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High-Performance Technique on the Base of ICP-MS for Obtaining High-Resolution Records of Climate-Sensitive Elements in Bottom Sediments of Lake Hovsgol (Mongolia)

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Abstract

To obtain high-resolution records of elemental paleoenvironmental change proxies in the bottom sediments of Lake Hovsgol (Mongolia), a high-performance technique is proposed. It consists of extraction of sediment samples with 1 % HNO_3 followed by multi-elemental ICP-MS measurements of extracts. In comparison with the complete decomposition of bulk samples, this method provides a maximal number (44) of climate-sensitive elemental signals (variation of contents of extractable elements along sediment core depth) and, at the same time, their maximal response to the global paleoclimate change. The highest sensitivity (variability >100 %) to climate change is characteristic for C_{inorg}, P, Ca, V, Ni, Se, Br, Sr, Mo, Sb, I, W and U, and the lowest one (25–30 %) – for As, Rb, and Pb. On the basis of memory effect studies, an algorithm of ICP-MS measurement (VG PlasmaQuad II quadruple spectrometer) is proposed; this method does not require intermediate rinsing of spectrometer measuring path between core samples analysed subsequently. It allows increasing the output of serial analysis up to 200 samples per day.

Keywords: ICP-MS, Lake Hovsgol sediments, sequential extraction, paleoenvironmental change proxies

1. INTRODUCTION

Modern paleoenvironmental reconstructions are based on high-resolution records of various proxies of paleoclimate changes in ice cores and in sedimentary cores from seas and lakes. Bottom sediments of large, old continental lakes, such as Lake Baikal (Russia) and Lake Hovsgol (Mongolia), are of great interest for paleoenvironmental reconstruction in the intracontinental part of Asia. Numerous studies of Lake Baikal bottom sediments carried out during last two decades have shown that geochemical indicators are very useful paleoenvironmental proxies [1–11]. The use of high-performance methods and their optimisation are the main factors for obtaining high-resolution paleoenvironmental records. Thus, many sediment cores from Lake Baikal were analysed with high and ultra-high resolution due to optimisation of high-performance methods of analyses, such as SR-XFA (scanning of raw cores) [12, 13] and ICP-MS [7, 8].

Comprehensive and detailed studies of Lake Hovsgol sediments aimed to obtaining paleoreconstructions have started rather recently [14–17]. Certainly, they require high-performance and valid techniques, in particular, for multielemental analysis on the basis of modern instruments.

Obtaining high-resolution elemental proxies caused by paleoclimate changes allows to determine the transition boundaries when paleoenvironmental conditions change. This is one of the most important tasks for paleoenvironmental reconstructions. The necessity of such identification is especially important while studying long drilling cores where traditional biogenic indicators ($SiO_{2\ bio}$, C_{org}, *etc.*) are considerably distorted or completely disappear due to diagenetic processes just at the boundary of 150 ky BP [16]. The method proposed in this paper is just aimed to the solution of this important task.

In this paper, the sequential extraction procedure (based on nitric acid) for revealing climate-sensitive elements in Lake Hovsgol bottom sediments is proposed and studied, and ICP-MS measurement algorithm for multi-elemental express routine analysis of cores is optimised.

2. EXPERIMENTAL

2.1. Sampling, sample preparation, weak acid extraction and sequential extraction procedure

The core X105-2, 110 cm long was taken in the central part of Lake Hovsogol from the depth of 241 m (50°56′40″ N, 100°21′25″ E). This core was dated by ^{14}C AMS method [15], it covers the last 30 ky. The core was cut along and sampled at 1 cm intervals. Sub-samples of wet sediment (~3 g) were weighed, dried at 60 °C to constant mass [2] and ground in a mortar. Dried samples were heated at 600 °C during 1 h (in order to remove the major part of organic matter), and mass losses were calculated.

To study losses on ignition, extraction kinetics, stability of solutions and some other items, a "test" sample was prepared by mixing equal quantities of Holocene (10 samples) and Pleistocene (10 samples) sediments (except diagenetic horizons) from the core X105-2. Dried and ignited (mass loss 8.7 %) aliquots of the sample were decomposed by microwave method and analysed with ICP-MS according to [18].

Kinetics of extraction with 1 % HNO_3 was done with dried and ignited sample "test". The sub-samples (160 mg) were placed in polypropylene tubes and 45 ml of 1 % HNO_3 was added. Extracts were taken after 5, 10, 20, 40 min, 1, 2, 4, 8 h, 1, 2, 3, 4, 5, 6, 7 days and 2, 3, 4 weeks. Extracts were stabilized with 0.01 % EDTA (SIGMA, 99.995 % purity) immediately after centrifugation and separation of supernatant from solid phase. All extracts were analysed by ICP-MS simultaneously after finishing the kinetic experiment.

Investigation of solutions stability (during a week) was done with ignited "test" sample after 20 h of extraction and separation of supernatant from solid phase. Stabilized (with 0.01 % EDTA) and non-stabilized extracts were studied.

An influence of the percentage of weak nitric acid on the magnitude of elements extraction was studied with 1, 2 and 4 % HNO_3 and with ignited "test" sample after 20 h of extraction.

The sequential extraction procedure was performed with 50 mg of ignited sub-samples under the conditions presented in Table 1.

All the reagents used were of analytical grade, and distilled water was prepared with redistiller GFL 2104 Cesellschaft fьr Labortechnik MBH (Germany). Indium (10 ppb in measurable solutions) was used as an internal standard.

TABLE 1

Sequential extraction procedure of Lake Hovsgol sediments (50 mg sub-samples)

Stage I[a]	Stage II[b]	Stage III (thermal acid decomposition of residue)[c]
1 % HNO_3 (15 mL)	70 % HNO_3 (0.5 mL)	70 % HNO_3 (3 × 1 + 2 mL), 60 % $HClO_4$ (1 mL), 50 % HF (5 mL), 30 % H_2O_2 (30 μL)
Room	80 °C	90 °C
20 h	2 h	During 24 h

[a] Tubes (polypropylene, V = 15 mL) were centrifuged (10 000 g), and solutions were measured from the same tubes (upper part of extracts was taken).

[b] After measuring the first stage extracts, they were decanted, tubes were rinsed twice with 10 mL distilled water. The hot acid extracts of stage II were diluted with 14 mL of distilled water (next steps – see comments for stage I).

[c] Residues were transferred to glass carbon crucibles (V = 40 mL) and evaporated to dryness. After this, precipitates were evaporated twice with adding 1 mL HNO_3, then 2 mL HNO_3 with 30 μL H_2O_2 were added. Solutions were kept to mature for 2 h (room temperature) and diluted with 40 mL of 1 % HNO_3.

