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International Journal of Coal Geology 68 (2006) 127 – 134
International Journal of COAL GEOLOGY
www.elsevier.com/locate/ijcoalgeo

Anomalous gold contents in brown coals and peat in the south-eastern region of the Western-Siberian platform

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Received 12 January 2005; accepted 9 January 2006
Available online 24 March 2006

Abstract

One hundred twenty-two samples of Jurassic and Paleogene brown coals and 1254 peat samples from the south-eastern region of the Western-Siberian platform were analyzed for gold by the neutron-activation method. Mean content of Au in Jurassic coals is 30±8 ppb, in Paleogene coals is 10.6±4.8 ppb, and in peat is 6±1.4 ppb. Concentrations of gold as high as 4.4 ppm were found in coal ash and 0.48 ppm in the peat ash. Coal beds with anomalous gold contents were found at Western-Siberian platform for the first time.

Negative correlation between gold and ash yield in coals and peat and highest gold concentrations were found in low-ash and ultra-low-ash coals and peat. Primarily this is due to gold's association with organic matter.

For the investigation of mode of occurrence of Au in peat the bitumen, water-soluble and high-hydrolyzed substances, humic acids, cellulose and lignin were extracted from it. It was determined that in peat about 95% of gold is combined with organic matter. Forty to sixty percent of Au is contained in humic acids and the same content is in lignin. Bitumens, water-soluble and high-hydrolyzed substances contain no more than 1% of general gold quantity in peat.

The conditions of accumulation of high gold concentrations were considered. The authors suggest that Au accumulation in peat and brown coals and the connection between anomalous gold concentrations and organic matter in low-ash coals and peat can explain a biogenic–sorption mechanism of Au accumulation. The sources of formation of Au high concentration were various Au–Sb, Au–Ag Au–As–Sb deposits that are abundant in the Southern and South-Eastern peripheries of the coal basin.

Keywords: Gold; Geochemistry; Brown coals; Peat; Western-Siberian platform; Russia

1. Introduction

The greatest amount of information on anomalous gold contents in coals has been accumulated for the past hundred years (Goldschmidt and Peters, 1933; Bouška, 1977; Boyle, 1979; Gayer and Rickard, 1994; Baruah et al., 1998), particularly during the last 20 years (as reviewed by Yudovich and Ketris (2004)).

High gold contents in coal can be considered as potential source of noble metals. Although much attention have been paid to the problems of gold accumulation in coal deposits, the geochemistry of gold in coals leading to different concentrations, conditions of gold in coal layers and the mechanisms of formation of anomalous gold concentration are still not well understood. Goldschmidt and Peters (1933) proposed biogenic–sorption mechanism of Au accumulation in coals. Boyle (1979) while studying gold geochemistry paid attention to the important role of hydrothermal

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0166-5162/$ - see front matter
doi:10.1016/j.coal.2006.01.004

processes in formation of anomalous gold concentrations. Seredin (2002) explained a fluid–hydrothermal model of Au accumulation in germanium-bearing coals of Prymorye, Eastern Russia. Shor et al. (1996) demonstrated the mechanism of infiltration concentration of noble metals in coals under stable conditions in the Western-Siberian platform.

Recently new data on gold distribution in peat and brown coals of the south-eastern region of the Western-Siberian platform was collected by the authors. We found coal layers and peat deposits with anomalously high Au concentrations. Investigations into coal or peat of different ages within certain section made it possible to determine the main relationship regulations in gold accumulation and migration during the process of coal formation.

2. Methods

Twenty-two Jurassic coal deposits (Tyumenskaya suite), seven Paleogene coal deposits (Novomihaylovskaya suite), and 15 deposits of peat at the south-eastern part of the Western-Siberian platform were investigated (Fig. 1).

Coal samples from Tyumenskaya suite were taken from core of oil-exploration and oil-prospecting boreholes from the depth 2 to 3 km.

Paleogene coals were sampled both from cores of prospecting holes (Tuganskoe, Talovskoe, Vershininskoe, Kolpashevskoe, and Timskoe coal deposits), and at the outcrops (Regenskoe and Lagernosadskoe deposits).

The peat samples were taken with peat bore from 0.05 to 0.1 m intervals. A total of 1254 peat samples, 53 Jurassic coal samples, and 69 samples of Paleogene coals of Western-Siberian platform were studied.

