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GEOCHEMISTRY

Inorganic Geochemistry of the Oil of West Siberia: First ICP-MS Data

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The evolution in innovation technologies and analytical devices has raised geochemistry to a higher level. As is known, modern petroleum geochemistry is mainly composed of organic geochemistry. The trace element composition of oils was studied usually in combustion products, whereas works on direct determination of the trace element composition of hydrocarbons are scanty and generally related to a very small number of elements and/or heavy fractions [1]. The rapid progress in the method of mass spectrometry with inductively coupled plasma (ICP-MS) has made it possible to study the trace element composition of not only rocks, but also complex organic compounds, for instance, oil and its derivatives. A series of works has recently been reported on the geochemistry of asphaltenes and bitumens, i.e., solid components of oil [2, 3]. We analyzed for the first time the trace element composition of crude oil from West Siberia by the ICP-MS method. More than 50 trace, rare earth, and other elements were determined in oils from the Shaim and Srednii Ob fields (see [4–6] for geological data). The analyses were conducted using an ELEMENT2 high-resolution mass spectrometer following the technique developed at the Laboratory of Radiogeology (Zavaritskii Institute of Geology and Geochemistry) [7, 8]. The measurement results are shown in the table.

Oils from West Siberia are characterized by extremely low contents of the majority of elements. The PM-normalized trace element contents are equal to ~0.1 u for the most depleted ultramafic rocks and ~0.001 for oils. It should be noted that the PM-normalized contents of trace elements in Triassic basalts of West Siberia, from where oil samples were also taken, are approximately 10 u (Fig. 1).

The table shows that crude oils of the Shaim and Srednii Ob fields have relatively high contents (>1 g/t) of major (Mg, Al, Fe, Na, Ti) and transition elements (Cr, V, Ni, Cu, Zn). In the Ni–Cu–Cr diagram [3] for the resinous–asphaltene fractions, these oils belong to the chromium type. Their data points fall at the continuation of the trend outlined by the authors of [3] for the West Siberian province. The contents of other trace elements in these crude oils are lower (<1 g/t), but often higher than in some rocks. The Cs, Rb, Sr, and Zr contents in the oils are comparable with those in ultramafic rocks. The U content in oils is similar to that in the basaltoids and significantly higher than that in ultramafic rocks, chondrites, and intermediate rocks [9]. Such a high U content in oils is presumably related to the reducing conditions and, correspondingly, to the presence of a geochemical barrier. These conditions could also promote the high Pb content (up to 0.3 ppm). The Ag content is also relatively high (up to 0.1 ppm), while the Au content is low (<0.002 ppm).

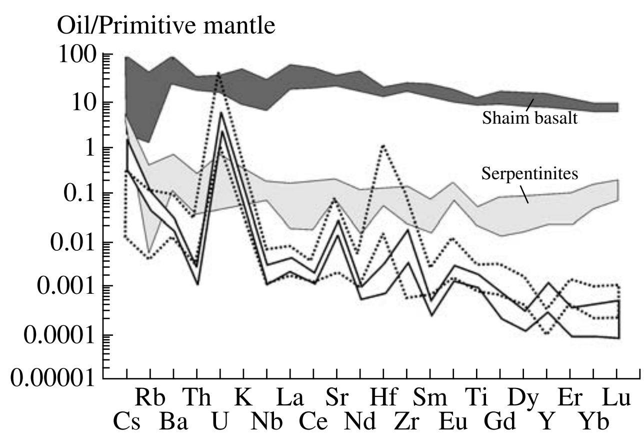

Fig. 1. Primitive mantle-normalized [11] spidergrams for oils of the Shaim (solid lines) and Srednii Ob (dashed line) oil–gas fields of West Siberia.

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Results of ICP-MS analyses of oil of West Siberia (ppm)