TABLE 2

Instrumental operating conditions and parameters data acquisition (VG PlasmaQuad II)

Condition/parameter	Setting
RF power, W	1350
Reflected power, W	<5
Cooling argon gas flow rate, $\min^{-1}$	13.5
Auxiliary argon gas flow rate, $\min^{-1}$	0.8
Nebulizer argon gas flow rate, $\min^{-1}$	0.98
Spray chamber (Scott type) temperature, °C	17
Nebulizer type	Babington
Sampler cone (nickel) internal diameter, mm	1
Skimmer cone (nickel) internal diameter, mm	0.7
Sample uptake rate, mL/min	1
Sample uptake time, s	40
Scan mode	Scanning
Scanning mass range	6–13, 23–39, 41–238
Points per mass unit	25
Dwell time, ms	10.24
Detector dead time, ns	30
Time per sweep, s	0.1
Integrated measurement time, s	60
Repeats	1
Integration range, units of atomic mass	0.8

2.2. Multi-elemental ICP-MS measurements of serial samples extracts

The samples of core X105-2 prepared according to conditions described in Table 1 were analysed with quadrupole ICP-MS spectrometer VG PlasmaQuad II using semiquantitative technique. Before each measurements set, the instrument was tuned and calibrated by standard solution "tune" having widely different masses (^{9}Be, ^{59}Co, ^{115}In, ^{140}Ce, ^{209}Bi, ^{238}U – 10 ppb). The calibration curve (taking into account sensitivity factors of the elements) is approximated by a second-degree polynomial fit. In this case, the systematic inaccuracy of calibration of elements which are not included in the "tune" calibration standard is not worse than ±30 %, while relative changes of elements concentrations between samples in the set measured are determined with a precision not worse than 10 % RSD. Samples were measured by separate sets: 1 % HNO_3 extracts, 70 % HNO_3 extracts, and solutions of thermal acid decomposition of the residue. In each set, the samples were measured subsequently with core depth increase in the following order: blank sample – control sample – 10 samples – control sample – 10 samples – control sample, *etc.* An averaged sample prepared by mixing of 0.5 mL from each measured solution sample in a set was used as a control sample tracing a temporal instrument drift for all the range of scanned masses. The rinsing of spectrometer measuring path (3 % HNO_3, 1 min) was done before and after each control sample, but it was not done between unknown samples measurements. Other parameters with which the measurements were performed are given in Table 2.

Interference correction was done using PQ SIMPLEX 2.0 software (improved from first version [19]). The final choice of isotopes, which were used for concentration calculation, was done by combining of principles of "minimal calculated concentration" and "most reliable isotopes" (essentially free from oxides and having a relatively high abundance). The typical masses were: ^{7}Li, ^{9}Be, ^{11}B, ^{12,13}C, ^{23}Na, ^{25}Mg, ^{28,29}Si, ^{31}P, ^{34}S, ^{43}Ca, ^{45}Sc, ^{47}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{71}Ga, ^{74}Ge,

^{75}As, ^{77}Se, ^{79}Br, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{98}Mo, ^{108,104}Pd, ^{109}Ag, ^{111}Cd, ^{120}Sn, ^{121}Sb, ^{127}I, ^{133}Cs, ^{135}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{174}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta, ^{182}W, ^{187}Re, ^{195}Pt, ^{202}Hg, ^{208}Pb, ^{209}Bi, ^{232}Th, ^{238}U.

It is possible to measure 60 elements (K and Al were out of detection range in most of the samples) reliably in solutions of 1 % HNO_3 (see Fig. 6). Some of these elements cannot be determined reliably in strong acid extracts (C, Re) and in solutions of thermal acid decomposition of residue (C, Na, Si, Re, Bi) but some other elements can be determined additionally (Ag, Pd, Pr, Au and Ag, Pt, respectively).

3. RESULTS AND DISCUSSION

3.1. Loss on ignition, kinetics of extraction with 1 % HNO_3 and stability of solutions

The main reason for ignition was the intention to remove major part of organic matter in order to obtain record of inorganic carbon. Another reason was a suspicion that organic matter is able to "cement" mineral particles and to decrease its accessibility for extragent effect. It was found out that considerable losses (in comparison to dried sample) are characteristic for Br (30 %), I (98 %) and Hg (70 %). Losses of other elements are within the range of determination errors (typically less than ±10 %), *i.e.* cannot be determined reliably, so we may assume that losses are negligible.

Kinetics of extraction with 1 % HNO_3 was done with dried and ignited sample "test". The initial kinetic profiles were normalized – every concentration in extracts was converted to the dried sample (ignited series were corrected to loss on ignition as well) and divided by its mean values over the ignited profiles; normalized profiles for each serial sets with similar shapes were combined in stacks (just averaged). Kinetic profiles of extracted elements from ignited "test" sample are presented in Fig. 1. It is evident that it is impossible to reach chemical equilibrium in sediment–extragent system over any reasonable time for most elements. It means that exact extraction time must be kept for all investigated samples in order to obtain comparable