Au content was determined by neutron-activation method in the nuclear–geochemical laboratory of the Tomsk Polytechnic University (TPU). The analyses were made at the nuclear research reactor of the Scientific Research Institute (SRI) of Nuclear Physics at Tomsk Polytechnic University. The method of traditional instrumental neutron-activation analysis (INAA) with samples of 200 mg weight (analyst A. F. Sudiko) and a specially developed neutron-activation method (SDNAA) of Au determination from the samples of 5 to 10 g (analyst V.M. Levitskiy) were used. The detection limit of Au^{198} isotope for INAA is

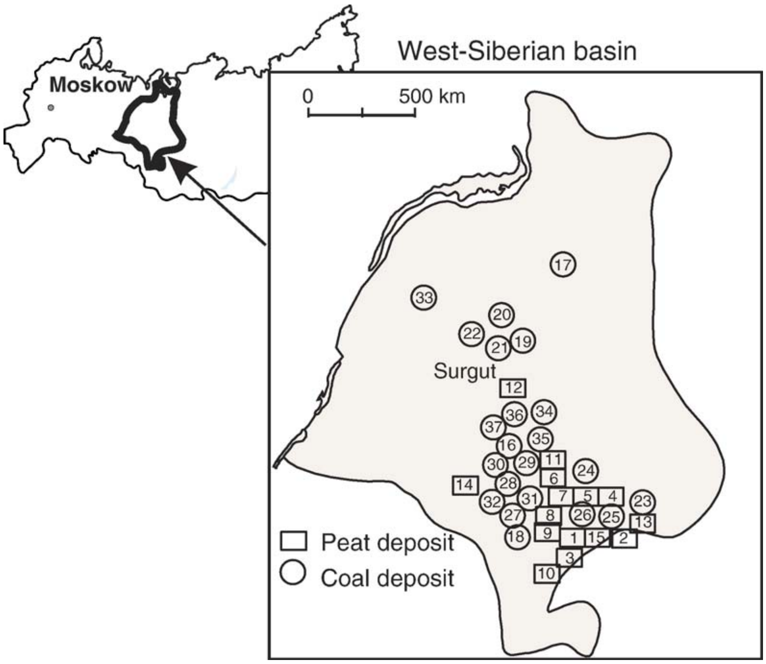

Fig. 1. Location of studied sections: 1 — peat: 1 — Klyukvennoe; 2 — Chistoe; 3 — Vodorazdelnoe; 4 — Berezovaya Griva; 5 — Semiozerye; 6 — Kolpashevskoe; 7 — Suhovskoe; 8 — Vasyuganskoe; 9 — Gusevskoe; 10 — Arkadevskoe; 11 — Aygarovskoe; 12 — Saim; 13 — Puhovskoe; 14 — Western Moiseevskoe; 15 — Petropavlovskiy Ryam; 2 — brown coal: 16 — Mildgeno; 17 — Urengoiskoe; 18 — Verhnetarskoe; 19 — Kavrinskoe; 20 — V. Tromeganskoe; 21 — Konitlorskoe; 22 — Ay–Pimskoe; 23 — Tuganskoe; 24 — Kolpashevskoe; 25 — Lagernosadskoe; 26 — Talovskoe; 27 — Tabaganskoe; 28 — Shirotnoe; 29 — Gerasimovskoe; 30 — Luginetskoe; 31 — Severo–Kalinovoe; 32 — Archinskoe; 33 — Yahlinskoe; 34 — Trassovoe; 35 — Stupenchatoe; 36 — Grigorievskoe; 37 — Prigranichnoe.

10 ppb (for 200 g weight) and for the SDNAA it is 1 ppb (for 5–10 g weight).

For the analyze quality control, a part of the samples was ashed. Gold concentration in ashes was studied parallel to the basic sample. By converting coal or peat to ash and vice versa the comparison of results was made.

Modes of occurrence of elements were studied on the basis of standard methods of group peat composition research. The group composition was studied by the successive extraction of bitumens, water-soluble and highly hydrolysable matters, and humic and fulvic acids by Instorf's method (Lishtvan and Korol, 1975). This method was used for the extraction of bitumens by benzol. Then the residue was treated with a HCl solution (5%) in a water bath for the 5 h. In this way water-soluble and highly hydrolysable matters were extracted. The residue was treated with NaOH at the temperature of 80 °C. After repeating the treatment 3 times the solution of humate mixture of Na was formed. Then this solution was filtered and oxidized by the hydrochloric acid. At this part the humic acids were in the residue and fulvic acids were in the solution. Cellulose was extracted from the insoluble residue with the H_2SO_4. Half of gold was determined in the residue and half was ashed at the temperature of 550 °C. The ash was also studied in Au concentration.

