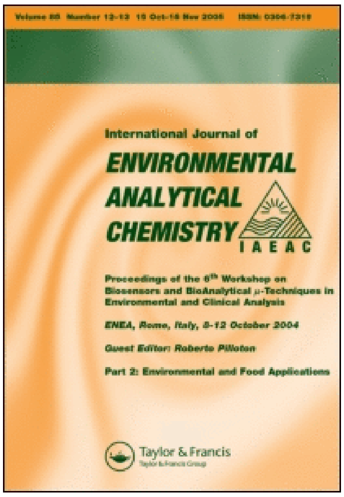

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Reference Samples of Lake Baikal Bottom Sediments - An Essential Part of Regional Collection of Reference Samples

Lev L. Petrov[a]; Yury N. Kornakov[a]; Ludmila A. Persikova[a]; Elena A. Anchutina[a]
[a] Institute of Geochemistry, Irkutsk, Russia

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REFERENCE SAMPLES OF LAKE BAIKAL BOTTOM SEDIMENTS - AN ESSENTIAL PART OF REGIONAL COLLECTION OF REFERENCE SAMPLES

LEV L.PETROV*, YURY N. KORNAKOV, LUDMILA A. PERSIKOVA and ELENA A. ANCHUTINA

Institute of Geochemistry, P.O. Box 4019, Irkutsk 664033, Russia

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The development of a special regional minimum collection of reference samples from natural environments of lake Baikal is presented. The set of environments and the list of parameters to be attested as well as the phases of development of any samples are discussed. Already developed and certified samples of lake Baikal bottom sediments (BIL-1 and BIL-2) are described in detail.

Keywords: Geochemical mapping; analytical data quality; reference samples; bottom sediments; homogeneity; interlaboratory analytical program

INTRODUCTION

In recent years the projects of geochemical mapping have increased the interest in many regions of the world[1]. In particular, investigations on the anthropogenic impact on the ecosystem are carried out in lake Baikal region in the context of national[2] and international programs ("Geoecology of Russia", "Baikal-Drilling Project", "Investigation of lake Baikal and its basin with the aim of protection as a World Natural – Heritage Site and Reference Site of the Sustainable Development", "Global changes of environment and climate", etc.).

The lake Baikal's region is unique (Figure 1). A number of significant territories are still virgin, but a number of areas are subject to important anthropogenic impacts. Thus, the analytical researches covered a very large set of substrates as well as the maximum range of components.

* Corresponding author. Fax : +7-3952-464050. E-mail : petrov@igc.irk.ru.