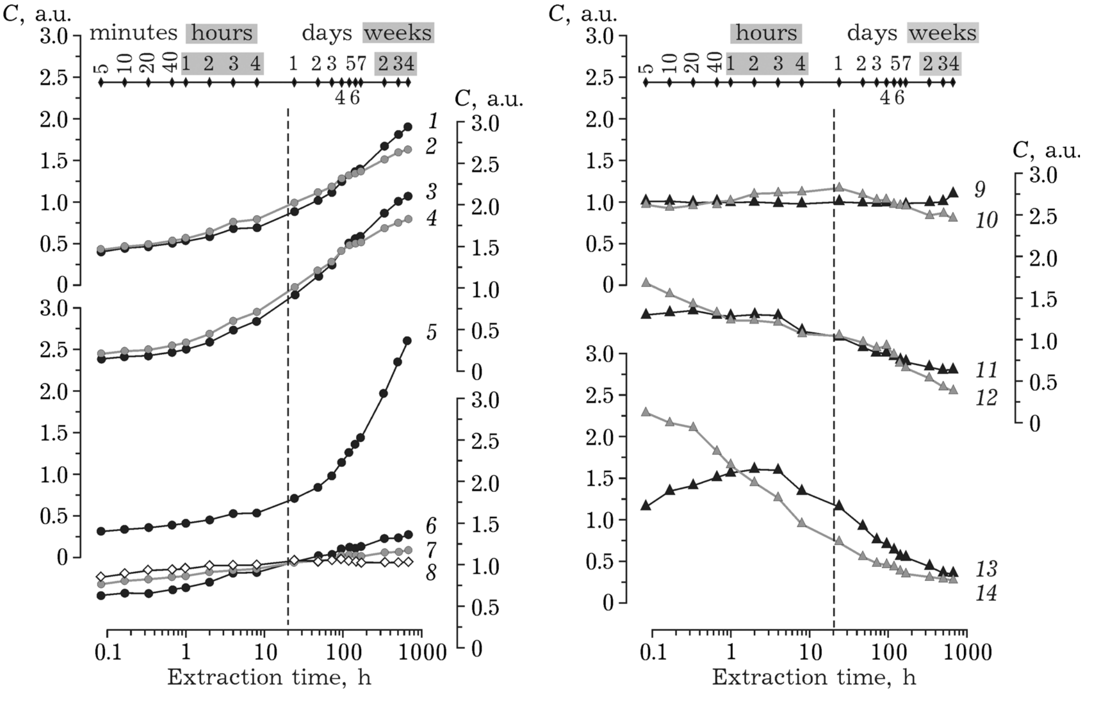

Fig. 1. Kinetics of extraction of elements from ignited Lake Hovsgol bottom sediments ("test" sample, see text) with 1 % HNO_3: *1* – Li, Na, Rb, Tl; *2* – Be, Mn, Mg, Sc, K, V; *3* – Si, Fe; *4* – Cr, Zn, Ga, Co, Ni; *5* – Ti, Cs, Cu; *6* – B, Pb, Th, Ba, Cd, Ta; *7* – Sr, LREE (La, Ce, Pr, Nd, Sm, Eu); *8* – P, As, Re, Ca, Ge, Y, HREE (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), U; *9* – Se, Br, Sn, Nb; *10* – S, Bi, Hf, Zr; *11* – Mo; *12* – I; *13* – Sb; *14* – W.

data. We chose extraction time equal to 20 h which was rather compromise. It is optimal for preparing of several hundred samples (including night time) on the one hand, and no sense to wait longer in terms of "stability" (concentration of Mo, I, Sb, W tend to decrease and elements of the stacks 1–5 tend to increase), on the other hand. We suppose that climate-sensitive element signals obtained in the sediment core (see below) are due first of all to mineral composition of the sediments which is controlled mainly by paleoenvironmental conditions. The processes of extraction have secondary influence and are able to amplify contrast factor for major part of element signals (this is disable effect) as it will be shown below.

After separation of supernatants from solid phases the solutions are stable at least during a week except Zr, Sn and Hf, concentration of which decreases to 26, 48 and 42 %, respectively. The losses of the elements are absent if solutions are stabled with EDTA (0.01 %). So, if it is impossible to measure samples immediately after extraction period, the solutions must be separated and recommended to be stabilized.

The shapes of kinetic profiles for major part of elements extracted by 1 % HNO_3 from dried "test" sample are similar to ones obtained with ignited sample but quantities of extracted elements varied greatly. As we assumed, the quantities of elements extracted from dried sample are less then ones extracted from ignited sample for major part of elements. At time extraction of 20 h, the maximal difference is characteristic for Th (13 times) and Br (10 times). As for the latter, it seems unusual because Br during ignition considerably escapes (30 %). We assume that a part of Br in sediments is subjected to diagenetic transformations and included in secondary minerals which are able to return Br readily into extract if organic mater was removed. Other elements extracted from ignited sediment exceed ones extracted from dry sediment not so much (Tl, V, Ni, Ge, Se, Mg, Re, Fe, Si, B, Ga, Sn, S, Rb, Sc, Al, K, Li, Mo, Na, Cr, W, Bi – from 1.2 to 3.2 times). On the contrary, some elements are extracted better from dried sediment: Pb, Ti, Ta, Cd, Zr, I, Cu (from 1.2 to 3.8 times). The difference for rest elements (Nb, Ba, Hf, Ca, Mn, Y, REE, Sb, Cs, Sr, U, Co, P, As, Zn, Be) does not exceed ±10 %.

Kinetic profiles of elements obtained from dried sample which have shapes character not similar to ignited one are shown in Fig. 2.

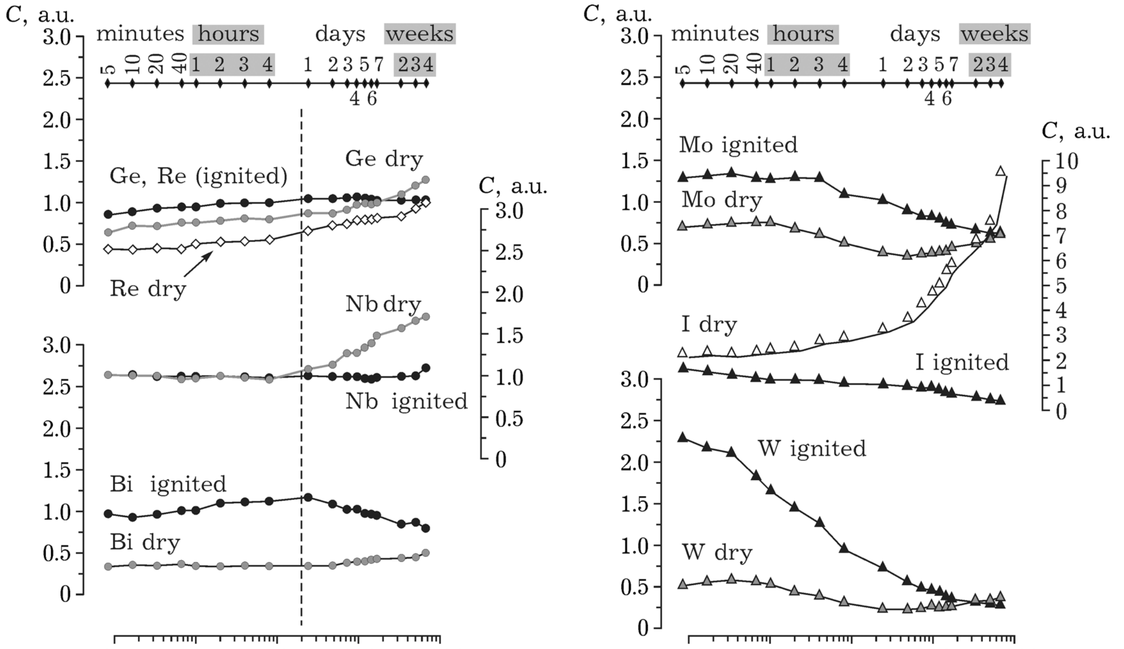

Fig. 2. Comparison of element extraction kinetics with 1 % HNO_3 from dried (grey symbols) and ignited (black symbols) "test" sample.

The discrepancy in shapes characters is found out only for Ge, Re, Nb, Bi, Mo, I and W. In all cases kinetic profiles obtained with dried sample have well-marked tendency to increase since 1 day (Re, Nb, I) or 2 days (Ge, Bi, Mo, W) in comparison to ones obtained with ignited sample. Such discrepancies are probably due to change of physical state of mineral phases during ignition. It should be kept in mind if weak acid extraction is done with dried or ignited sediments.