3. Results

3.1. Gold concentration in Jurassic coals and coal ash

The average concentration of gold in Jurassic coals from the south-eastern part of the Western-Siberian platform (30 ppb for 22 coal deposits) substantially exceeds its Clarke value for sedimentary rocks (Table 1). Analytical results of coal ash and calculation of weighted average concentration in ash shows 260 ppb of Au with an average coal ash content of 11.7%.

In some coal layers Au concentration in coal ash exceeds 1 ppm with maximum of 4.4 ppm. This suggests that gold does not volatilize from coal during ashing. The highest gold concentrations are for coal deposits from the southern part of the studied region. High gold concentrations are determined not only for coals, but also for the coaly shale where up to 220 ppb of Au were found. It has been noted that towards the central part of the Western-Siberian platform Au concentrations in coals decrease.

Significant Au concentrations in coal ash are found in the low-ash coals with ash content of about 5%, mostly thin ultra-low-ash layers with ash content of 1.4–2.5%. Gold concentrations in coals with various ash contents are presented in Table 2.

Table 1
Average gold concentration in coals and coal ash of Jurassic age, ppb

Deposit, show of coal	Number of samples	A^d, %	In coal	In the coal ash
Ay–Pimskoe	2	15.2	1.2	7.9
Archinskoe	2	12.1	<1	<10
V. Tromeganskoe	1	2.2	42	1900
Gerasimovskoe	5	8.8	22	250
Grigorevskoe	2	11.7	<1	<10
Kavrinskoe	1	15.7	<1	<10
Konitlorskoe	2	6.6	8.1	123
Luginetskoe	4	19.5	41	208
Mildgeno	7	2.1	0.9	42.8
Nizgne–Tabaganskoe	1	11.5	86	750
Prigranichnoe	2	18.6	<1	<10
Severo–Kalinovoe	5	3.3	56	1700
Stupenchatoe	2	3.9	47	1200
Trassovoe	2	13.4	37	283
Shirotnoe	2	4.6	41	902
Yuzgno–Tabaganskoe	3	28.0	74.2	265
Yahlinskoe	10	3.8	1.2	30.5
Average	53	11.7±1.8	30±8	260±63

A^d — ash yield on the dry matter, %.

Correlation between Au contents (C_{Au}) in ash and ash contents is best described by an exponential function (Fig. 2B). There was no distinct correlation noted between gold content and ash content for the coal. It can be approximately described by the power function (Fig. 2A).

3.2. Gold concentration in Paleogene coals and coal ash

Paleogene coals in the region are mainly represented by the middle- and high-ash brown coals and lignites. Gold concentrations in brown coals and lignites are lower than in Jurassic coals but they are considerably higher than the Clarke value for sedimentary rocks. The average concentration calculated for seven coal deposits is 10.6 ppb (Table 3).

Generally these coals considerably differ from the Jurassic ones with low ash content. For coals with average ash content (10–20%) gold concentrations are similar to the Jurassic coals. Reverse correlation between Au concentrations in coal ash and ash contents is obvious. This makes it possible to suggest that gold is connected with the organic matter.

Table 2
Gold concentration in coals and carbonaceous rocks of different ash yield, ppm

A^d, %	Average ash yield of interval, %	Number of samples	In the coal ash	In coal
60–80	70.2	11	0.051	0.034
50–60	54.8	7	0.065	0.037
20–50	32.9	7	0.14	0.046
5–20	10.3	16	0.36	0.027
<5	2.4	13	1.4	0.034

Table 3
Average Au concentration in coals and coals ash of Paleogene age, ppb

Deposit, show of coal	Number of samples	A^d, %	In coal	In the coal ash
Vershininskoe	2	12.2	22	180
Kolpashevskoe	2	11.5	24	210
Lagernosadskoe	16	32.8	44	134
Regenskoe	1	17.3	<10	<20
Talovskoe	44	32.1	2	6.2
Tuganskoe	2	12.4	<10	Not determined
Timskoe	2	Not determined	<10	Not determined
Average	69	18.2±3.4	10.6±4.8	88±36

3.3. Gold concentration in peat and peat ash

Average Au concentration (6.0 ppb) in peat from the south-eastern region of the Western-Siberian platform was calculated as average value for 15 deposits (1254 samples) (Table 4). This concentration is close to the average Au contents for peat deposits from the south of Western-Siberia (Matuhina et al., 2003) estimated from analyzing 248 samples from 10 deposits. Both these average concentrations considerably exceed Au Clark value for sedimentary rocks and the earth's crust.