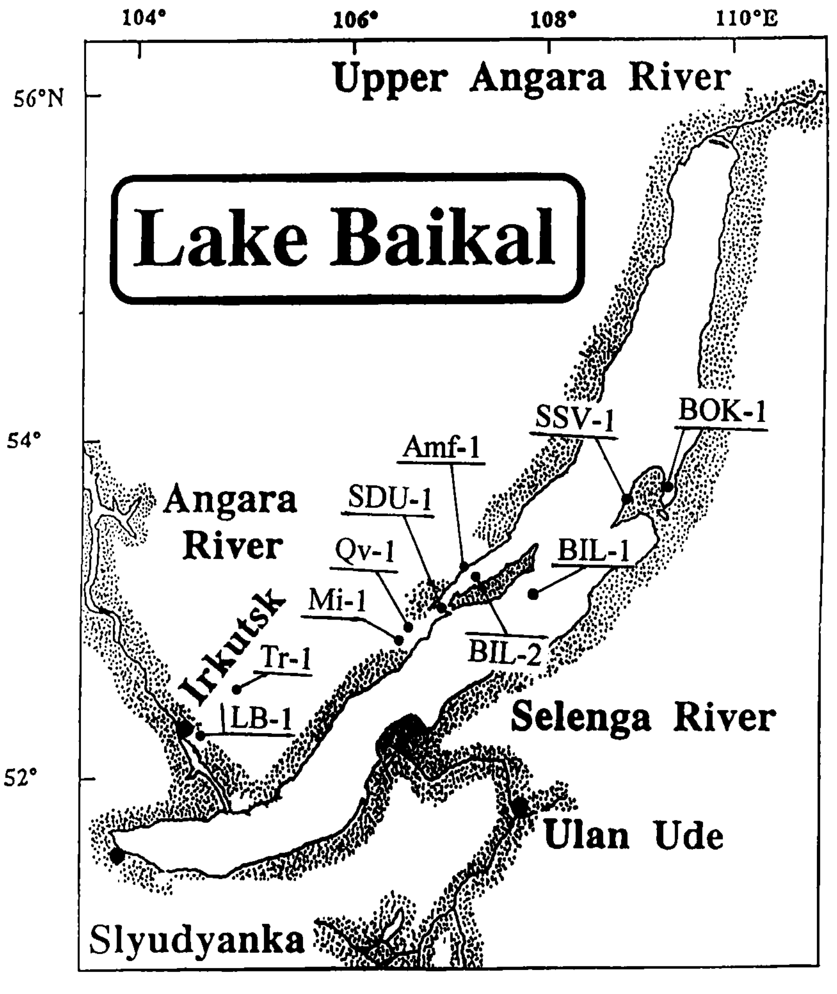

FIGURE 1 The locations of the RSs material sampling

The study of the compositions of different natural media (crystal rocks, sediments, soils, waters, plants) as well the participation of many analytical labs are crucial peculiarities of such projects. In this context, the problem of the analytical informations correlation of paramount importance [1,2].

The quality of analytical information in large regional projects can be assured by a special control of the analytical data quality (CAWO)[3]. This system is defined by a number of conditions, the principal of which is the use of a compulsory collection of reference samples (CMC). The building of this collection in its turn is defined by a number factors[3,4], the main of which are as follows:

- Optimum overlapping of compositions of substrates under analysis by use of the minimum number of samples;
- Quantity of attested components for a certain certified reference samples. The samples with more attested indicators are chosen when the matrices are similar;
- Samples availability;
- Possibility to extend the collection and the samples interchangeability;

A necessary condition when CMC develops is the coordination of reference samples.

The development of the optimum system of the reference samples for the different environments of the region requires the development of standard samples, which characterize directly the environments of lake Baikal: bottom sediments, water and biota. These include (Figure 1):

- bottom sediments (BIL-1 and BIL-2)
- dry water residue (SOVB-1)
- biota samples: perch (BOK-1) and sponge (GB-1)
- turf podsol soil (P-1)
- plant samples: birch leaf (LB-1) and grass mixture (Tr-1),
- coal ash (ZUK-1 and ZUA-1)
- crystal rocks and minerals from stone necklace of Baikal – dunite (SDU-1), sviatonossite (SSV-1), quartz (QV-1), microcline (Mi-1) and amphibole (Amf-1).

The soil and plant samples are necessary for monitoring explorations and works on appraisal of anthropogenic pollution. The reference samples of coal ashes, likewise, are of great importance, because the most power stations of the region use coals only from local deposits. The RMs of crystal rocks from the Baikal shores are necessary as well.

For a part of the above-listed natural and man-made environments, the reference samples already available are: dunite SDU-1(SRS* 4233–88) sviatonossite SSV-1(SRS 6104–91), coal ashes ZUK-1(SRS 7125–94) and ZUA-1(SRS 7177–95). The information on these samples has been detailed in earlier publications[5,6]. Further, the results of researches and parameters of two developed reference samples of the lake Baikal bottom sediments (BIL-1 and BIL-2) will be adduced. In our opinion these samples are the central fragment of the reference samples for the lake Baikal region.

* SRS – State Reference Sample.

EXPERIMENTAL

Works to develop two samples of lake sediments were begun with a sample of lake Baikal bottom silt (BIL-1). This standard sample was developed primarily as the bearer of the metrological function. On the other hand, it is supposed that the concentration of priority toxic elements and pollutants, as well as other components, will serve as the original "count point" for an estimation of the technogenic pollution of the lake's ecosystem. According to Goldyrev[7] the lake Baikal deep-water bottom sediments are rather similar in terms of the fluctuations in the concentrations of macro and microcomponents.