3.2. Influence of percentage of weak nitric acid on magnitude of elements extraction

We investigated elements extraction from ignited "test" sample with 1, 2 and 4 % nitric acid (under the same condition as for stage I of sequential extraction procedure, see Table 1). The choice of concentration range of nitric acid was done for the next reasons: (i) 1–4 % HNO_3 is a typical range for measurable solutions in ICP-MS, so use of more concentrated extragent requires dilution of initial extracts, this will decrease sample prepare rate; (ii) more concentrated nitric acid has no advantages in terms of revealing and contrasting paleoenvironmental changes elemental signals (as it follows from the results obtained while running sequential extraction procedure of the core studied; see below). Data obtained are presented in arbitrary units in Fig. 3. It is seen that the increase of extraction is practically linear and proportional to nitric acid strength for the major part of the elements. Increase of extraction in 4 % HNO_3 media in comparison to one of 1 % HNO_3 does not exceed 25 % for approximately half of the elements (stacks *1–4*). Extraction of Ca, Se, U, Ge, Sr, Y, S, Br (stack *4*) and Si, As, REE (stack *3*) practically does not depend on HNO_3 strength, it means that mobile forms of these elements are associated mainly with phases which are able to be dissolved readily (sulphates and carbonates mainly) or to desorb the elements into weak acid media (some authigenic facies and clay minerals, *e.g.* montmorillonite). Extraction of rest elements depends on acid strength stronger – concentrations of the elements in 4 % HNO_3 exceed ones in 1 % HNO_3 1.4–9.3 times except P (1.1) and Mn (1.3). The latter together with Zn are characterized by more expressed extraction in 1–2 % HNO_3 interval, and than extraction is suppressed (P) or slightly decreases (Mn, Zn). Nb, Ta and Zr, Hf, on the contrary, have inverse extraction

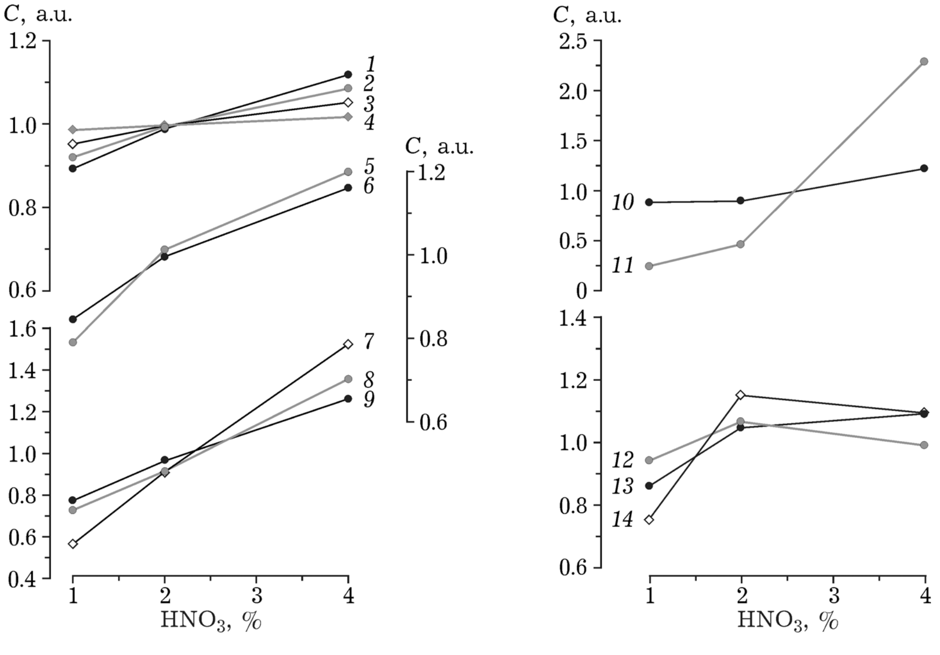

Fig. 3. Extraction (20 h) of the elements from ignited "test" sample (see text) with 1–4 % HNO_3: *1* – Li, Mg, B, I, Mg; *2* – Be, Sc, Cd, Ba, Pb; *3* – Si, As, REE; *4* – Ca, Se, U, Ge, Sr, Y, S, Br; *5* – Fe, Sb, Ga, Mo; *6* – K, V, Co, Cr, Ni, Th; *7* – Sn, Cs, W, Bi; *8* – Ti; *9* – Cu, Rb, Tl; *10* – Nb, Ta; *11* – Zr, Hf; *12* – P; 13 – Mn; *14* – Zn.

profiles – extraction is more expressed in 2–4 % HNO_3 interval, especially for Zr, Hf.

Increase of concentration of HNO_3 from 1 to 4 % formally corresponds to increasing of extraction time with 1 % HNO_3 from 1 to 2–7 days (the time is not equal for different elements and groups, cf. Fig. 1). Evidently, the increasing of extraction time is not identical to increasing of acids strength (especially for Mo, I, Sb, W, Si, As, P, HREE, Nb, Ta, Zr, Hf, Bi, Th, cf. Fig. 1). So, it should be kept in mind while choosing extragent percentage.

3.3. Sequential extraction procedure

In order to study elemental composition of different fractions of multi-component systems (soils, bottom sediments, *etc.*), different variants of the method of sequential extraction with specific extragents are used [20–25]; first it was proposed by Tessier *et al.* in 1979 [26].

While studying Baikal sediments, we have shown that extraction with hot concentrated HNO_3 allows to increase “contrast range” of elemental signals (which are proxies of paleoenvironmental change) and to reveal ones which were masked with bulk content of the elements in the samples [7].

In this study, we also used nitric acid as an extragent, however, in difference with [7], the procedure of sequential extraction was used. At the first stage of this procedure the elements were extracted from the sediments with a weak nitric acid (1 % HNO_3). A weak acid is able to extract exchangeable and mobile elements from mineral phases characterized by different resistance to it. We expected that it could give a greater contrasting effect to paleoclimate proxies – variation range of extracted elements along the core depth in response to global paleoclimate changes. Of course, a lot of different acids (*e.g.* hydrochloric acid, acetic acid, *etc.*) are widely used in geochemistry practice for mobile elements extraction from sediments, but our choice is based on the fact that nitric acid gives least interference at ICP-MS analysis. For example, using of hydrochloric acid and other chlorinated compounds does not allow to determine reliably such elements as V, Cr, As, Se due to interferences with molecular ions ClO^+, $ArCl^+$. Another reason is that nitric acid does not form insoluble salts, which are able to precipitate from solutions. On the base of data obtained during investigations of “test” sample (see above) it was impossible to choose optimal weak acid extraction mode. In other words, it was impossible to forecast how these or those extraction conditions will effect onto elements signals obtained from the core sediments. So, we decided to use ignited samples and initial boundary conditions – extraction with 1 % HNO_3 and compromise extraction time (20 h, see Table 1).

