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GEOLOGY

The ICP-MS Determination of Rare Earths and Other Metals in Baikal Crude Oil: Comparison with Crude Oils in Siberia and the Russian Far East

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Hydrocarbon shows were already known half a century ago on the eastern coast of Lake Baikal. Zamaraev and Samsonov studied crude oils in the Klyuchi–Tolstyi Cape area and concluded that Tertiary sediments have the highest crude oil potential [1]. Based on findings of Sinian spores in the crude oils, M.M. Mandel'baum et al. assumed that they are related to deep Precambrian rocks. However, new data obtained by A.E. Kontorovich et al. suggest that aliphatic hydrocarbons of Baikalian crude oil lack 12- and 13-methylalkanes that are typical of ancient crude oils in the Siberian Craton. Hydrocarbons in bitumens and crude oils also lack normal alkanes as a result of biodegradation [2]. Hydrocarbon seeps in Lake Baikal can be related to the destruction of the gas hydrate layer [3].

The present paper reports pioneering results of the determination of concentrations of REEs and other metals in crude oils. Samples of Baikalian crude oil were taken at the end of 2004 from crude oil slicks on the lake surface (107°21′59″ E, 52°39′16″ N) and in April 2004–2005 on the ice surface north of Tolstyi Cape (107°21′43″ E, 52°39′01″ N) (Fig. 1). The Baikalian resinous black crude oil has high viscosity and density. For the sake of comparison, we used samples of crude oils from deposits in the West Siberian Depression, southern Siberian Craton, and Sakhalin Island shelf. Crude oil from the southern Siberian Craton (Atov deposit) is confined to Lower Cambrian rocks. This type of crude oil is characterized by relatively low contents of resin and sulfur but high contents of light fractions [4]. Crude oils from the West Siberian Depression and Sakhalin Island shelf are confined to Mesozoic and Cenozoic rocks, respectively.

Minor elements in crude oils can be determined by both dry and wet versions of the ashing method [5, 6, and others]. The available literature data were primarily obtained by spectral analysis of the ash residue and neutron activation analysis. These methods make it possible to determine a limited number of elements. The inductively coupled mass spectroscopy (ICP-MS) yielded a wider range of minor elements in crude oils of the Kaliningrad Ridge [7]. Only LREEs were determined from the entire REE range. The analysis error was very high (30%) for the majority of elements.

We used the high-precision version of the ICP-MS method [8] for the determination of minor elements. Crude oil samples were decomposed in two stages. After treatment in concentrated nitric acid with a minor addition of hydrogen peroxide, the samples were subjected to thermal ashing in a muffle furnace. We varied the weight of crude oil samples from 1 to 15 g depending on the possible content of determinate elements. The sediments were decomposed in a mixture of HF and HNO_3 in the microwave furnace. The analysis was carried out in a Plazma Quad PQ 2+ inductively coupled mass spectrometer at the Irkutsk Analytical Center. In order to take into account the influence of the temporal drift of the instrument, the prepared sample was spiked with 10 ng g^{-1} of internal standards of In and Bi. The accuracy of results obtained was checked with the BIR-1, DNC-1, JB-2, and BHVO-1 international standards of rocks. The detection limit was determined for each element on the basis of procedure blanks (Fig. 2).

The quality of crude oil sample decomposition was checked by two procedures of incineration (with and without the introduction of an ash-free filter). The loss

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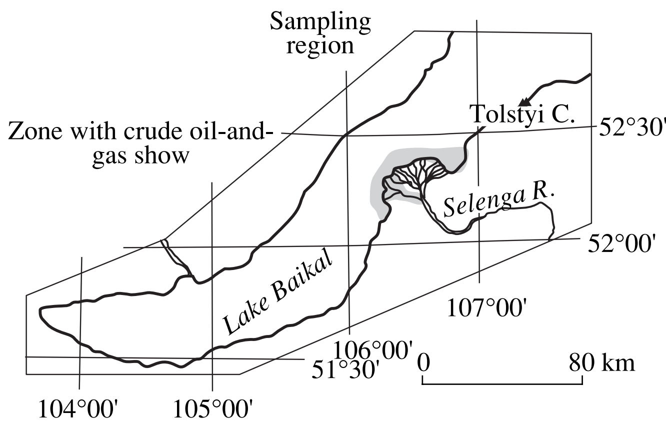