The sampling of the BIL-1 bottom silt was performed in the middle of the basin to the East of Olkhon island from a depth of about 1600 m (Figure 1), with the bottom scooper "Okean", on board of a research vessel.

The bottom sediments of Maloye More (BIL-2) were accepted because of the available analytical information and knowledge of the sampling site. As a result, the south basin of Maloye More between the mouths of the Kurma and Sarma rivers was chosen for sampling (Figure 1). The material was received as the composition of 13 separate subsamples collected in a coast zone, from a depth of 5–15 m, with a small scoop from a motor boat. All subsamples consisted, basically, of fine sand.

From each point about 30–40 kg of material was selected. The total initial weight of sample was about 400 kg. Thus, all received material was dried up in the field conditions and cleared of foreign coarse fragments of an organic origin, as well as the impurity and rubbish associated with the human activity.

The granulometric features of the initial sample materials are as follow : the prevailing particles size of 0,05–0,01 mm and 0,01–0,001 mm are characteristic of BIL-1, but the prevalence of 1,0–0,1 mm and 0,1–0,01 mm fractions are typical for BIL-2.

The ***mineral composition of deep-water bottom sediments BIL-1*** was very complicate and represented aleuropelitic composition of the terrigeneous material, diatomaceous sediments autigeneous products, characteristic of top horizons of sediments with the transition conditions of mineral genesis from oxidation to reduction conditions. This was the material selected for RS. The terrigeneous material was presented argely by hydromicas and highly hydrated varieties. Montmorillonite and structurally imperfect caolinite was present in somewhat lesser amounts. The quartz, field spar, pyroxenes, micas, amphiboles, chlorites, garnet, and accessory sphene and zircon were identified in rough fractions of silt. Diatomaceous components were of dominant importance among authigenous formations. The opal concentration in BIL-1 ranged up to 16 %. The characteristic water enriching the oxygen of bottom layers defines the oxidizing nature of geochemical processes. The autigeneous minerals of this zone are represented by hydrogoethite, psilomelane, vernadite. The minerals of the reduction zone are represented by vivianite, hydrotroilite, melnikovite, pyrite and marcasite.

The mineral composition of the coastal sediments (BIL-2) represents in more than half of the sample leucocratic minerals (quartz, field spar, K-field spar). The essential group (more than 35 %) consists in melanocratic minerals, including monoclinic pyroxenes, amphibole and biotite. Ore minerals make about 5 % of the standard mass. Among them, ilmenite (3,4 %), magnetite (up to 1 %) and martite-hematite, limonite, leucoxene and pyrite are recognized. Appreciable quantities of scapolite, carbonates (basically calcite), epidote, zoisite, garnet, sphene and apatite and lower amounts of rutil and zircon are also present. This rather impressive list of minerals making an integrated image of reference sample BIL-2, is in agreement with an idea of a "stone necklace".

From all the above it is evident that the initial material of samples BIL-1 and BIL-2 differed in particles size as a minimum by one order. The preparation of samples by crushers largely eliminates these differences as it is shown in Table I.

TABLE I Particle size distribution (%) of BIL-1 and BIL-2 reference samples

Fraction µm	*BIL-1*			*BIL-2*		
	Fritsch particle sizer	*Sieve analysis*	*Average*	*Fritsch particle sizer*	*Sieve analysis*	*Average*
80–71	0.2	0.5	0.4	0.46	0.29	0.38
71–63	0.2	0.8	0.5	0.58	0.35	0.47
63–50	0.3	2.2	1.5	1.10	2.20	1.65
50–45	0.1	1.6	0.8	0.56	1.97	1.27
45–40	0.2	0.2	0.2	0.58	0.90	0.74
40–36	0.8	1.7	1.3	0.48	3.89	2.19
36–25	1.2	4.9	3.0	2.22	16.81	9.52
< 25	97.0	88.1	92.3	94.02	73.55	83.78

The estimation of the homogeneity of the prepared reference samples BIL-1 and BIL-2 was carried out on the basis of the approach described elsewhere[5,6]. Briefly the main aspects of this procedure are the following:

- Division of all certified elements into sets of homogeneous groups according to the value of potential inhomogeneity (S_r) estimated for each element;
- Selection of an element indicator for each identified group;

TABLE II Inhomogeneity error estimates (σ_{inhom}) of element indicators for bottom sediments BIL-1 and BIL-2

Element-indicators	C_M, %	Δ_D	σ *inhom*	σ_{inhom}/Δ_D		*Element (component) groups, similar in potential inhomogeneity to element indicator*
			Bottom sediments BIL-1			
Rb	0.0093	0.0018	0.000048	0.00268	(<1/37)	SiO_2, Al_2O_3, FeO, MgO,Na_2O, K_2O,
Fe_2O_3 total	7.02	0.196	0.0081	0.041	(<1/24)	Ba, Ce, Cs, Ga, Ge, Hf, La, Lu, Nd, Pb,
CaO	1.85	0.108	0.0036	0.033	(<1/30)	Sc, Sm, Ta, Tb, Th, U, Y, Yb, Zn.
TiO_2	0.69	0.04	0.00357	0.089	(<1/11)	P_2O_5, LOI, As, B, Be, Co, Cr, Cu, Eu,
Zr	0.0156	0.00183	0.00013	0.071	(<1/14)	F, Li, Mo, Nb, Ni, S_{total}, Sn, V.
MnO	0.40	0.0208	0.0022	0.105	(<1/9)	Ag, Sb.
			Bottom sediments BIL-2			
Sr	0.055	0.0082	0.00015	0.018	(<1/56)	SiO_2, Al_2O_3, FeO, Ba, Co, Cr, Cu, La,
Fe_2O_3 total	5.395	0.15	0.0032	0.021	(<1/48)	Li, Pb, Sc, V, Zn.
K_2O	1.515	0.098	0.0032	0.033	(<1/30)	MgO, Na_2O, Ni, Rb, Sn, Y, Yb.
CaO	7.18	0.23	0.011	0.047	(<1/21)	
TiO_2	0.758	0.044	0.0036	0.082	(<1/12)	
Zr	0.0204	0.0024	0.00022	0.091	(<1/11)	LOI, Nb.
MnO	0.119	0.013	0.0013	0.0995	(<1/10)	
P_2O_5	0.139	0.0084	0.00114	0.135	(<1/8)	

Notes: C_M = arithmetic mean; Δ_D = maximum permissible certification error at 95% Cl; σ_{inhom} = inhomogeneity distribution error.

- Collection of experimental data for all selected element indicators;
- Application of the values obtained from the element indicators to all elements of the corresponding groups.

For a reasonable separation of BIL-1 elements into potential inhomogeneity groups a diagram was used, where along the abscissa S_r^{lat}. the data on variability of the element concentrations in the silts and along the ordinate, the appropriate estimation of variability for various particle size fractions S_r^{fr}, were plotted. All necessary data for construction of such diagnostic diagram were found in the literature[8]. For BIL-2 the material received during a preliminary sampling was used for the construction of a similar diagram.

Then, the following steps were accomplished:

a. The elements to be certified were divided by potential inhomogeneity;
b. The element indicators were chosen to establish the inhomogeneity error σ_{inhom};
c. An experimental estimation of σ_{inhom} was carried out on the basis of analysis of 100 subsamples by X-ray fluorescence;
d. A correlation between the obtained values and the values allowable by normative documents are given in Table II.

The listed data allow to ascertain, that all elements in sample BIL-1 and the majority of elements in sample BIL-2 to be attested are homogeneous with respect to the Russian Standard requirements[9].

For phosphorus the inhomogeneity error (σ_{inhom}) in excess of 1/8 of maximum permissible certification error (Δ_D) accounts for uncertainty of certified concentration.

As the samples BIL-1 and BIL-2 were developed not simultaneously, the conditions of realization of its Interlaboratory Analytical Programs (IAP) have appeared to be different. So, the IAP for sample BIL-1, 67 organizations of Russia and States of former USSR owning various analytical methods were involved, but for BIL-2 the number of participants was only 42. The number of IAP Western Countries participants also varied: for BIL-1, 8 labs (including IAEA analytical service), and for BIL-2, only 1 lab. The use of analytical methods in the IAP (Table III) was rather similar. All this was reflected in the number of parameters to be certified in the samples (Table IV).