At the second stage of sequential elements extraction we used, like in [7], hot concentrated nitric acid which is able to dissolve some autigenic minerals and to extract some quantity of elements additionally due to strong oxidation state.

Finally, at the third stage of this procedure, we dissolved the residues of the samples completely (thermal acid decomposition) in order to reveal paleoclimate change signals, which are due to variations of non-extractable elements.

Evidently, sum of all the stages of the sequential extraction procedure allows to determine bulk elements distribution in the core studied.

The profiles of elements distribution by depth of the core X105-2 obtained while realizing the sequential extraction procedure in comparison with climate biogenic indicators ($SiO_{2\ bio}$, C_{org}, diatoms [15]) are presented in Figs. 4 and 5. Data are presented in arbitrary units – every concentration was divided by its mean values over the profiles. The boundaries of global aleoclimate changes shown in Figs. 4, 5 are obtained by radiocarbon dating of the core [15]: Holocene/Pleistocene – 11.5 ky BP, a warm period Bølling-Allerød (BA, 15–13 ky BP) in the end of Pleistocene is shown by a dashed rectangle, a cold period Younger Dryas (YD, 13-11.5 ky BP) – by a grey rectangle.

As it follows from Fig. 4, most of elements (44 of 60) extracted with 1 % HNO_3 give a clearly expressed paleoenvironmental change signals – elements contents change considerably at the boundary Holocene/Pleistocene or within transitional periods (BA–YD) in the end of Pleistocene. To assess the degree of signals variability in response to global paleoclimatic conditions change, we used a parameter CF (contrast factor) determined as percentage of

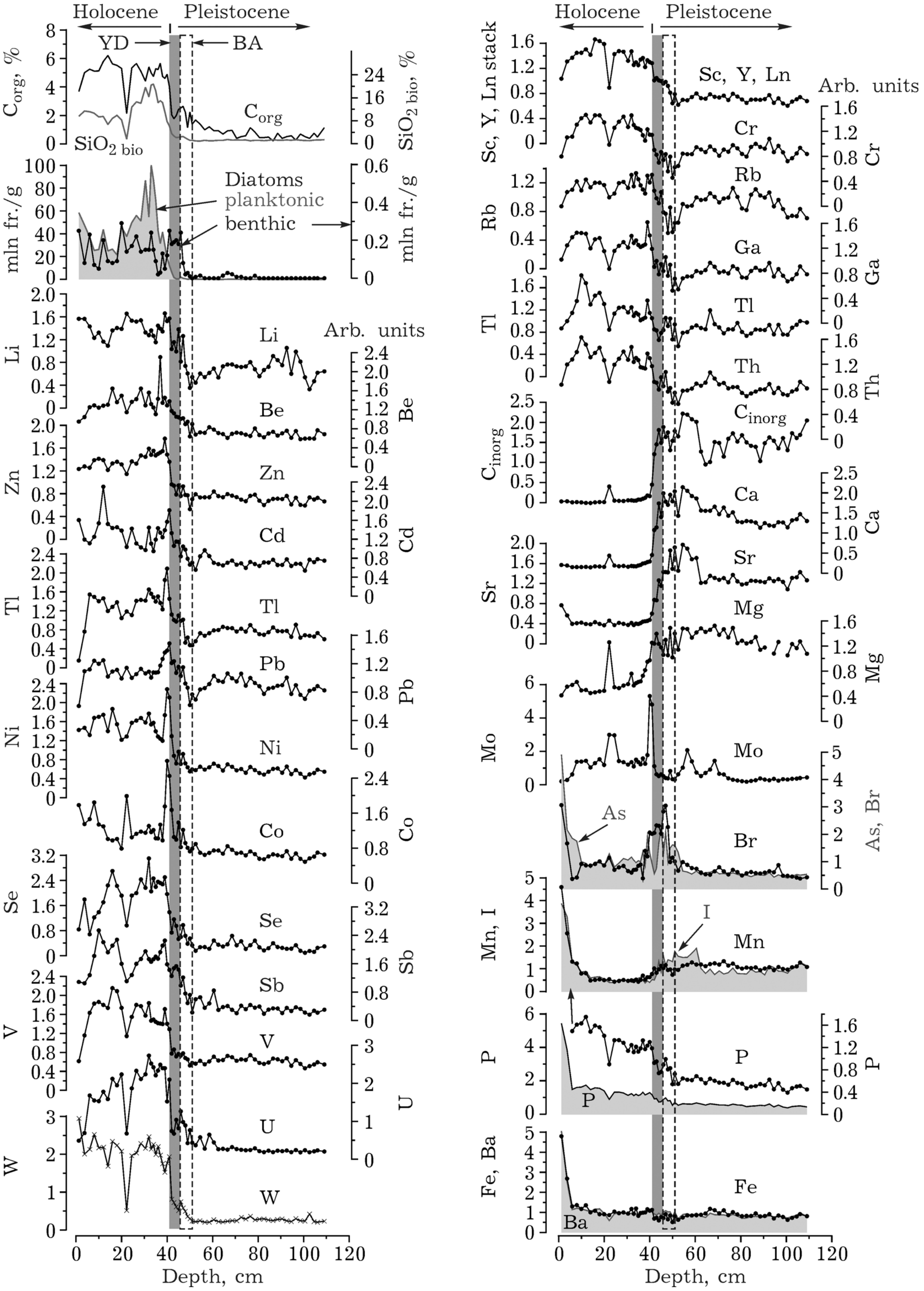

Fig. 4. Climate-sensitive and diagenetic element signals (arbitrary units, see text) are obtained by 1 % HNO_3 extraction of sediments of the X105-2 core (Lake Hovsgol) in comparison to biogenic paleoenvironmental indicators (C_{org}, $SiO_{2\ bio}$, diatoms).

