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Microelement Composition of Boundary Cenomanian-Turonian Sediments of Mountain Crimea and Northern-Western Caucasus As The Evidence of Global Anoxic Event

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Abstract

To study the origin of sedimentary rocks of Mountain Crimea and Northern-Western Caucasus, a composition of rock samples was studied and the geochemical ratios of the elements in them were determined. Analytical data were obtained on the basis of a comprehensive approach including determination of total and organic carbon by CHNS-analysis, as well as macro- and microcomponents by atomic emission spectrometry with inductively coupled plasma (ICP-AES) and electrothermal atomic absorption spectrometry (ETAAS) after microwave-assisted sample preparation. For low contents of rare earth elements (REEs) preliminary cation-exchange matrix separation on Dowex AG 50W-X8 was used. That, in combination with calculated interelement correction coefficients, permitted ICP-AES determination of all REEs, Y and Sc with good precision (RSD below 10%) and detection limits (DLs) varying from 0.025 μg g^{-1} (Eu, Ho, La, Lu, Y, Yb, Sc) to 0.10 μg g^{-1} (Dy, Er, Gd). Noble metals were determined by ETAAS using slurry technique with DLs 2 ng g^{-1} (Au, Pd) and 2.5 ngg^{-1} (Pt) after preconcentration on a powdered chelating sorbent POLYORGS-IV.

The accuracy of data was confirmed by the analysis of standard reference materials (limestone KH and black shale SChS-1).

Data obtained for samples of black shales and host rocks from cross-sections of Mountain Crimea and Northern-Western Caucasus show the principal differences in accumulation conditions of sediments in these geological regions.

Key words: Sediment rocks, rare earth elements, noble metals, ICP-AES, ETAAS

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1. Introduction

Chemical composition of geological samples and ratios of elements in them are tightly connected with the origin of Earth matter and often serve as indicators of geological processes. Very widely distributed in geological history are the formations containing black shales - sedimentary rocks enriched with organic matter (OM). During the last several dozen years sedimentologists, geochemists, paleontologists, paleooceanographers and paleoclimatologists paid to black shales special attention, because in the geological record of these sediments a number of global and sub-global oceanic anoxic events (OAE) are reflected. During the Cretaceous epoch there were three main events: Barremian-Albian (OAE1), Cenomanian-Turonian (OAE2), and Coniacian-Santonian (OAE3). Black shales of OAE2 are critical, in part, for understanding the mechanisms driving the climate and ocean systems during the period of extreme warmth. Traditionally two main environments are considered for OAE2 black shale formation: stagnant basins and upwellings.

The signs of this event are recorded in sediments in the West, Central and East remote areas of Mediterranean. Similar rocks are found in the sections of Mountain Crimea and Northern-Western Caucasus [1,2].

The most information on the differences in the accumulation conditions of black shale layers and host rocks (limestones and marls) could be obtained from the study of distribution of individual elements with different mobility, as well as groups of elements - lithophilic, chalcophilic, siderophilic. Very informative is the group of rare earth elements (REEs). Each group characterizes the various aspects of sediment accumulation, and comprehensive approach increases the validity of conclusions.

In the present study, comparative investigation of cross-sections from the South-Western part of Mountain Crimea (Aksudere and Selbukhra), and cross-sections of Great Caucasus (Novorossiisk-Lazarevskoye zone), was carried out. Information on the substantial composition of rocks was obtained, including data on total and organic carbon, macro- (CaO, MgO, Fe_2O_3, TiO_2, MnO, P_2O_5, S) and microcomponents (Ba, Co, Cr, Cu, Ni, Li, V, W, Sr, As, Sc, Y, REEs, as well as Ag, Au, Pt, Pd, Se). The analytical procedure developed was based on ICP-AES and ETAAS determination after microwave decomposition of samples. For REEs determination, preliminary cation-exchange separation on Dowex AG 50W-X8 was used. For noble metal preconcentration, the chelating sorbent POLYORGS IV was applied.

2. Experimental

2.1. Instrumentation

A CEM MARS5 microwave digestion system equipped with temperature and pressure regulation through a sensor vessel was used for the mineralization of the samples. The sample carousel was capable of holding 12 TMF PTFE digestion vessels (XP-1500 Plus) with a capacity of 100 ml. The maximum working pressure and temperature in the vessels were adjusted to 17.2 bar (250 psi) and 190°C, respectively. Ramp to temperature - 10 min, holding at temperature - 10 min.

Atomic emission determination of macro- and micro components was carried out using ICP-AES spectrometer IRIS Intrepid II XDL (Thermo Electron) with CID detector; the wavelength range was 165-1050 nm. Autosampler Cetac ASX-520 was used to introduce the solutions into the source. The instrument operating conditions are listed in Table 1. Analytical lines used for the analyte determination are given in Table 2.