TABLE III The use of the various methods of analysis at the Interlaboratory Analytical Program

Analytical method	*BIL-1*		*BIL-2*	
	N, %	*n*	*N, %*	*n*
Emission spectrometry (arc, ICP)	31,4	47	29,7	41
Neutron activation analysis	12,8	38	9,5	37
Atomic absorption spectrometry	11,0	24	13,0	21
X-ray fluorescence analysis (XRF)	10,8	35	10,5	29
Photometry	9,9	19	13,6	17
Flame photometry	6,6	7	7,7	6
Titrimetry	6,6	7	7,7	8
Gravimetry	5,8	8	5,4	6
Chemical spectral analysis	2,2	10	1,7	12
Mass spectrometry	1,5	12	-	-
Chromatography	0,7	6	0,8	6
Potentiometry	0,4	2	0,4	1
Fluorimetry	0,1	2	-	-
Atomic fluorescent spectrometry	0,1	1	-	-
Coulometry	0,05	1	-	-
Polarography	0,05	1	-	-

Notes : N, % = persentage quantity of the analytical information obtain by use of every method ; n = quantity of the elements (components) obtain by use of every method.

TABLE IV Certified values (A), uncertainty of certified concentration at 95% Cl (Δ_{RS}), values of representative analytical subsampless mass (m) in reference samples BIL-1 and BIL-2

N°	*Element component*	*BIL-1 (GSO N° 7126- 94)*			*BIL-2 (GSO N° 7176–95)*		
		A (%)	*Δ_{RS}(%)*	*m, g*	*A (%)*	*Δ_{RS} (%)*	*m, g*
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
1	SiO_2	61.07	0.26	0.35	62.46	0.26	0.21
2	TiO_2	0.69	0.03	0.07	0.76	0.03	0.21
3	Al_2O_3	13.57	0.13	0.22	14.22	0.22	0.24
4	Fe_2O_3 total	7.02	0.15	0.13	5.39	0.1 1	0.21

N°	*Element component*	*BIL-1 (GSO N° 7126- 94)*			*BIL-2 (GSO N° 7176–95)*		
		A (%)	Δ_{RS}*(%)*	*m, g*	*A (%)*	Δ_{RS} *(%)*	*m, g*
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
5	FeO	1.60	0.09	0.6	3.50	0.14	0.21
6	MnO	0.40	0.02	0.13	0.12	0.01	0.09
7	CaO	1.85	0.09	0.13	7.09	0.21	0.38
8	MgO	2.00	0.07	0.22	3.12	0.12	0.27
9	Na_2O	1.96	0.07	0.13	3.11	0.09	0.27
10	K_2O	2.21	0.08	0.13	1.51	0.05	0.27
11	P_2O_5	0.345	0.015	0.07	0.139	0.008	0.59
12	LOI	8.34	0.18	0.6	1.78	0.08	0.59
13	H_2O^+	(4.50)	(0.42)		-	-	-
14	CO_2	(0.07)	(0.03)		(0.74)	(0.19)	-
15	SO_3	(0.35)	(0.05)		(0.050)	(0.028)	-
16	C organic	(2.24)	(0.18)		-	-	-
17	Ag	($0.170 \cdot 10^{-4}$)	($0.054 \cdot 10^{-4}$)		($0.040 \cdot 10^{-4}$)	($0.022 \cdot 10^{-4}$)	-
18	Au	($0.004 \cdot 10^{-4}$)	($0.0027 \cdot 10^{-4}$)		-	-	-
19	As	0.0018	0.0003	0.26	-	-	-
20	B	0.0034	0.0006	0.35	(0.0012)	(0.0011)	-
21	Ba	0.071	0.007	0.22	0.053	0.008	0.38
22	Be	0.00027	0.00004	0.6	(0.00013)	(0.00004)	-
23	Ce	0.0080	0.0005	0.40	(0.00041)	(0.0005)	-
24	Co	0.0018	0.0002	0.26	0.0017	0.0002	0.40
25	Cr	0.0066	0.0004	0.6	0.0158	0.0010	0.56
26	Cs	0.0006	0.0001	0.13	-	-	-
27	Cu	0.0052	0.0007	0.15	0.0018	0.0003	0.40
28	Dy	($4.6 \cdot 10^{-4}$)	-	-	-	-	-
29	Er	($2.6 \cdot 10^{-4}$)	($0.6 \cdot 10^{-4}$)	-	-	-	-
30	Eu	0.00014	0.00002	0.15	(0.00014)	(0.00004)	-
31	F	0.060	0.006	0.6	(0.038)	(0.027)	-
32	Gd	($5.8 \cdot 10^{-4}$)	($0.5 \cdot 10^{-4}$)	-	-	-	-