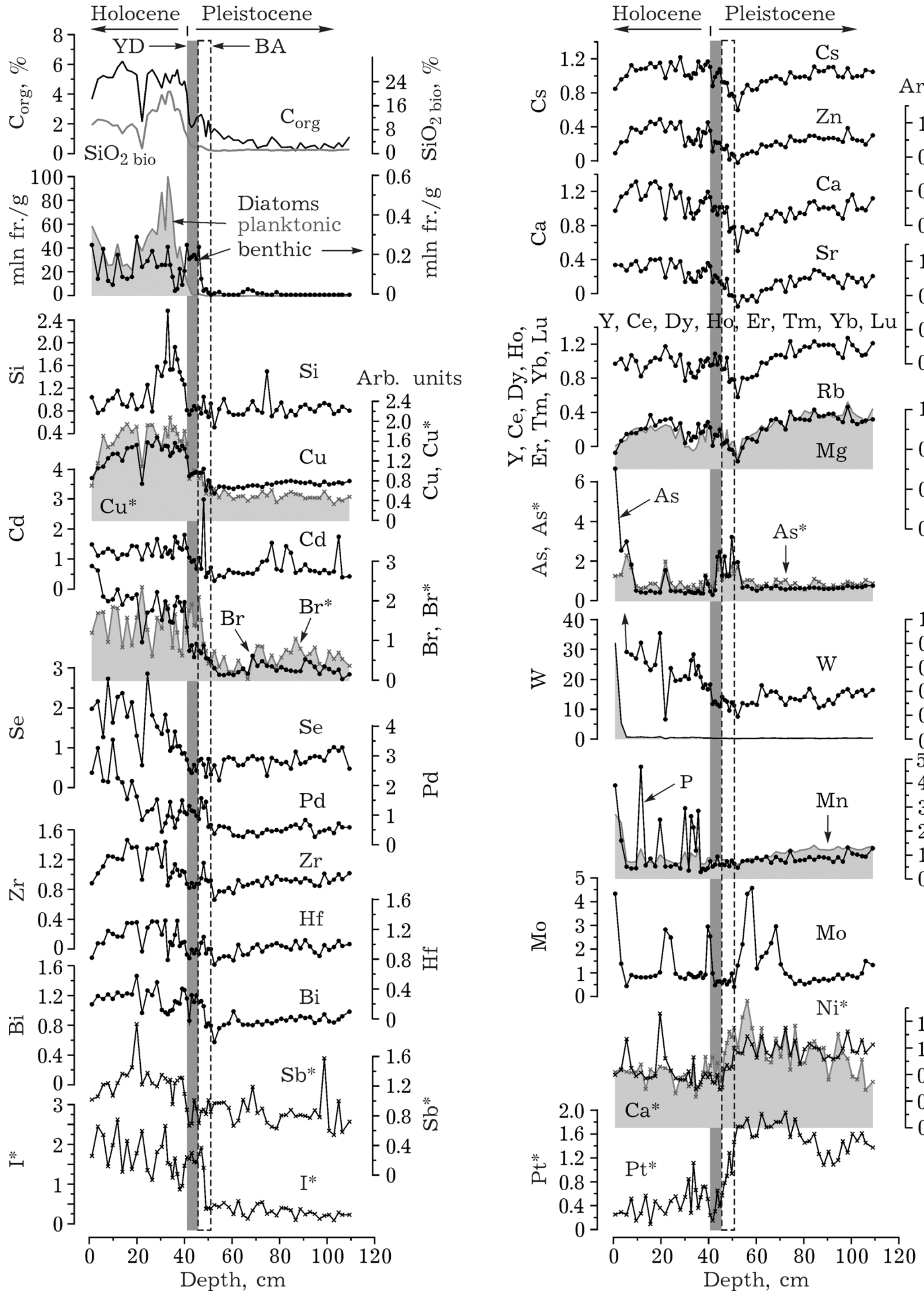

Fig. 5. Climate-sensitive and diagenetic element signals (arbitrary units, see text) are obtained by hot 70 % HNO_3 extraction (marked by circles except Mg and Mn) followed by thermal acid decomposition (marked by "x" on the profiles and by * superscript of element symbols) of sediments of the X105-2 core (Lake Hovsgol) in comparison to biogenic paleoenvironmental indicators (C_{org}, $SiO_{2\ bio}$, diatoms).

change of average signals values in Holocene and Pleistocene parts of the core (except diagenetic horizons) while crossing of the Holocene/Pleistocene boundary (for As, Br the Pleistocene part was averaged within BA and YD periods only).

The most variability of the signals (CF > 100 %) is characteristic for C_{inorg}, P, Ca, V, Ni, Se, Br, Sr, Mo, Sb, I, W and U, the least one (CF = 25–30 %) – for As, Rb and Pb.

The contrast factors and the number of paleoclimatic change elemental signals revealed sequentially with 70 % HNO_3 and with thermal acid decomposition of the residue are considerably less (25 and 8, respectively, see Fig. 5).

Paleoenvironmental change-induced element signals obtained with 1 % HNO_3 are divided into three classes: (i) with high contents in Holocene and low ones in Pleistocene core intervals (Li, Be, Zn, Cd, Tl, Pb, Ni, Co, Se, Sb, V, U, W, Sc, Y, lanthanides (Ln), Cr, Rb, Ga, Ti, Th, Mo and P); (ii) with reversal distribution (C_{inorg}, Ca, Sr, Mg, Mn, I), and (iii) elements the contents of which are higher in transitional climate periods (BA–YD) – As and Br. Paleoenvironmental change proxies obtained at subsequent stages of extraction procedure are divided into three similar groups (see Fig. 5), and profiles of some elements become inverse to stage I (Ca, Rb, Y, lanthanides – in extracts of 70 % HNO_3, I, Ni – in residues, see Fig. 5), and additional climate-sensitive elemental signals appear (Cu, Pd, Zr, Hf, Bi, Cs – in extracts of 70 % HNO_3, Cu, Pt – in residues, see Fig. 5).

The direct extraction of sediments with 70 % nitric acid (estimated by the sum of stage I and II) has no advantages in comparison with 1 % HNO_3 both by number of and by contrast factors of proxies. In this case, seven climate-sensitive signals disappear (Li, Ti, Cr, Co, Ga, Rb, Mo), and seven other ones appear (Cu, Zr, Pd, Cs, Hf, Bi, Ge).

In the bulk samples, only 22 elements remain climate-sensitive (P, Cu, Se, Sb, La, Ce, Pr, Nd, Sm, Gd, Tb, W, Th, U – 1st class; C_{inorg}, Mg, Ca, Mn Sr – 2nd class; As, Br, I – 3rd class). Their contrast factors are lower than in nitric acid extracts ones.

Some elements (W, Mo, As, Br, I, Mn, P, see Figs. 4 and 5) complicated by diagenetic processes are revealed, as well as purely diagenetic ones – Ba, Fe, accumulating in the upper part of the core.

Hence, if we have no aim to study the elements geochemistry in detail, sediments extraction with 1 % nitric acid, due to a simple sample preparation and its high throughput (it is possible to prepare several hundreds samples simultaneously), is the most suitable for obtaining of paleoenvironmental change proxies in lake sediments, as revealed in Lake Hovsgol ones.

