is considered as the most important parameter governing the relation between the noble metal chemical forms in carbon-bearing rocks and indicating the possibility of their quantitative extraction for analytical or technological purposes.

1. Kholin Yu.Y. A Quantitative Physical-Chemical Analysis of Equilibria on the Surface of Complexing Silicas. Functionalized Materials. V.2. Kharkov. Oko. 1997. 137 p.
2. Varshal G.M., Velyukhanova T.K, Korochantsev A.V., et al. // Geokhimiya. 1995. № 8. S.1191-1198.