Table 1 Operating parameters for the ICP-AES IRIS Intrepid II XDL

ICP RF power 1150 W
Nebulizer gas flow - 0,72 L min^{-1}
Auxiliary gas flow - 0,5 L min^{-1}
Pump rate 100 rpm -1,80 mL min^{-1}
Rinse time - 90 s

Table 2 Analytical lines used for ICP-AES determination

Element	Analytical line, nm	Element	Analytical line, nm
As	193.759 (173) *	Mn	257.610 (130)
Al	396.152 (85)	Mo	202.030 (165)
B	208.959 (161)	Na	818.326 (41)
Ba	455.403 (74)	Nd	386.333 (87)
Ca	317.933 (105)	Ni	231.604 (145)
Ce	418.660 (80)	P	214.914 (156)
Co	228.616 (147)	Pr	410.072 (82)
Cu	327.396 (102)	S	182.034 (184)
Dy	369.481 (97)	Se	196.090 (171)
Er	369.265 (91)	Sc	361.384 (93)

(Table 2 continued)

Element	**Analytical line, nm**	**Element**	**Analytical line, nm**
Eu	381.967 (88)	Sm	359.260 (260)
Fe	237.373 (142)	Sr	460.733 (73)
Gd	335.047 (100)	Tb	350.917 (96)
Ho	345.600 (97)	Ti	323.657(104)
K	766.491 (44)	V	292.402 (115)
La	408.672 (82)	W	224.845 (149)
Li	670.784 (50)	Y	324.228 (103)
Lu	261.542 (128)	Yb	328.937 (102)
Mg	285.213 (118)	Zn	213.856 (157)

* In brackets is given the order of the spectrum.

Atomic absorption determination was carried out on ETAAS spectrometer «SOLAAR MQZ» with Zeeman and D_2-background correction (Thermo Electron). The instrument operating conditions and analytical lines used for determination of analytes are given in Table 3.

Table 3. Parameters for GF-AAS measurements (SOLAAR MQZ)

	Pd	Pt	Au	Ag	Se
Lamp type, power	HCL, 15 mA	HCL, 15 mA	HCL, 10 mA	HCL, 4 mA	HCL, 15 mA
Wavelength, nm	247.6	265.9	242.8	328.1	196.0
Slit width, nm	0.5	0.5	0.5	0.5	0.5
Signal measurement, s	2	2	2	3	2
Background correction	Zeeman	Zeeman	Zeeman	Zeeman	Zeeman
Drying temperature, ^{0}C	105	115	115	105	105
Drying time, s	35	30	30	35	35
Ashing temperature, ^{0}C	700	700	700	500	1200
Ashing time, s	20	25	15	90	20
Ashing temperature, ^{0}C	1050	1200	1000		
Ashing time, s	20	10	10		
Atomization temperature, ^{0}C	2500	2500	2300	2500	2300
Matrix modifier				$C_6H_8O_6$, 0.1 mg L^{-1}	$Ni(NO_3)_2$, 0.1 g mL^{-1}

Organic carbon was determined on CHNS-analyzer EA 1108 (Carlo Erba) using pyrolytic decomposition of samples at 1000^0C (sample masses for C_{org} determination were 4.2-5 mg) (Table 4).

Table 4. Operating conditions for CHNS analysis

Column	GC, «Porapac QR», column length – 2 m
Detector	katharometer
Left furnace temperature	1000^0C
Right furnace temperature	500^0C
Oven temperature	70^0C
Filament temperature	190^0C
Carrier	He
Carrier flowrate	120 mL min^{-1}
Total runtime	13 min

2.2. Reagents, standards, standard reference materials and samples

2.2.1. Standard solutions

Multielement stock standard solutions ICP-MS-68A-A (10 mg L^{-1}, High-Purity Standards) and 11355 ICP Multi Element Standard IV (1000 mg L^{-1}, Merck) were used for the determination of macro- and microcomponents.

Stock standard solution for the determination of REEs, Y and Sc was ICP-MS-68A-A 10 mg L^{-1} (High-Purity Standards). Besides that, the solution prepared by dissolving the appropriate amounts of the oxides of 99.99% pure obtained from Merck (Germany) was used.

Stock standard solutions of Ag (1010 mg L^{-1} in 10% HNO_3; Pt, Pd, Au (1000±10 mg L^{-1} in 5 % HCl (SIGMA® GERMANY) were used for the determination of noble metals.

For the determination of Se, S, and P standard solutions (1000 mg L^{-1}, Russian GSO 7782-2000, 6693-93 and 7018-93, respectively) were used.

Calibration solutions were prepared by stepwise dilution of stock solutions with acids.

For separation of REEs from the matrix, glass columns (19×0.7 cm ID) fitted with fritted glass disks in the bottom were packed with 5 ml of swollen cation exchanger Dowex AG 50W-X8 (100-200 mesh) from Bio-Rad.

For noble metal preconcentration, a chelating POLYORGS IV sorbent with methylpyrazole groups chemically bound on polystyrene-divinylbenzene resin [3] was used in powdered form (100 mesh).

2.2.2. Standard reference materials

Standard reference materials Limestone KH (Germany), and Black shales SChS-1 and SLg-1 (Russia) were used to validate preconcentration and determination procedures.