3.4. ICP-MS measurements for serial analysis. Metrological characteristics

Besides a high-performance samples prepare, the obtaining of high-resolution paleoenvironmental records requires optimisation of measurement process itself, which is limiting in most cases. In this work, we refused intermediate rinsing of measurement path of ICP-mass-spectrometer between sequentially analysed samples in the series. Below we present some metrological characteristics justifying such approach, as well as characterizing this technique as a whole.

3.4.1. Detection limits

Detection limits (DL, 3σ test) of the elements in 1 % nitric acid extracts are presented in Fig. 6. As it follows from data obtained, for most elements detection limits are <0.1 μg/L, it is considerably lower (10–4600 times) of their minimal concentrations in the solutions measured. DL for Be, Sr, Cu, Mn, I, P, Hg, Zn and Ni are within 0.1–1 μg/l, and for Se, Ti, Cr, Li, B, Mg, Si, Br, S, Fe, Ca, Na, C they are >1 μg/L (maximal DL values are obtained for two latter ones: Na – 60 and C – 4000 μg/L). Such high values are due to impurities in the plasma argon gas (carbon, [27]) and in the blank sample (Na, Ca and some others).

Minimal concentrations of Ta, Hf, Sn, Se, and C in the solutions are comparable with detection limits (they increase DL 1.2–2 times). Rhenium at its minimal concentrations cannot be determined reliably.

Thus, with the selected mode of samples prepare (extraction with 1 % HNO_3), the mass-

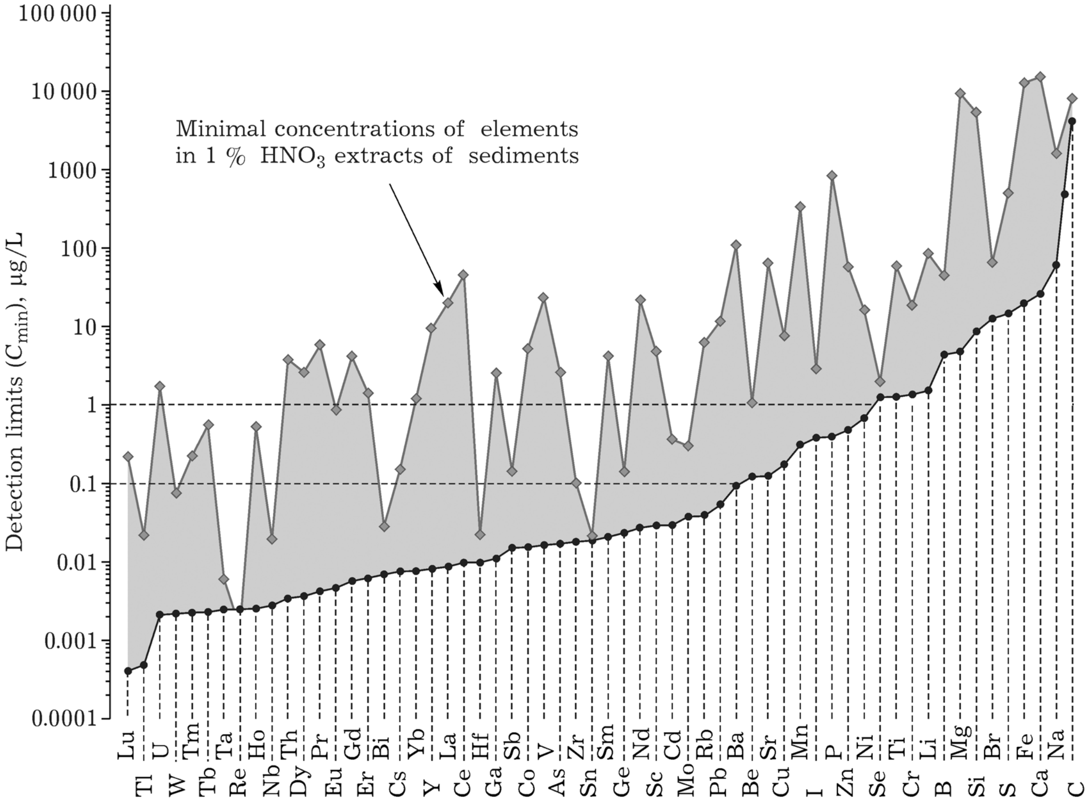

Fig. 6. Comparison of detection limits (DL) of the elements and of their minimal concentrations in 1 % HNO_3 sediment extracts (core X105-2, Lake Hovsgol) by results of ICP-MS analysis.

spectrometer used allows to determine major part of elements in samples studied reliably.

3.4.2. Memory effects

While determining elements by ICP-MS method, main throughput decreasing factor is the necessity to rinse mass-spectrometer measuring path in order to prevent cross-contamination. We supposed that for reliable determination of paleoenvironmental change-induced signals at sequential samples measurement (along the core), rinsing was not necessary as samples have the same type of composition within current paleoclimatic periods, but abruptly different types when paleoclimatic periods change. It was sufficient here to show that memory effects and maximal cross-contamination, which is due to them, do not exceed minimal variability of the proxies (CF = 25 %, see above).

In order to study memory effects, we used the "test" sample (see above). It was extracted with 1 % HNO_3 and measured in the same experimental conditions as for serial samples (see Table 2). The measurements were done seven times repeatedly in the following order: blank (1 % HNO_3) – extract of "test" sample – blank – 10 min rinsing (3 % HNO_3). Memory effects calculations were done as follows:

$$M, \% = (C_{bl\,2} - C_{bl\,1})/(C_{extr} - C_{bl\,1})100 \qquad (1)$$

where $C_{bl\,1}$ and $C_{bl\,2}$ are elements concentrations in blank samples measured just before and after the "test" sample extract, C_{extr} are elements concentrations in the "test" sample extract.