N°	Element component	BIL-1 (GSO N° 7126- 94)			BIL-2 (GSO N° 7176–95)		
		A (%)	Δ_{RS}(%)	m, g	A (%)	Δ_{RS} (%)	m, g
1	2	3	4	5	6	7	8
33	Ga	0.0016	0.0002	0.22	(0.00130)	(0.00025)	-
34	Ge	0.00014	0.00002	0.49	(0.00013)	(0.00002)	-
35	Hf	0.00039	0.00007	0.35	(0.00067)	(0.0001)	-
36	Hg	($0.030 \cdot 10^{-4}$)	($0.018 \cdot 10^{-4}$)	-	-	-	-
37	Ho	($1.0 \cdot 10^{-4}$)	($0.2 \cdot 10^{-4}$)	-	-	-	-
38	La	0.0045	0.0006	0.13	0.0019	0.0003	0.51
39	Li	0.0037	0.0004	0.15	0.00085	0.00016	0.38
40	Lu	0.000040	0.000005	0.6	(0.000041)	(0.000014)	-
41	Mo	0.00029	0.00005	0.40	(0.00016)	(0.00005)	-
42	Nb	0.0012	0.0002	0.35	0.0010	0.0002	0.51
43	Nd	0.0039	0.0005	0.22	(0.0021)	(0.0002)	-
44	Ni	0.0054	0.0006	0.07	0.0031	0.0006	0.24
45	Pb	0.0021	0.0003	0.49	0.0014	(0.0002)	0.40
46	Pr	($8 \cdot 10^{-4}$)	($2 \cdot 10^{-4}$)	-	-	-	-
47	Rb	0.0093	0.0005	0.22	0.0039	0.0007	0.21
48	S total	0.165	0.013	0.49	-	-	-
49	Sb	($0.95 \cdot 10^{-4}$)	($1 \cdot 10^{-4}$)	-	-	-	-
50	Sc	0.0013	0.0002	0.26	0.0019	0.0003	0.51
51	Se	($0.97 \cdot 10^{-4}$)	($0.1 \cdot 10^{-4}$)	-	-	-	-
52	Sm	0.0007	0.0001	0.15	(0.000430)	(0.000025)	-
53	Sn	0.00032	0.00005	0.35	0.00037	0.00007	0.46
54	Sr	0.0266	0.0030	0.15	0.058	0.003	0.38
55	Ta	0.000084	0.000015	0.6	-	-	-
56	Tb	0.00009	0.00001	0.22	-	-	-
57	Th	0.00127	0.00013	0.35	(0.00048)	(0.00010)	-
58	Tm	($0.42 \cdot 10^{-4}$)	($0.06 \cdot 10^{-4}$)	-	-	-	-
59	U	0.00120	0.00011	0.6	(0.0003)	(0.00032)	-
60	V	0.011	0.001	0.40	0.0105	0.0010	0.56

N°	Element component	BIL-1 (GSO N° 7126- 94)			BIL-2 (GSO N° 7176–95)		
		A (%)	Δ_{RS}(%)	m, g	A (%)	Δ_{RS} (%)	m, g
1	2	3	4	5	6	7	8
61	W	($4.3 \cdot 10^{-4}$)	($0.9 \cdot 10^{-4}$)	-	-	-	-
62	Y	0.0030	0.0004	0.35	0.0024	0.0004	0.46
63	Yb	0.00029	0.00004	0.22	0.00027	0.00005	0.46
64	Zn	0.0096	0.0014	0.13	0.0064	0.0011	0.38
65	Zr	0.0156	0.0013	0.40	0.0204	0.0022	0.38
66	SiO_2biogen.	(14.59)			(1.07)		

Note : In parenthesis the approximate values.