2.2.3. Samples

Information about samples taken from cross-sections Aksudere and Selbukhra is presented in Figs. 1,2.

2.2.4. Procedures

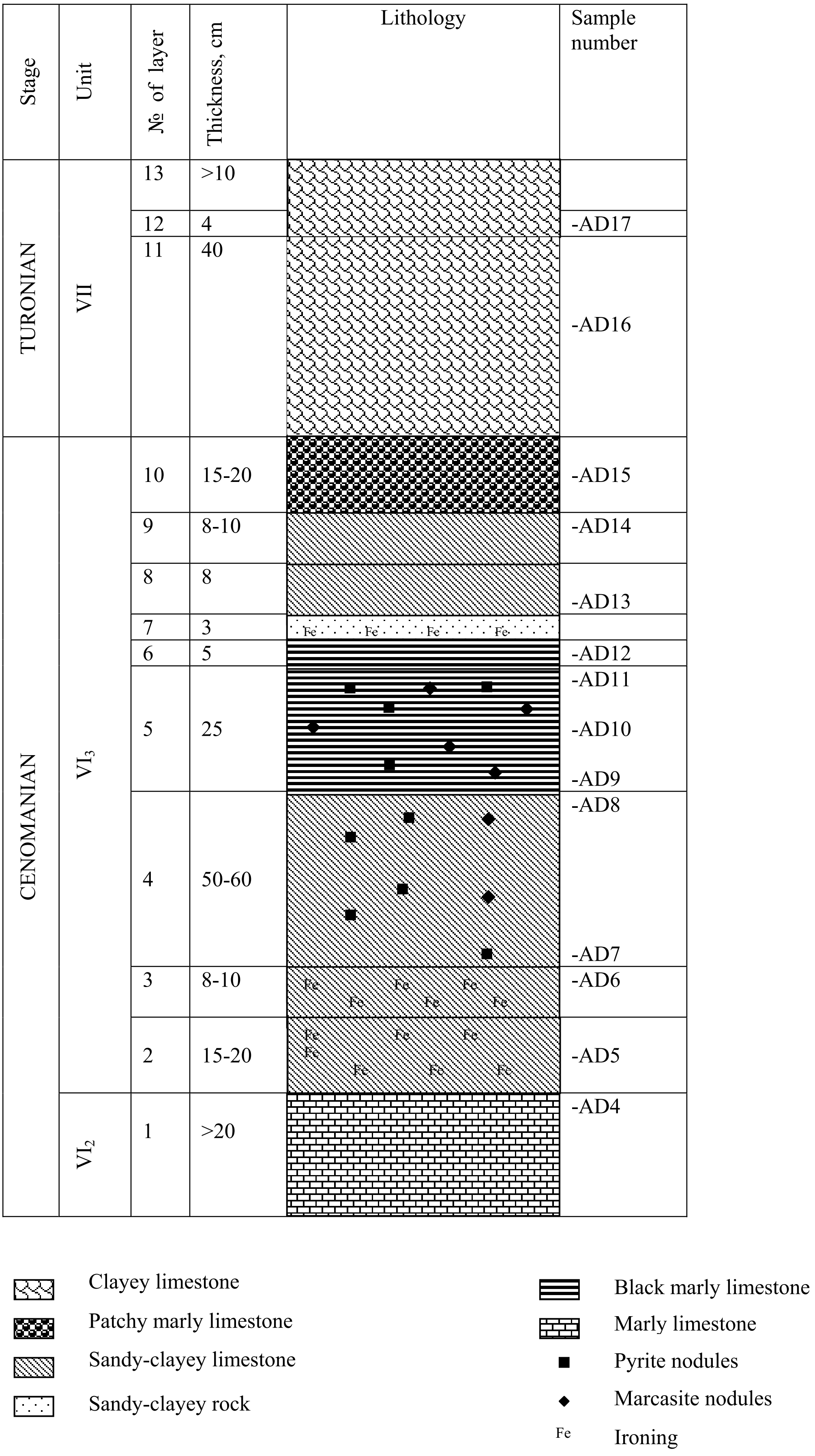
For the *determination of organic carbon* the sample was treated with 10 % HCl to remove carbonates and thoroughly washed with water to absence in washing waters of chloride ions. After that the sample was dried at 110^0C up to constant weight and analyzed for carbon, nitrogen, and hydrogen on the CHNS-analyzer.

Decomposition of samples. Sample (2 g) was weighed into the liner, conc. HF and HNO_3 were added, the vessels were closed and placed into the microwave oven. After heating for 20 min at 180 ^{0}C the samples were transferred into glassy carbon crucibles, heated up to dryness, twice treated with conc. HCl and diluted to 100 ml with 1M HCl. For ICP-AES determination of macro- and microcomponents, 1 and 5 ml aliquots of the solution were diluted to 50 and 25 ml, respectively.