Fig. 1. Schematic map of the crude oil sampling area and crude oil-and-gas shows in the Selenga River estuary [3].

of elements in the course of incineration was controlled by the dilution of the crude oil sample with standard multielement solutions (1-800-lab Spex Co.) before and after the decomposition. Comparison of results showed that the application of a filter in the course of ashing makes it possible to detain elements of the iron group, as well as Li, Be, Sc, Zr, Mo, and W, in the sample. At the same time, the detection limit is also significantly enhanced. Therefore, it is unreasonable to use a filter in the case of low concentrations of determinate elements (REE, Zr, Y, Th, U, Be, Co, and others). Traces of Zn, Sr, Ba, La, and Ce can be present in the filter. The breakdown of Nb and Ta is incomplete in this method.

Concentrations of minor elements in crude oils are commonly increased in the case of high contents of resin and asphaltenes [9]. This is typical of the Baikalian crude oil. In general, the concentrations of metals in this type of crude oil turned out to be higher than those in the deposits (table). The concentrations of REEs in the Baikalian crude oil are two or three orders of magnitude higher, although the slope and shape of spectra are comparable if the data were normalized to the average composition of the continental crust [10] (Fig. 3). The spectrum of sample N-10 of Baikalian crude oil is similar to the spectra of shales at crude oil shows in the upper continental crust. The $(La/Yb)_N$ value in the analyzed crude oil samples varies from 0.07 to 3.4.

The ratio Y/Ho is an essential parameter. The behavior of these elements is similar in many geochemical processes. The Y/Ho ratio varies from 27 to 29 in mantle rocks and decreases to 23 in the continental crust. This ratio decreases to 15 in the intensely differentiated granitoids under the influence of a fluid phase that contains H_2O, F, Cl, Li, B, and P. This type of fluid phase fosters the formation of complex compounds of REEs [11]. In surface crude oil slicks from Lake Baikal and in crude oil from the Atov deposit, the Y/Ho ratio is 35 and 30, respectively, which is close to the mantle values. In the crude oil slick from the Baikalian ice sur-

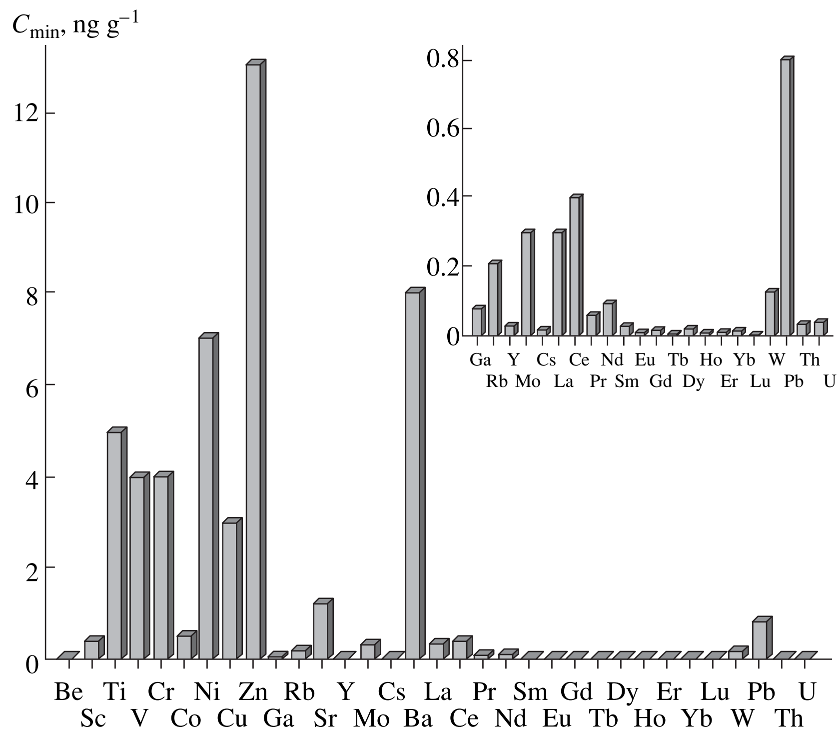

Fig. 2. Detection limits (C_{min}, criterion 3σ, and probability $P = 0.997$) for elements determined in the crude oil mass of 15 g. Inset shows elements with a low detection limit.