RESULTS AND DISCUSSION

The reference samples BIL-1 and BIL-2 were certified according to Russian Standards for concentrations of 49 and 30 elements, respectively, with a precision fulfilling current metrological ("fitness for purpose") requirements. The concentration of 17 additional components in BIL-1 and 18 in BIL-2 were established approximately as information values. The RS have passed the State requirements and have assigned official names in the State list of standard samples: SRS 7126–94 (BIL-1) and SRS 7176-95 (BIL-2). The validity for 10 years of both BIL-1 and BIL-2 samples was assigned, according to Russian Standard Document requirements.

The details of the matrix composition of RS lake sediments BIL-1 and BIL-2 as well as those of sediments from other basins are given in Figure 2. Thus, the reference samples BIL-1 and BIL-2 forming a distinguished differing pair, allow to ensure the necessary metrological support in analysis of samples of lake sediments, including those of the Baikal region. The standard sample BIL-2, as well as BIL-1, is unique and has no analogs in Russia.

In an international collection of multielement reference samples of recent sediments[10] two RMs of bottom sediments developed by International Atomic Energy Agency (IAEA) SL-1 and SL-3 are known, one sample is available in Japan (JLK-1) and four samples were created in Canada (LKSD –1, –2, –3, –4). Besides, in the analysis of bottom sediments it is possible to use the reference sample of the estuarine sediment developed in USA (NBS-1646), the Canada marine sediments (MESS-2, BCSS-1, PACS-1), and the sea silt MAG-1 (USA).

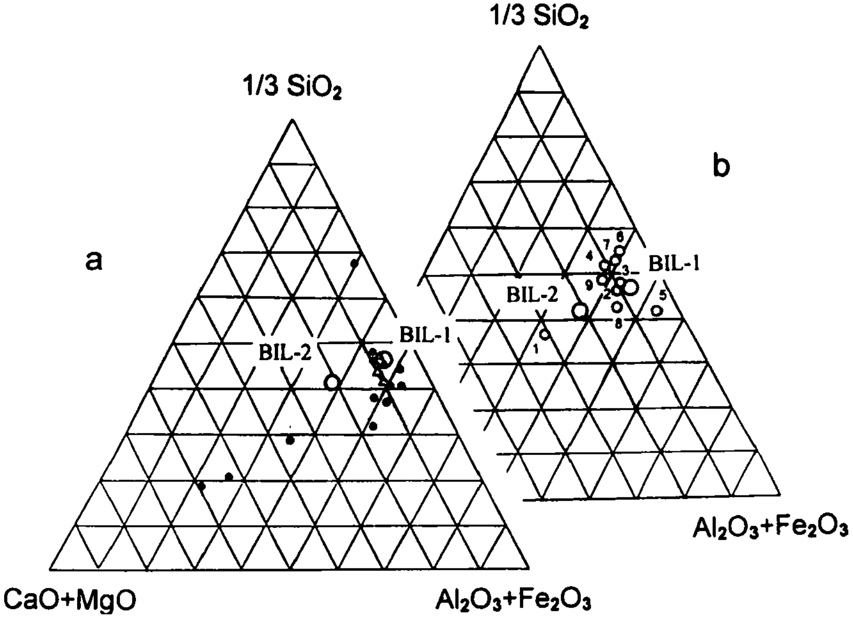

FIGURE 2 The positions of the BIL-1 and BIL-2 samples on the diagrams of compositions: a) bottom sediments of various World's basins; b) reference materials of the various water basins bottom sediments. *Notes*: empty large circles – BIL-1 and BIL-2; triangular symbols – the compositions of lake Baikal individual samples of deep-water bottom sediments; filled small circles – the compositions of the bottom sediments of various World's basins; empty small circles – the reference materials of the bottom sediments : (1- 4) Lake sediments LKSD-1, –2, –3, –4; (5) Lake sediment JLK-1, (6) Estuarine sediment NBS1646, (7) Marine sediments BCSS-1, (8) Marine sediments PACS-1, (9) Marine mud MAG-1

A well-known set of reference samples of deep-water bottom sediments of Pacific ocean and Red Sea (SDO-1, –2, –3, –8, –9) are created in Russia.