For *REEs separation* Dowex AG 50W-X8 resin was previously prepared. The swollen sorbent was washed with 20 ml 2M HCl to obtain H^+-form [4]**.** To separate REEs, Y and Sc from the matrix and preconcentrate the metal ions, 10 ml aliquot of the solution was placed into the column. Matrix components were eluted with 40 ml of 2M HCl, then REEs with 50 ml 6M HCl with flow rate 1.2 mL min^{-1}. The eluate obtained was evaporated to 0.5 ml, diluted up to 5 ml and placed in autosampler cups.

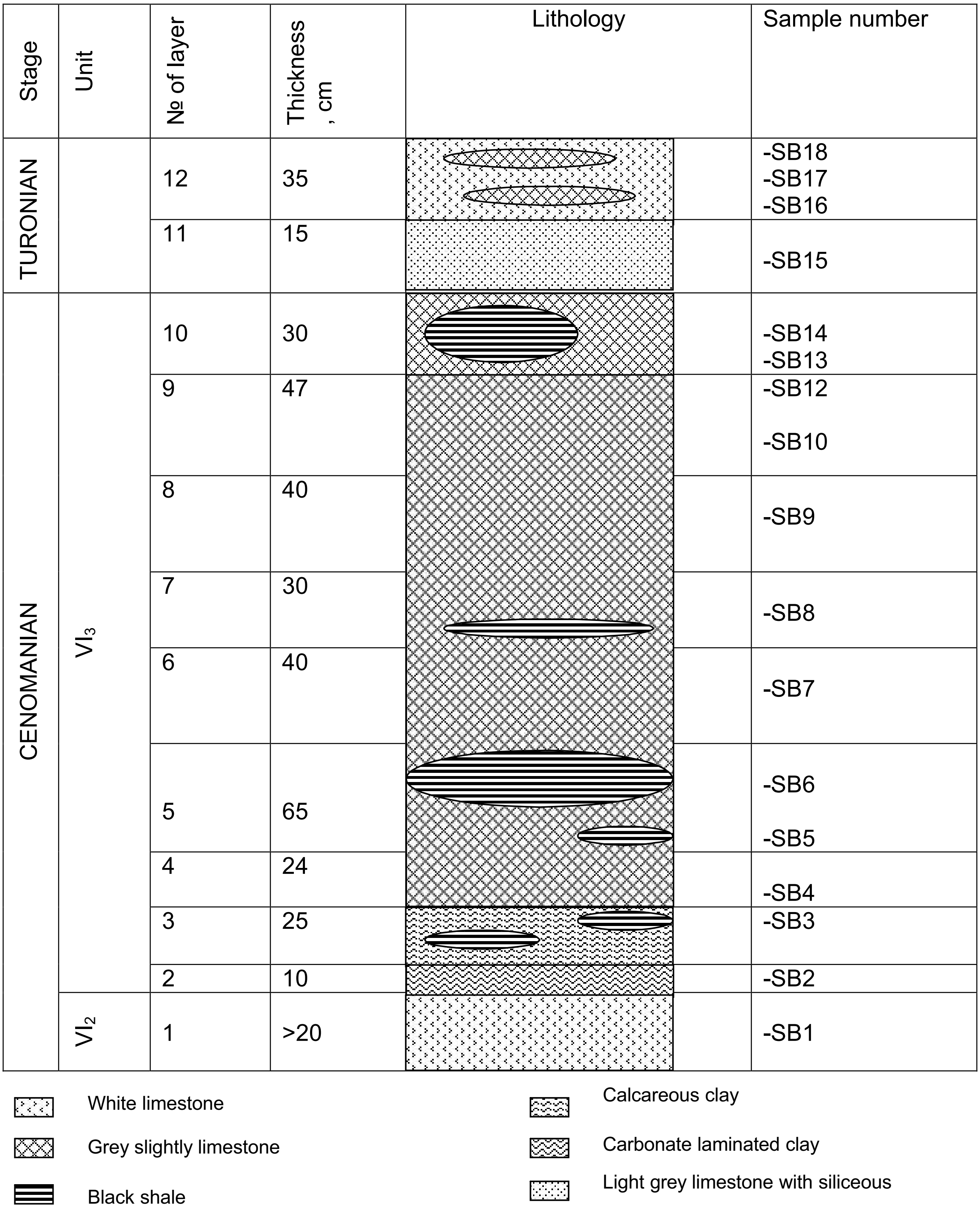
Preconcentration of noble metals was carried out in the batch mode. The sorbent POLYORGS IV (100 mg) was placed into a glass, 80 ml of sample solution was added, and the mixture was boiled on the hot plate for 1 h. (Sorption procedure could be carried out under microwave heating [5]). After that the sorbent was filtered through a membrane filter, washed with 1M HCl, transferred into 2 ml volume with 2% HCl and mixed thoroughly. 10-20 μL of the slurry were introduced into the graphite furnace atomizer of the atomic absorption spectrometer and analyzed.