Gold concentrations in peat range from 0.6 to 16 ppb with maximum of 160 ppb; in peat ash maximum of 480 ppb was found.

Increased Au contents are characteristic of low-ash domed and transitional peat deposits. Bernatonis et al. (1991) noticed that gold contents in peat deposits decrease from domed peat deposits (7.8 ppb) to transitional peat ones (4.7 ppb) and low-land peat deposits (2.3 ppb). Thus Au contents in peat of certain type from various deposits can significantly differ (Table 4).

Deposits from the right bank of the Ob River, set on the eluted sandy grounds without clay strata, are enriched with gold. In constant, peat bogs from the left bank, overlying clay-carbonate deposits, contain considerably less amount of gold.

Bernatonis et al. (2002) showed that gold concentrations in the domed peat of the Great Vassyugan bog increase towards the north-western direction from 1.9 (area no. 5) to 8.1 (area Yuginskiy) and to 34.8 ppb (riverheads of Vassyugan River). A similar tendency is noted for transitional and low-land peat of the Vassyugan bog. These facts demonstrate regional lateral heterogeneity of gold distribution.

In the cross-section of the peat deposit, Au distribution is also very heterogeneous (Fig. 3). Au-enriched horizons are notable against the background of horizons with lower contents. The gradual upward increase of Au concentrations, followed by a decrease at this top was established with detailed sampling of the horizons. Such variations do not correlate with changes in the ash content, leading speculation that composition of water supplying the peat bogs might be of great importance. In many locations high Au contents are found within near-surface and near-bottom areas of the

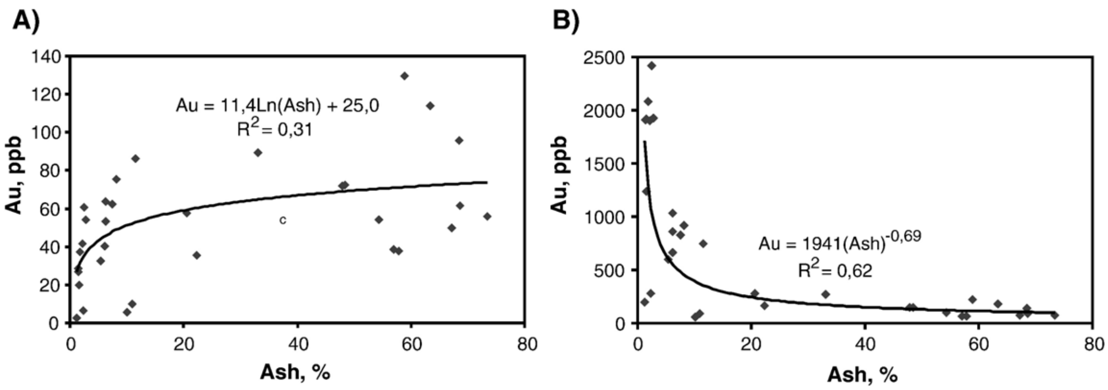

Fig. 2. Dependence of gold concentration on ash yield: A) in coals and B) in coal ash.

Table 4
Gold concentration in peat and peat ash of the south-east part of the Western-Siberian platform, ppb