The data presented in Figure 2a allow to estimate the relationship between the compositions of samples BIL-1 and BIL-2, as well as its situation in a field of recent fresh water and, certainly, of marine sediments. Figure 2b allows a definite conclusion about the compositions relationship of the samples under discussion with the above listed samples.

It is interesting to discuss a range of elements, which managed to be certified in the developed samples and also the list of elements included in the certificates as recommended. With reference to data presented in the Table IV it can be seen that, in both samples, the rock forming components are attested completely (SiO_2, TiO_2, Fe_2O_3 total, FeO, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, LOI). In this case both samples are close in the concentrations of three main components (SiO_2, TiO_2, Al_2O_3), differ in the concentrations of MgO, FeO, MnO and alkalis and very much in the CaO concentration. Among the certified trace elements in RS BIL-1 and BIL-2, the Ba, Co, Nb, Sc, Sn and V concentrations are very close in between, but such elements as Ni, Pb, Y, Yb, Zn, Zr differ in concentrations up to 2 times, and Cr, Cu, La, Li, Rb and Sr, in 2.5 and higher. Among other elements, of which concentrations are attested only for BIL-1 (for BIL-2, usually appear in rank "approximate values") it should be noted the distinctions of concentrations for Be and Ce in 2 times, for B and Th in 3 times, for Ag and U in 4 times. When the amount of certified parameters in sample BIL-1 is compared with that of the other above mentioned RS of lake bottom sediments, it is apparent that the sample BIL-1 is attested on a level with the best World standards collection. The sample BIL-2 is comparable with samples SL-1, SL-3 and NBS-1646 in the quantities of attested parameters. Unfortunately, the concentrations of many matrix components are not certified in samples MESS-2, SL-1 and SL-3, being unable to plot them on the diagram (Figure 2b).

The range of elements to be certified is primarily defined by the necessity of the reference samples for monitoring the anthropogenic or technogenic impact on the natural environment. These include the foremost toxic pollutants: As, B, Ba, Be, Cd, Co, Cr, Cu, F, Hg, Pb, Sb, Se, Sr, Tl, V and Zn. In the ecogeochemical programs it is of first importance the control over the cycling of biophyllic elements: Fe, Mn, Mg, Ca, K and P, as well as B, Co, Cu, Mo, Se and Zn. Diversified Ti, Mn, Nb, Sn and Au mineralization on the Baikal coast define the necessity of these elements attestation in RS to be developed. It is of first importance for researches of Baikal's environments to have the samples with certified SiO_2 and SiO_2 biogenic, C and Corganic, Stotal and Ssulphate, Ntotal, as well as Br, I, F, Cl, Th and U.

CONCLUSION

As indicated above, the reference standards of bottom sediments of lake Baikal BIL-1 and BIL-2 are certified accordingly on 49 and 30 components. The concentrations of 17 components are provided as "approximately values". The use of these RS are already supporting important researches, connected with lake Baikal. For further extension of the compulsory minimum collection of the RMs of natural environments of lake Baikal region it has been suggested to develop a number of RMs of ground and water based biota, including birch leaf (LB-1), grass mixture (Tr-1), Canadian eladea (EK-1), perch muscle (BOK-1) and dry water residue (BVSO-1). At the moment the possibility of development of the Baikal's ultra fresh water RM is under active study.

The approach suggested here envisages the system development of special collection of RS. The authors research program pursue two goals. First, the set of reference samples to be created should provide the metrological support for analytical researches in Baikal region, which has been recently announced by UNESCO as World Heritage Site. The second is to record the certified data of the selected reference samples as the analytical "image" or "count point" for future researches.

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