Fig. 1. Section of boundary Senomamian-Turonian sediments Aksudere



Stage	Unit	№ of layer	Thickness, cm	Lithology	Sample number
TURONIAN	VII	13	>10		
		12	4		-AD17
		11	40		-AD16
CENOMANIAN	VI$_3$	10	15-20		-AD15
		9	8-10		-AD14
		8	8		-AD13
		7	3	Fe Fe Fe Fe	
		6	5		-AD12
		5	25		-AD11 -AD10 -AD9
		4	50-60		-AD8 -AD7
		3	8-10	Fe Fe Fe Fe Fe Fe	-AD6
		2	15-20	Fe Fe Fe Fe Fe Fe Fe	-AD5
	VI$_2$	1	>20		-AD4

Fig.2. Section of boundary Senomian-Turonian sediments at the southern slope of Selbukhra mountain



Stage	Unit	№ of layer	Thickness , cm	Lithology	Sample number
TURONIAN		12	35		-SB18 -SB17 -SB16
		11	15		-SB15
CENOMANIAN	VI_3	10	30		-SB14 -SB13
		9	47		-SB12 -SB10
		8	40		-SB9
		7	30		-SB8
		6	40		-SB7
		5	65		-SB6 -SB5
		4	24		-SB4
		3	25		-SB3
		2	10		-SB2
	VI_2	1	>20		-SB1

3. Results and Discussion

3.1. Determination of macro- and microcomponents of black shales and host rocks

Analytical scheme used for the sediments investigated is given in Fig. 3. Major components and some microelements were determined directly by ICP-AES and ETAAS in the solutions obtained after sample decomposition, and REEs and noble metals – after preliminary separation of the elements from the matrix. Accuracy of results obtained is confirmed by the analysis of SRMs (Table 5).

Table 5. Results of ICP-AES determination of elements in SRMs KH and SChS-1 in comparison with certified data (n=3); P=0.95

	SRM SChS-1				SRM KH			
Element	found %	RSD %	$U_c(x)$, %	Certified %	found %	RSD, %	Uc(x), %	Certified %
Al_2O_3	16.9±0.30	0,95	1.3	16.8±0.30	2.43±0.05	1,1	2.2	2.41±0.08
Fe_2O_3	5.40±0.10	0,93	1.9	5.57±0.12	0.92±0.01	0,59	2.6	0.93±0.10
MnO	0.058±0.006	5,2	7.9	0.057±0.006	0.085±0.005	3,5	4.5	0.087±0.004
MgO	2.50±0.05	1,2	2.4	2.67±0.09	0.70±0.06	4,3	5.9	0.723±0.050
CaO	1.13±0.08	3,5	4.9	1.14±0.06	48.0±0.2	0,23	0.3	47.79±0.12
TiO_2	0.91±0.04	2,2	3.9	0.91±0.05	0.15±0.008	3,3	4.3	0.134±0.007
P_2O_5	0.80±0.05	3,8	3.8	0.86±0.06	0.11±0.01	4,6	5.5	0.121±0.006
	$\mu g\ g^{-1}$	$\mu g\ g^{-1}$		$\mu g\ g^{-1}$	$\mu g\ g^{-1}$	$\mu g\ g^{-1}$		$\mu g\ g^{-1}$
Ba	740±10	0,74	1.2	720±12	41.2±1.6	2,1	8.9	48.8±6.2
Co	15±1	3,6	8.5	13±2	5.1±0.8	8,6	16.1	4.7±1.2
Cr	129±5	2,1	4.9	128±10	19.8±2.1	5,8	17.9	18.7±5.8
Cu	34±3	4,8	11.3	34±6	10.3±1.1	5,8	13.6	9.3±2.2
Li	60±1.6	1,4	5.9	56±6	9.0±1.2	7,2	12.0	8.5±1.5
Mo	1.3±0.4	16,9	21.5	1.7±0.3	3.6±0.2	3,1		-
Ni	43±3	3,8	8.9	39±6	24.7±3.2	7,0	15.9	21.7±6.1
S	6500±50	0,42	2.7	6200±300	2298±19	0,45		-
Sc	27±3	6,0	10.5	23±4	2.7±1.0	20,0	30.9	2.3±1.1
Sr	160±6	2,0	5.8	150±15	500±8	0,87	6.3	488±54
V	142±10	3,8	8.3	148±18	19.1±1.0	2,8	12.4	24.6±4.0
Zn	92±8	3,6	7.8	96±11	38.9±1.0	1,4		-