Average concentrations of minor elements in crude oils and sediments of Lake Baikal versus crude oils from deposits in Siberia and the Russian Far East

Element	Crude oil, ng · g^{-1}								Sediments, µg · g^{-1}
	sample N-10	sample N-11	sample N-0	sample N-6	sample N-7	sample N-9	sample N-2	sample N-8	
V	2850	2195	710	138	1623	18349	11	3300	132
Cr	630	322	12	32	18	16	22	8.57	78
Co	1007	966	58	3.7	6.1	11	2	4.08	21
Ni	7480	12745	940	234	242	827	12	213	46
Cu	220	296	23	4.27	282	100	130	21	32
Rb	24	12	0.36	0.37	2.9	6	2.8	2.6	114
Sr	240	80	11	9	17.3	410	30	11.5	296
Y	10	5.3	0.18	0.25	0.20	0.22	0.62	0.37	24
Zr	20	71	1.24	1.48	1.4	0.64	5.77	0.06	86
Cs	2.2	1.18	0.06	0.18	1.8	1.14	0.18	0.071	7.2
Ba	311	377	13	55	7.7	347	31	3.8	665
La	21	8.46	0.24	0.37	0.092	0.25	0.51	0.16	43
Ce	39	12.4	0.39	0.56	0.20	0.60	1.17	0.40	88
Pr	4.76	1.34	0.060	0.077	0.017	0.073	0.14	0.082	10.1
Nd	16	6.38	0.25	0.16	0.22	0.24	0.76	0.25	38.6
Sm	2.83	0.41	0.032	0.081	0.14	0.066	0.12	0.055	6.54
Eu	0.89	0.38	0.026	0.042	0.031	0.09	0.03	0.057	1.56
Gd	2.64	1.07	0.010	0.085	0.052	0.05	0.12	0.084	7.13
Tb	0.65	0.17	Not det.	Not det.	0.010	Not det.	Not det.	0.016	1.09
Dy	2.18	0.85	0.013	0.029	0.085	0.046	0.15	0.093	4.58
Ho	0.77	0.15	0.011	0.015	0.014	0.035	0.021	0.023	0.93
Er	0.43	0.43	0.022	0.035	0.029	0.051	0.076	0.069	2.42
Yb	1.21	0.44	0.040	0.047	0.14	0.089	0.05	0.086	2.56
W	Not det.	2.88	0.36	0.6	0.20	0.91	0.20	0.34	2.06
Pb	94	Not det.	2.5	3.1	11.2	7.39	11	5.62	1.6
Th	7.0	2.05	0.08	0.43	0.094	0.19	ç.Ó.	0.044	12.5
U	13	3.92	0.048	0.06	0.16	0.32	0.071	0.033	2.98

Note: (Samples N-10, N-11) Lake Baikal; (N-0) Sakhalin Island shelf; deposits in West Siberia: (N-6) North Kharampur, (N-7) West Agan, (N-9) Petelin; deposits in the Siberian Craton: (N-2) Atov, (N-8) Malobalyn.

face, this ratio is as low as 13, which is consistent with the range determined in other crude oil samples (5–17).

Strontium isotope measurements were carried out with an MI-1201TM mass spectrometer at the Institute of the Earth's Crust, Irkutsk (M.N. Maslovskaya, analyst; Yu.M. Malykh and E.I. Demonterova, prepared samples). The $^{87}Sr/^{86}Sr$ ratio in the Baikalian crude oil turned out to be equal to 0.70876 ± 0.00040. This value is within the interval limit defined for crude oils from various provinces (0.7083–0.7104) [12].