Element	1	2	3	4	5	6	7	8
Na	74.63	25.24	18.79	26.69	27.37	26.85	1.39	4.59
Mg	11.42	3.50	4.19	2.92	3.15	2.87	0.47	0.92
Al	2.73	1.78	1.93	2.31	2.58	2.32	1.12	1.37
Sc	0.76	0.81	0.78	0.63	0.52	0.47	0.12	0.11
Ti	2.00	1.76	1.38	1.05	1.40	1.34	2.89	2.75
V	12.11	6.89	8.53	6.49	6.80	6.10	10.45	11.63
Cr	44.25	29.85	34.97	30.22	28.18	24.68	28.49	32.74
Mn	0.40	0.16	0.17	0.16	0.14	0.14	0.12	0.59
Fe	82.10	90.36	94.54	96.36	87.76	91.71	52.17	48.92
Co	0.013	0.017	0.015	0.015	0.015	0.013	0.012	0.007
Ni	1.57	4.29	1.69	1.58	1.64	1.71	10.11	4.58
Cu	1.33	1.37	1.33	1.31	1.24	1.26	1.77	2.06
Zn	4.05	2.88	2.85	2.50	2.39	2.66	4.98	5.85
Ga	0.2509	0.0876	0.0796	0.0558	0.0477	0.0470	0.1535	0.1557
As	0.0005	0.00049	0.0073	0.0005	0.0004	0.0010	0.6819	0.8396
Rb	0.0594	0.0465	0.0452	0.0321	0.0272	0.0245	0.0019	0.0070
Sr	0.3981	0.2461	0.2705	0.3242	0.3214	0.3007	0.2114	0.6509
Y	0.0045	0.0015	0.0015	0.0011	0.0018	0.0011	0.0004	0.0010
Zr	0.1527	0.0358	0.0287	0.0336	0.0505	0.0285	0.1236	0.2042
Nb	0.0018	0.0012	0.0009	0.0008	0.0010	0.0008	0.0021	0.0041
Mo	0.0336	1.1012	0.0672	0.1365	0.0249	0.0255	0.0987	0.0599
Ru	0.0055	0.0059	0.0059	0.0056	0.0051	0.0054	0.0033	0.0058
Rh	0.0003	0.0003	0.00029	0.0003	0.0007	0.0004	0.0003	0.0002
Pd	0.0069	0.0038	0.0013	0.0016	0.0022	0.0013	0.0106	0.0164
Ag	0.0537	0.0429	0.0791	0.0449	0.1475	0.0141	0.0042	0.0030
Cd	0.0151	0.0189	0.0134	0.0149	0.0119	0.0133	0.0139	0.0072
In	0.0466	0.0181	0.0143	0.0116	0.0086	0.0089	0.0001	0.0004
Sn	0.3690	0.4209	0.3563	0.3903	0.2971	0.3427	0.2499	0.1454
Sb	0.0014	0.0012	0.0021	0.0013	0.0018	0.0018	0.0039	0.0049
Te	0.0047	0.0047	0.0046	0.0046	0.0041	0.0044	0.0002	0.0003
Cs	0.0107	0.0074	0.0068	0.0040	0.0028	0.0027	0.0003	0.0004
Ba	0.1808	0.1233	0.1081	0.1219	0.1434	0.1430	0.3217	0.2840
La	0.0026	0.0020	0.0019	0.0014	0.0017	0.0014	0.0024	0.0039
Ce	0.0029	0.0021	0.0022	0.0017	0.0022	0.0018	0.0037	0.0055
Pr	0.0004	0.00027	0.00025	0.0002	0.00029	0.0002	0.00052	0.00066
Nd	0.0012	0.0009	0.0009	0.0006	0.00079	0.00075	0.00145	0.00271
Sm	0.0002	0.00011	0.00009	0.00011	0.00016	0.00009	0.00035	0.00028
Eu	0.0004	0.00022	0.00019	0.00020	0.00023	0.00021	0.00051	0.00040
Gd	0.00036	0.00019	0.0002	0.00010	0.00019	0.00013	0.00049	0.00045
Tb	0.00004	0.00002	0.00003	0.000013	0.000023	0.000015	0.00005	0.00005
Dy	0.00018	0.00009	0.0001	0.00007	0.00013	0.00007	0.00029	0.00033
Ho	0.00004	0.00002	0.00002	0.000012	0.000024	0.000014	0.00006	0.00006
Er	0.00014	0.00005	0.00005	0.000034	0.000074	0.000042	0.00019	0.00019
Tm	0.00002	0.00001	0.000009	0.000005	0.000011	0.000007	0.00002	0.00003
Yb	0.00017	0.00005	0.00005	0.000035	0.000071	0.000043	0.00013	0.00019
Lu	0.00003	0.00001	0.000009	0.000005	0.00001	0.000007	0.00002	0.00003
Hf	0.00086	0.00023	0.00017	0.00021	0.00032	0.00018	0.01208	0.01260
W	0.0028	0.0059	0.0028	0.0022	0.00198	0.0019	0.0002	0.0001
Re	0.00002	0.0012	0.00003	0.00002	0.000008	0.00028	0.00564	0.00272
Os	0.00004	0.00006	0.00004	0.00005	0.00002	0.00004	0.00006	0.00005
Ir	0.00003	0.000002	0.000006	0.000009	0.000006	0.000004	0.00037	0.00027
Pt	0.00013	0.00013	0.00005	0.00012	0.00033	0.00017	0.00094	0.00119
Au	0.0002	0.00012	0.00011	0.00013	0.00019	0.00012	0.00039	0.00002
Hg	0.0011	0.0019	0.0009	0.0009	0.0020	0.0009	0.0019	0.0028
Tl	0.0316	0.0186	0.0125	0.0120	0.0098	0.0087	0.0459	0.0332
Pb	0.0419	0.0414	0.0302	0.0458	0.3046	0.0642	0.1401	0.1036
Bi	0.0237	0.0108	0.0082	0.0204	0.1714	0.0246	0.0008	0.0002
Th	0.0002	0.0001	0.0001	0.0001	0.0002	0.0001	0.0007	0.0019
U	0.1304	0.0627	0.0656	0.0593	0.1072	0.1031	0.3409	0.2002

Note: Oil fields: (1) Northern Danilovsk (borehole 6567), (2) Danilovsk (borehole 2459), (3) Dorozhnyi (borehole 1746), (4) Ust'-Teterev (borehole 1856), (5) Ubinsk (borehole 1236), (6) Lovinsk (borehole 9556), (7) Eastern Pridorozhnyi (borehole 402/2), (8) Kustovaya (borehole 1182/26). (1–6) Shaim field, (7, 8) Srednii Ob. Contents are given in ppm. Analysts O.P. Lepikhina, O.Yu. Popova, and others.