Where: $u_c(X) = +\sqrt{u^2(X) + u^2(SRM)}$

$$u^2(SRM) = \frac{\Delta^2}{3}$$

$$\Delta = \frac{\Delta_+ - \Delta_-}{2}$$

$$u(X) = +\sqrt{\frac{\sum_{i=1}^{N}\left(X_i - \bar{X}\right)^2}{N-1}}$$

- half-width of the interval where the certified standard value lies

$$U_c(X) = \frac{u(X)}{X} \cdot 100\%$$

- relative combined standard uncertainty

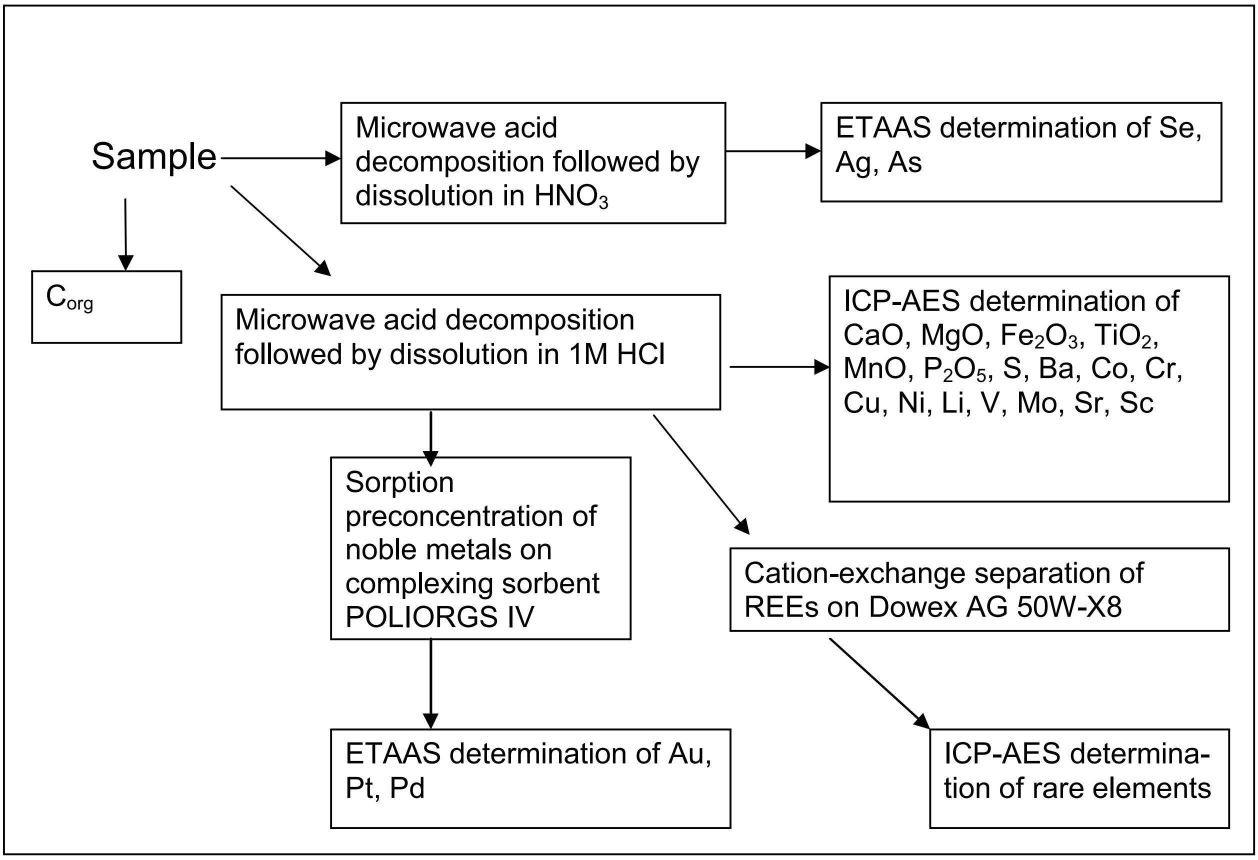


Fig. 3. The scheme of analysis

3.2. Determination of rare elements

Instrumental analysis of geological samples on rare elements (REEs, Sc and Y) is often problematic because of low contents of these elements and complex matrices that hamper determination. Among the sediment rocks, the lowest contents of REEs are observed in carbonaceous ones [6], additional problems for which arise from the presence of high quantities of Ca and Mg. In turn, black shales in carbonaceous rocks are additionally enriched with macro- and microcomponents, in part, with iron, possessing a “rich” emission spectrum and interfering with REE lines. Even high-resolution ICP-AES instrumentation does not enable the direct determination of all REEs in solution after sample decomposition [7, 8]. As a result, direct analysis of the solutions of SRM SChS-1 (without matrix separation of interfering elements) ensures the correct determination only of Ce, La, Nd, Sc, Y (Table 6), whereas analysis of SRM KH, which contains lower concentrations of REEs, permits the determination of only Ce, Sc and Y.

Table 6. Overlapping emission lines of rare elements

Analyte	Line	Interfering element	Line of interferent
Dy	353,170	Tb	353,170
Eu	381,967	Nd	381,970
Gd	335,047	Ho	335,049
Ho	345,600	Sc	345,589
Sc	424,683	Ce	424,657
Y	324,228	Ho	324,220

Other elements are detectable after separation of matrix and preconcentration of rare elements. Cation exchange techniques are well-developed [9] and differ depending on analytical purposes and possibilities. Nature of objects analyzed (sea water, rocks, minerals) and their element composition need different matrix separation procedures; besides, column parameters and differences in the quality of ion exchangers require a preliminary study of column characteristics on model solutions and reference materials. Determination methods (ICP-MS, ICP-AES, NAA, etc.) differing by sensitivity, interferences, requirements to analyte (phase composition, solution composition, etc.) play the key role in the procedure development. For these reasons, the use of procedures developed earlier for similar objects is often hindered, and modification of techniques is required. In our case, the separation of rare elements on Dowex was adapted on model solutions to carbonaceous sediments (in part, black shale layers), and to ICP-AES determination.