As it follows from Fig. 7, *a*, memory effects for most elements are <3 % except Br (20 %) and I (26 %) for which they are rather great, probably due to the sorption of molecular and/or hydride forms on the surface of spray chamber and of tubes supplying solutions [28–30]. While studying more diluted solutions (3- and 9-fold) we found out that memory effects for Br and I do not depend on the concentration, therefore, considering

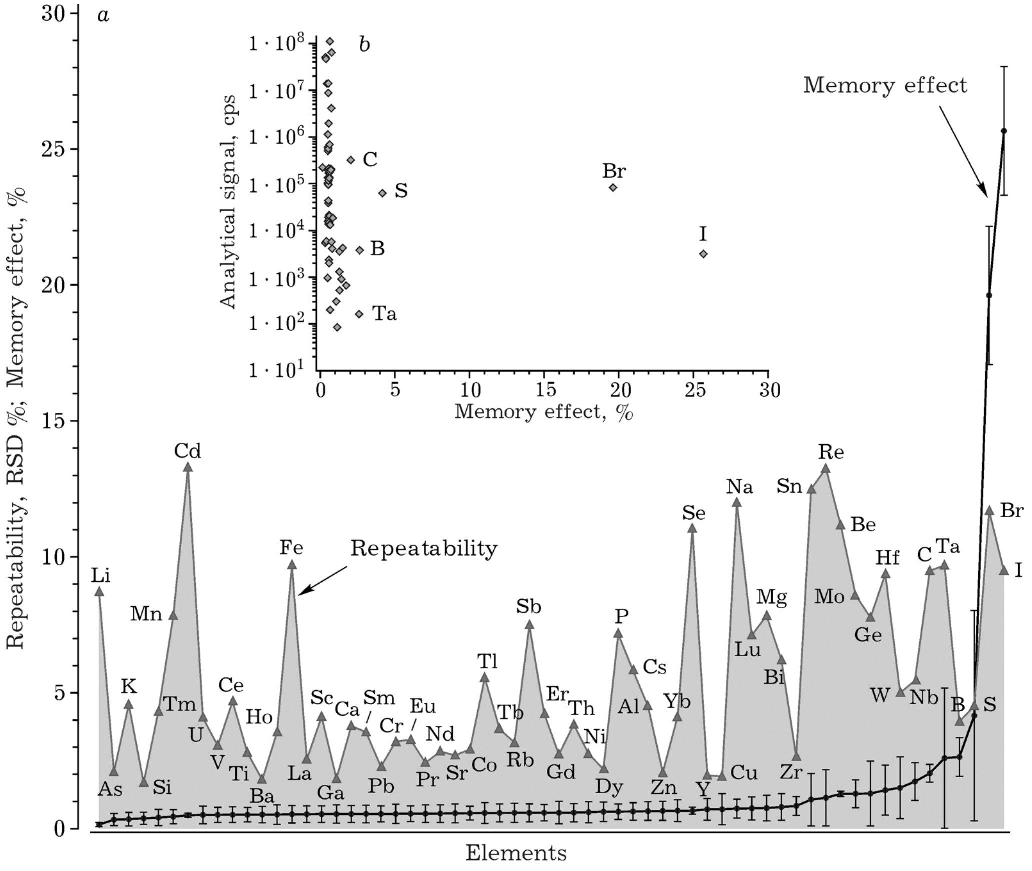

Fig. 7. Memory effects (standard deviations are marked by bars, $n = 7$, panel *a*) and their dependence on analytical signals magnitudes (panel *b*) at ICP-MS measurements of 1 % HNO_3 extracts of the "test" sample in comparison to repeatability of elements determination (RSD, %, $n = 7$, panel *a*).

them as constant ones, one can correct accurately the profiles obtained initially.

Dependence of memory effects on the magnitudes of analytical signals is shown on Fig. 7, *b*. It suggests that all the elements (except Br, I), independently on their concentration range (analytical signals change by 6 orders of magnitude) are removed from measuring system of mass-spectrometer during the time uptake of next sample (40 s, see Table 2) practically completely.

As minimal variability of paleoenvironmental change-induced signals (determined as CF) in the core is 25 %, the contribution of memory effects is negligible, and maximal cross-contamination impact may be estimated as

$$3/(3^2 + 25^2)^{1/2} = 12\ \%$$

Refusal of intermediate rinsing allows to increase considerably the throughput of analysis up to 200 samples per day (~ 2 min per sample, see Table 2), that it provides high-performance technique for high-resolution paleoenvironmental records obtaining.

3.4.3. Repeatability of analysis

The technique proposed intends first of all for determination variability of paleoenvironmental change-induced signals in cores. It means that determination of absolute element concentration in extracts not so significant for our purposes. Systematic error within the limits of semiquantitative methodology is up to ±30 % (due to approximate mode of calibration, see section 2.2) but this error is a constant for every element in all samples in a series. In other words, calibration error does not change the shape of proxies profiles. Main attention is to be paid to the fact that repeatability of determination was not worse than minimal variability (CF = 25 %) of the proxies.

The repeatability was estimated by measurement of extracts of seven parallel sub-samples of the "test" sample (prepared in the same way as for stage I, Table 1). Data obtained are presented in Fig. 7, *a*. One can see repeatability better than 5 % RSD for most of the elements (13 % RSD is maximal value for Cd and Re) that is lower than minimal variability (CF = 25 %) of elemental signals. Thus, the technique developed allows to obtain elemental proxies of paleoenvironmental change in Lake Hovsgol sediments reliably.

4. CONCLUSIONS

On the base of sequential extraction procedure (1 % HNO_3, 70 % HNO_3, thermal acid decomposition of residue) of sediment core samples st. X105-2, it was ascertained that the first step of the procedure (extractions with 1 % HNO_3) provides maximal number (44) of high-sensitive element signals – proxies of paleoclimate changes recorded in Lake Hovsgol bottom sediments. The maximal response (signal variability expressed as contrast factor CF > 100 %) to global paleoclimate change over the past 30 ky (while crossing Holocene/Pleistocene boundary or boundaries of transitional periods Bølling-Allerød and Younger Dryas) is characteristic for C_{inorg}, P, Ca, V, Ni, Se, Br, Sr, Mo, Sb, I, W, and U, and the minimal one (CF = 25–30 %) – for As, Rb and Pb. At the same time, the weak acid sediment extraction method is quite simple and high-performance (it is possible to prepare several hundreds samples per day simultaneously).

An optimised algorithm of multi-elemental ICP-MS analysis of sample prepared was proposed. It is based on the fact that memory effects for the major part of the elements are <3 %, and maximal cross contamination is 12 %, it is considerably less than minimal variability (25 %) of paleoenvironmental change-induced element signals in the core studied. It allows us to exclude rinsing of spectrometer measuring path between samples analysed and so that increases the output of serial analysis up to 200 samples per day. Detection limits of the major part of the elements in the 1 % HNO_3 sedimentary extracts are 0.001–1 μg/L, this is considerably less than their minimal concentration in the solutions studied. The repeatability of determinations for the major part of the elements is characterized by relative standard deviation (RSD) not worse than 5 %. This algorithm together with high throughput of samples prepare is a reliable and high-performance technique for obtaining high-resolution paleoenvironmental change proxies in Lake Hovsgol bottom sediments. We expect that use of this technique will allow to determine paleoenvironmental transition boundaries in long drilling cores more reliably.

The idea on which the technique is based (revealing and/or amplification of climate changes-induced elemental signals via samples prepare operation) allows to adapt it for any bottom sediments for identification of paleoenvironmental change boundaries and to improve it (technique) for solution of specific geochemical tasks.

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