Deposit	Number of samples	A^d, %	In peat			In the peat ash	
			X_{av}	X_{min}	X_{max}	X_{min}	X_{max}
Chistoe	4	4.4	12.0	7.0	19.0	Not determined	180
Semiozerye	122	4.0	16.0	<1.0	97.5	Not determined	Not determined
Vodorazdelnoe-2	31	3.9	14.7	<1.0	90.3	<1.0	170
Puhovskoe	32	7.0	14.3	<1.0	160	<1.0	220
Saim	2	2.2	14.0	10.0	18.0	130	480
Berezovaya Griva	121	7.5	9.6	<1.0	112	<1.0	160
Klyukvennoe	94	13.2	3.3	<1.0	76.3	Not determined	Not determined
Aygarovskoe	72	2.5	3.1	<1.0	37.3	Not determined	Not determined
Kolpashevskoe	90	4.3	2.6	<1.0	17.4	<1.0	220
Vasyuganskoe	181	4.0	2.4	<1.0	15.9	Not determined	Not determined
Suhovskoe	142	12.7	1.9	<1.0	11.2	Not determined	Not determined
Gusevskoe	90	15.8	0.9	<1.0	11.8	Not determined	Not determined
Arkadevskoe	101	22.3	0.6	<1.0	10.0	<1.0	38.0
Western Moiseevskoe	131	2.4	30.8	4.0	360	Not determined	Not determined
Petropavlovsky Ryam	41	3.4	4.6	0.1	59.5	5.0	720
Average	1254	8.7±1.7	6.0±1.4	<1.0	160	<1.0	720

X_{av}; X_{min} and X_{max} — average, the least and the most concentration, ppb.

peat deposit. High contents of Ag (3–5 ppm) are also noted in the ash of sphagnum moss from the upper parts of peat deposits.

For studied peat deposits there is correlation found between Au concentrations and ash contents (Fig. 4). As it had been noted, high-ash peat is characterized by low gold concentrations, while for peat with decreased ash content higher gold concentrations were determined. The correlation of these parameters is described by exponential functions (Fig. 4).

3.4. Forms of gold occurrence in brown coals and peat

The high Au concentrations in low-ash coals and domed peat make it possible to suggest an important role of the organic matter in the process of gold accumulation. Correlation between Au contents in coals, peat and the ash content (Figs. 2 and 4) points to a predominant organic form of gold occurrence. According to the mathematical models of Ryazanov and Yudovich (1974) such distribution of gold in peat indicates a biogenic form of gold, in coal the organic form is also dominating.

In order to verify the important role of organic matter in the initial gold accumulation in coals, domed and low-land peat bogs characterized by near Clarke value and increased gold concentrations were studied. Low-land peat deposits are considered to be the predecessors of normal-ash and high-ash coals, and domed peat types to be the predecessors of low-ash coals. Arbuzov et al. (2003) showed that over 95% of gold is related to the humus acids (mainly humic) and to the unhydrolysable lignin–cellulose residuum.

Bitumen and a fraction of highly soluble and highly hydrolysable substance are characterized by low Au contents. From nine samples studied significant Au content (6.7 ppb) in the dry residuum was determined only in one sample taken from the domed low-ash peat (A^d=1.4%). Weak hydrochloric solutions used for extraction of highly hydrolysable matters also cause the extraction of absorbed forms of metals. This allows us to conclude connection between gold and organic matter. The calculations of the balance show that the major quantity of Au is present in the neutral unhydrolyzsable residuum, a lignin (Table 5). In the unhydrolysable residuum, Au can exist both in mineral form and as a compound of organic matter (for example, in high-molecular weights insoluble in NaOH humates and humins). According to Rakovskiy and Pigulevskaya (1978) the “neutral part” of unhydrolysable residuum insoluble in alkali can not be equated to the lignin because, based on nitrogen content, carboxyl groups, and on other indexes, it is nearer to the humic acids than to the lignin. Possibly this explains the high gold concentration in the unhydrolysable residuum as compared with the Au concentration in humic acids.

Such distribution by composition is typical both for domed and low-land peat deposits. Thus, it is obvious that in peat formation, Au was accumulated in organic matter mainly due to the humic acids and organic matter