Eliminating matrix interferences, this procedure enables the ICP-AES detection of all REEs, Sc and Y. In Fig. 4 an area near the analytical line Gd 335,047 is shown. It can be seen that in the sample solution the target element cannot be identified (curve 2), whereas after matrix separation a signal is easily detected (curve 3). The same picture is observed for other REEs.

Additional problem in ICP-AES determination of rare elements are their rich emission spectra causing mutual interelement interferences inside the group. In Table 6 overlapping lines of rare elements are given.

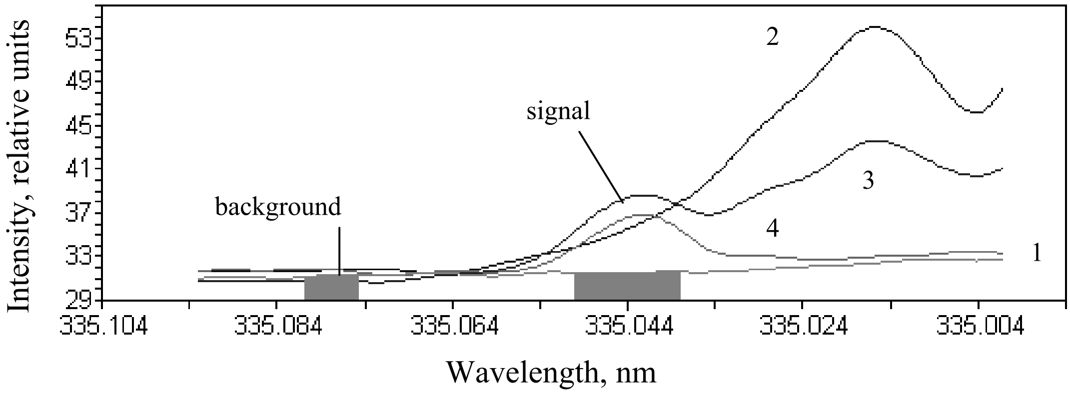


Fig. 4. The area around the analytical line Gd 335,047(100).
1 – blank, 2 – SRM SChS-1 (sample solution without separation of matrix), 3 - SRM SChS-1 (sample solution after separation of matrix on Dowex), 4 – standard solution (C_{Gd} 0.1 mg L^{-1})

The simplest way to avoid interference is to choose another line. This possibility was used for Dy and Sc, for which lines free from interferences can be used (369.481 and 361,384 nm, respectively). In the other cases the coefficients of interelement correction should be calculated. In Table 7 these coefficients are calculated for Gd 335.047, Ho 345.600, Y 324.228 and Eu 381,967.

Table 7. Interelement correction coefficients for ICP-AES determination of rare elements

Analyte	Line	Interfering element	Line of interfering element	Interelement correction coefficient
Gd	335,047	Ho	335,049	$7{,}8\cdot10^{-2}$
Ho	345,600	Sc	345,589	$2\cdot10^{-4}$
Y	324,228	Ho	324,220	$7{,}4\cdot10^{-4}$
Eu	381,967	Nd	381,970	$1{,}3\cdot10^{-3}$

By matrix separation and interelement correction, improved values for rare element concentrations in sediments were obtained. The data were confirmed by the analysis of SRMs КН and SChS-1 (Table 8). In the same table the detection limits of the determination are given.

Table 8.1. Comparative data on the determination of rare elements (µg g^{-1}) in the SRMs КН with and without matrix separation (n=3)

Element	Line, nm	Without separation µg g^{-1}	RSD,%	$U_c(X)$,%	With matrix separation µg g^{-1}	RSD,%	$U_c(X)$,%	Certified value µg g^{-1}	DLs on 3σ-criteria, µg g^{-1}
La	408.6				12.4±0.5	2.2		-	0.025
Ce	418.6	56.6±2.1	2.0		61±2.0	1.8		-	0.075
Pr	440.8				3.79±0.3	4.2		-	0.075
Nd	386.3				16.4±1.0	3.3		-	0.05
Sm	359.2				3.0±0.25	4.5	6.8	2.20±0.26	0.05
Eu	345.6				0.45±0.04	4.8	7.8	0.41±0.05	0.025
Gd	335.0				4.6±0.3	3.5		-	0.1
Tb	350.9				0.64±0.05	4.7		-	0.075
Dy	369.4				3.7±0.32	4.6		-	0.1
Ho	345.6				0.61±0.03	3.3		-	0.025
Er	369.3				1.8±0.1	2.8		-	0.1
Tm	346.2				0.22±0.03	9.1		-	0.05
Yb	328.9				0.82±0.05	3.3	6.4	0.86±0.074	0.025
Lu	261.5				0.13±0.02	8.4	15.4	0.120±0.03	0.025
Y	324.2	14.9±1.0	3.6		15±0.5	1.8		-	0.025
Sc	361.3	2.7±1.0	20	30.8	2.4±0.4	9.1	28.0	2.3±1.0	0.025

3.3. Determination of noble metals

In spite of the high sensitivity of modern instrumentation, the direct analysis of real samples on NM, similarly to other rare elements, is hampered by their low concentrations and the prevailing content of matrix constituents. The promising way of eliminating matrix effects is the preliminary sorption preconcentration [10]. Most selective to noble metals are N-containing complexing sorbents, particularly POLYORGS-IV [3], enabling the efficient separation of the noble metals from the matrix components, as well as from non-ferrous metals: Cu, Ni, Co, Fe, Mn.