The V/Ni ratio in porphyrines is also an essential parameter [9]. Together with the S content, this parameter is used for the assessment of redox conditions in the crude oil-forming medium. High V/Ni values are typical of crude oils formed in a relatively reducing environment. The concentrations of the mobile V can be lower than that of the inert Ni [13]. The highest V/Ni ratio (22.2) has been recorded in crude oil sampled from the Petelin deposit. In contrast, this ratio is minimal (0.23–2.4) in Paleozoic crude oils from the Kaliningrad Ridge [7]. This fact suggests that hydrocarbons in Lake Baikal formed in a relatively reducing environment or as a result of the removal of V in the course of biodegradation. In crude oils from the Kaliningrad Ridge, we can recognize two groups of minor elements. The first group includes lithophile elements (LE), such as La, Ce, Nd, Yb, Y, Th, and U, coupled with Mn and Fe. The second group includes naphtophile elements (NE), such as Ni, V, Pb, Co, and Cu, as well as chalcophile and siderophile elements, B, W, and Cr. The NE/LE ratio varies from 14 to 192 [7]. Thus, the values

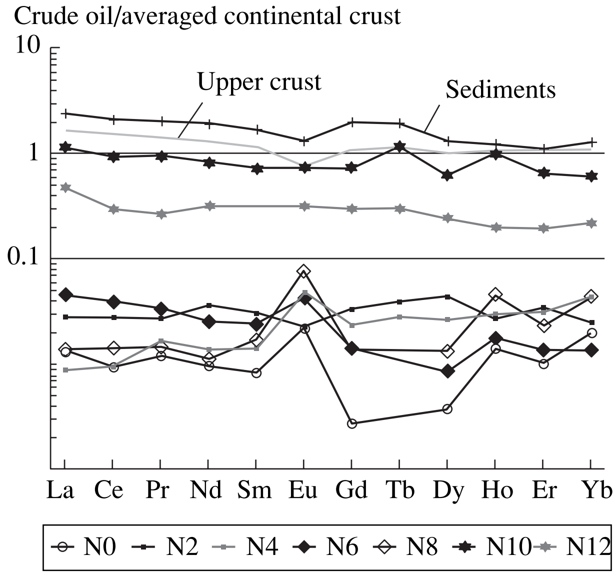

Fig. 3. Concentrations of rare earth elements in crude oils (multiplied by 10^3 and normalized to the averaged composition of the continental crust [10]). Sample location: (N-10, N-11) Baikal crude oil field and crude oil shows in the Tolstyi Cape area (asterisks), (N-2, N-8) crude oil fields in the Siberian Craton (boxes), (N-0) Sakhalin Island shelf (circles), (N-6, N-9) crude oil fields in West Siberia (diamonds). Sample numbers in the plot are as in the table. For the sake of comparison, the average compositions in the upper continental crust [10] and bottom sediments of the Tolstyi Cape crude oil show area are given.

of the NE/LE ratio in crude oils from the Atov deposit in the southern Siberian Craton (31) and the North Kharampur deposit in West Siberia (134) fall into the range of NE/LE values recorded for the Kaliningrad Ridge. The NE/LE ratio has the highest value in crude oils from Sakhalin Island and the Petelin deposit, West Siberia (1240 and 2475, respectively). This ratio is relatively low in two samples of Baikalian crude oil (96 and 280).

CONCLUSIONS

The concentrations of all REEs and other metals have been determined in the Baikalian crude oil by the ICP-MS method. Comparison of the data obtained show that the REE concentrations are nearly two orders of magnitude higher than those in crude oils from deposits in Siberia and the Russian Far East. The concentrations of REEs in Baikalian crude oil are three to four orders of magnitude lower than those in the present-day sediments of Lake Baikal, although their distribution patterns are rather similar. Baikalian crude oil is characterized by low V/Ni values, testifying to the formation of such crude oils either in a severe oxidizing environment or as a result of the significant loss of V in the course of biodegradation. With respect to the NE/LE ratio, Baikalian crude oil can be correlated with its counterparts from the North Kharampur deposit (West Siberian Depression) and the Kaliningrad Ridge.

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