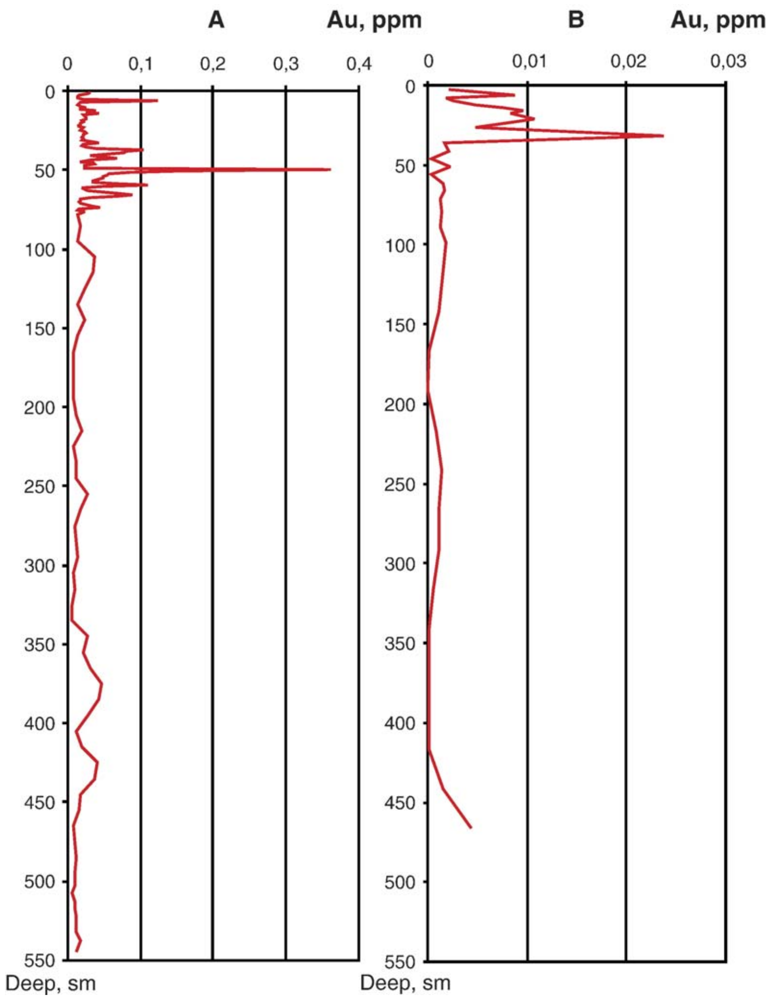

Fig. 3. Gold distribution across peat deposit: A) Western Moiseevskoe; B) Petropavlovskiy Ryam.

contained in the neutral part of unhydrolysable residuum.

4. Conditions of gold accumulation in peat and brown coals

In order to understand conditions for gold accumulation in peat and coals at least three basic points should be clarified:

- source of gold;
- mechanism of gold transportation and migration;
- mechanism of gold accumulation in peat and coals.

Gold ore deposits and gold-bearing rocks widely spread throughout the south-eastern, southern, and south-western margins of the peat deposit can be considered as source of gold in coals and peat of the Western-Siberian platform (Sherbakov and Kalinin, 2000). Formation of the weathering crust within folded regions since Triassic period resulted not only in formation of eluvial deposits (Roslyakov et al., 1995), but also in transformation of some part of Au into mobile form and its migration into the regions of ancient and modern areas of peat deposit formation.

Gold anomalies in coals and peat deposits occur on the periphery of the basin where known hydrothermal deposits of Au–Sb, Au–Ag and Au–As–Ag ores are located. Decreased Au concentrations towards the center of peat deposit can be explained by such positioning.

Relationship between anomalous Au contents and low-ash peat and coals allows us indicate mainly water Au migration to the areas of its accumulation. Forms of such migration were discussed by Yudovich and Ketris (2004). Probably in Western-Siberia Au was transported both in form of chlorides and Au-organic complexes.

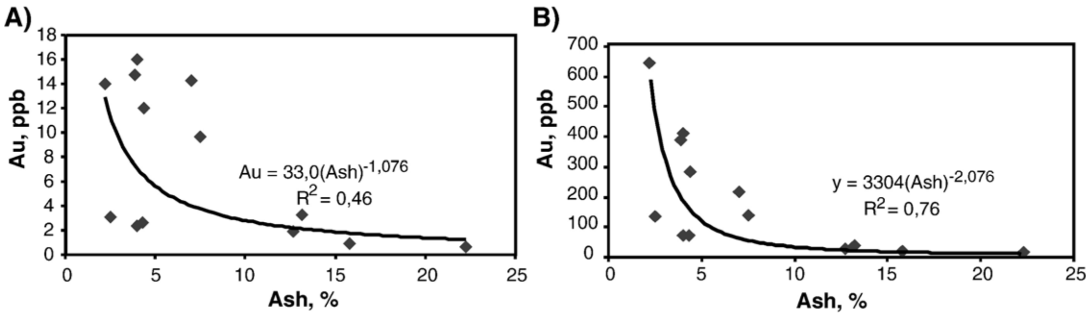

Fig. 4. Dependence of gold concentration on the ash yield: A) in peat and B) in peat ash.