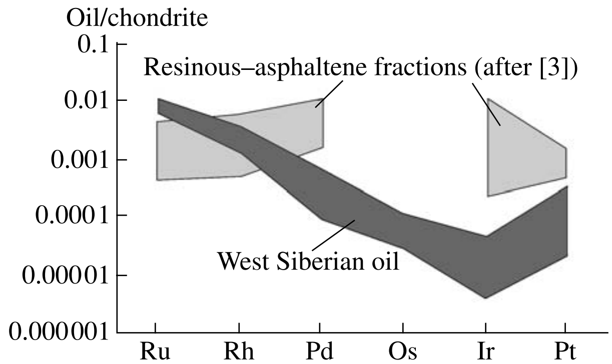

Fig. 2. PGE distribution in oils and resinous–asphaltene fractions.

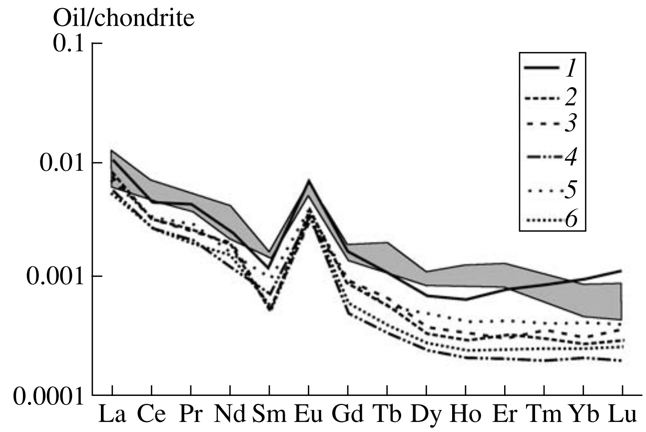

Fig. 3. Chondrite-normalized [12] REE distribution patterns for oils of the Shaim and Srednii Ob oil–gas fields. The number of the pattern corresponds to the sample number in the table. The shaded field shows the Srednii Ob oil.

Noteworthy is the significant concentration of PGE (Pt, Ir, Os, Ru, Rh, and especially Pd). Their total content reaches 0.01 ppm, which is higher than the content in virtually all rocks of the Earth [9]. Chondrite-normalized [10] PGE distribution is characterized by a gentle decrease from Ru to Pt with a negative Ir anomaly. Thus, the analyzed oils show a distinct Pd specialization (Fig. 2). The PGE distribution in oils sharply differs from that in resinous–asphaltene fractions [3].

The PM-normalized [11] trace element distribution in hydrocarbons exhibits positive U, Sr, Ti, Y, and Zr anomalies and negative Sm, Hf, Th, Nb, and Nd anomalies (Fig. 1). The oils taken from different fields are similar in the REE distribution patterns, with the exception of the positive Y anomaly in the Shaim oil and the negative Y anomaly in the Srednii Ob oil. The chondrite-normalized [12] REE contents in the oils of Western Siberia show a similar trend of the gradual enrichment in LREE. The REE contents are slightly higher in the Srednii Ob oil. It should be noted that the trace element content in asphaltenes [3] is approximately 100 times lower than that in crude oils. The REE distribution pattern is characterized by $(La/Yb)_n$ = 16–19, a high positive Eu anomaly, and a weak negative Sm anomaly (Fig. 3). The positive Eu anomaly can be related to both the abyssal genesis [11] and reducing environment [13], which is typical of hydrocarbons.

The elevated contents of transition elements (Ni, Co, Cr, V, and others) and PGE suggest "ultramafic" geochemical–metallogenic specialization of the oil and its mantle genesis [3]. However, such geochemical features can also be explained by the biogenic theory, according to which oil and hydrocarbons in the Earth's crust are generated from organic matter (kerogens and bitumens) under the influence of hydrocarbon flows. Host rocks (mainly clays) and some metals (Ni, Pt) serve as catalysts; i.e., geochemical specialization of the oils is promoted by catalytic metals accumulated in hydrocarbons.

Owing to the high sensitivity, accuracy, and capacity of simultaneous multielement analysis, the ICP-MS method developed in 1983 now represents one of the most perfect methods of atomic spectroscopy [14]. The use of high-resolution mass spectrometers with double focusing has made it possible to determine up to 70 elements (instead of the typical 15–20) in Mendeleev's Periodic Table. It is necessary to study the trace element composition of oils from other deposits and regions. The use of ICP-MS actually marks the beginning of a new stage in the study of the inorganic geochemistry of oil.

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