Water feeding these bogs is poorly mineralized, but they contain considerable quantity of organic admixtures, including humic acids. Such water is enriched with microelements. High Au contents in water of the region are proved by the presence of its high concentrations in the dry residuum after water evaporation (Yazikov et al., 2004).

In a peat bog, the gold can also be supplied by the fragmental material as suspensions and atmospheric dust falls. However, the established negative relation of gold concentration to the ash content indicates an insignificant role of clastogene material in accumulation of anomalous gold concentrations. The mass balance of clastogene gold in such coals does not exceed 10–20%. In the conditions of strong industrial environmental impact of the last 50–70 years, the dust-aerosol falls could have become a substantial source of the Au supply in peat bog. The high concentration of the metal in the hard residuum of snow indicates as much (Yazikov et al., 2004). Such mechanisms could be a cause of the enrichment of upper parts of peat beds, but it is unlikely that it could be realized in the period of the deposition of Jurassic and Paleogene coals.

Anomalous Au concentrations in low-ash peat and coals make it possible to suggest a biogenic–sorptive mechanism of Au, Ag, and Sb concentration. Such mechanism was proved by Goldschmidt and Peters (1933). Recently published data on Au contents in peat-forming vegetation and peat from the Great Vassyugan bog agree with this mechanism (Bernatonis et al., 2002). According to this information gold contents in plants are higher than in the peat formed from them. Taking into account that the domed peat bog is mainly fed by atmospheric precipitations, partly due to the capillary uptake of the ground water and extraction of nutritive matters by plant root system from the underlying soils, it is possible to conclude that ground water is the main source of gold. Plants extract the ionic gold from the underlying water horizons. Considerable enrichment of gold of the peat bogs set on the sandy soils in comparison with the peat situated on the clay deposits provide support to this mechanism.

Results of the study of relation of Au concentration to the ash yield also support this mechanism. The increase of ash yield is accompanied by the sharp decrease of the element concentration in coals, ash, and peat. This means that the clastogene material supply in modern or Paleogene peat was low in Au and served to dilute the biogenic–sorptive ash enriched by the metal. Therefore, the ash of low-land peat bogs and high-ash coals are depleted in gold. Theoretically, in the low-land peat with the more active hydro-geological regime, gold concentration must be higher, because the conditions for the metal sorption are substantially better than in domed peat. Despite this the low-land peat is lower in gold than the domed peat. Consequently, in coals and peat with anomalous Au concentrations, the biogenic concentration is the basic mechanism of its accumulation.

Gold release takes place during the process of humification with further formation of complex humate and other steady organic compounds. As sorption capacity of organic matter in relation to the ions of noble metals is very high even for the coals of high degree of metamorphism (Varshal et al., 1995), under

Table 5
Gold yield in fractions of group composition of doomed-moor peat

Group composition of peat	Gold yield, %	Au concentration, ppb	Gold yield in fractions, %
Initial peat	100	6.4	100
Benzol bitumen	5.3	0.4	0.3
Water-soluble and easily-hydrolysable matters	34.3	0.1	0.6
Humic acids	18.6	11.0	32.0
Fulvic acids	23.2	2.0	8.2
Cellulose	10.4	4.7	7.6
Lignin	8.2	40.0	51.3

natural conditions coals are not saturated with gold and can save it during all stages of coal formation.

5. Conclusions

Coal and peat of the south-eastern region of the Western-Siberian platform are enriched in gold. There are coal layers and peat beds with anomalous gold contents, which could be of commercial interest for the region.

The organic matter is the major Au transmitter and a concentrator in peat and coal, with 40–60% of the metal is contained in the humic acids of peat.

For the determination of the economic significance of exposed deposits, the development of technological schemes of the gold extraction and concomitant metals and their subsequent geological–economic evaluation is required.

Acknowledgements

The authors gratefully acknowledge Dr. Ya.E. Yudovich, Dr. G.M. Eskenazy for fruitful cooperation and discussion. We also appreciate Dr. C.A. Palmer and editor-in-chief Dr. J.C. Hower, undertaking a work at the improvement of this article.

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