Because of the strong binding of noble metals by the complex-forming groups of the sorbent, the metal desorption in this case is impossible, and the concentrate should be analyzed in the solid state. In the present work a slurry technique of ETAAS was used, permitting noble metal determination at ppb level.

Results obtained were confirmed by the analysis of SRM SChS-1. Applicability of the technique for Pd and Pt determination was confirmed by the analysis of SRM SLg-1. Detection limits of ETAAS determination of noble metals in real samples were found to be 2 ng g^{-1} (Au, Pd) and 2.5 ng g^{-1} (Pt).

Table 8.2. Comparative data on the determination of rare elements (μg g^{-1}) in the SRMs SChS-1 with and without matrix separation (n=3)

Element	Without separation μg g^{-1}	RSD,%	$U_c(X)$,%	With matrix separation μg g^{-1}	RSD,%	$U_c(X)$,%	Certified value μg g^{-1}
La	32.7±3.0	5.0	11.7	28.4±2.0	3.8	10.9	30±5
Ce	56±5.0	4.9	12.3	56±3.1	3.0	11.3	58±11
Pr				9.3±0.5	2.9		-
Nd	25.8±2.1	4.4	12.4	25±2	4.4	12.4	28±5
Sm				6.5±0.3	2.5	8.4	5.7±0.9
Eu				1.2±0.08	3.6	10.2	1.2±0.2
Gd				7.7±0.6	4.2	9.3	6.1±1.1
Tb				1.2±0.2	9.1	11.7	0.95±0.15
Dy				6.2±0.6	5.3	10.7	5.6±1
Ho				1.3±0.02	0.8		-
Er				3.3±0.09	1.5		-
Tm				0.5±0.03	3.3		-
Yb				2,9±0.1	1.9	10.1	2.9±0.5
Lu				0.4±0.03	4.1	11.3	0.44±0.07
Y	33.0±4.0	6.6	13.4	27.0±1.0	2.0	10.9	28±5.0
Sc	27.0±3.0	6.0	11.8	24.0±1.0	2.2	9.9	23±4.0

Table 9. Comparative data on the ETAAS determination of Au, Pt and Pd (ng g^{-1}) in SRMs SChS-1 and SRMs SLG-1 (n=3)

Element	SChS-1 (certifed content), ng g^{-1}	Found, ng g^{-1}	RSD,%	$U_c(X)$,%	SLg-1 (certifed content), ng g^{-1}	Found, ng g^{-1}	RSD,%	$U_c(X)$,%
Au	100±20	80±17	11.6	18,5	2500±300	2000±200	5.4	6.4
Pt*	1.3	-			2.2	2.3± 0.25	5.9	6.2
Pd*	1.2	-			2.3	2.5±0.20	4.4	4.8

* certified data are given in the SRM passport without the confidence interval

3.4. Composition of samples from cross-sections Aksudere, Selbukhra and Novorossiisk-Lazarevskoye zone

Data on the concentrations of macro- and microcomponents in the samples from Aksudere, Selbukhra cross-sections and Novorossiisk-Lazarevskoye zone are given in Table 10.

It can be seen that in Aksudere samples (limestone layers and black shale ones), high content of organic carbon is present. The samples from black shale layers are enriched with Fe, Al, S, as well as with microcomponents: As, Co, Cr, Cu, Mo, Ni, Zn, Li, W. In the samples from Selbukhra cross-sections, the differences in organic carbon content are well-defined in black and limestone layers, and total carbon varies from 11 to 27,3%. Black layers contain up to 10.9% of C_{org}, limestones - only 0.17-0.27%. Increased concentrations of S, As, Cu, Ni, V, Zn are also observed in the black shales. In the black shale layers from cross-sections of Novorossiisk-Lazarevskoye zone no carbonate carbon was found, whereas C_{org} varies from 0.64% to 10.2%. Relatively to limestones these samples are enriched with Fe, Al, Ti, P, S, As, Co, Cr, Cu, Ni, V, Y.

REE contents in most representative samples are normalized to shale [11] and shown in Fig. 5. One can see that REE contents in limestone samples (line 2) in all cases (excluding Selbukhra section), are lower in comparison with the samples from black shale layer (line 1). In addition, negative cerium anomalies are observed in some samples, which points to the presence of minerals formed in marine water, for example, autogenic phosphates and/or fish bones and scales.

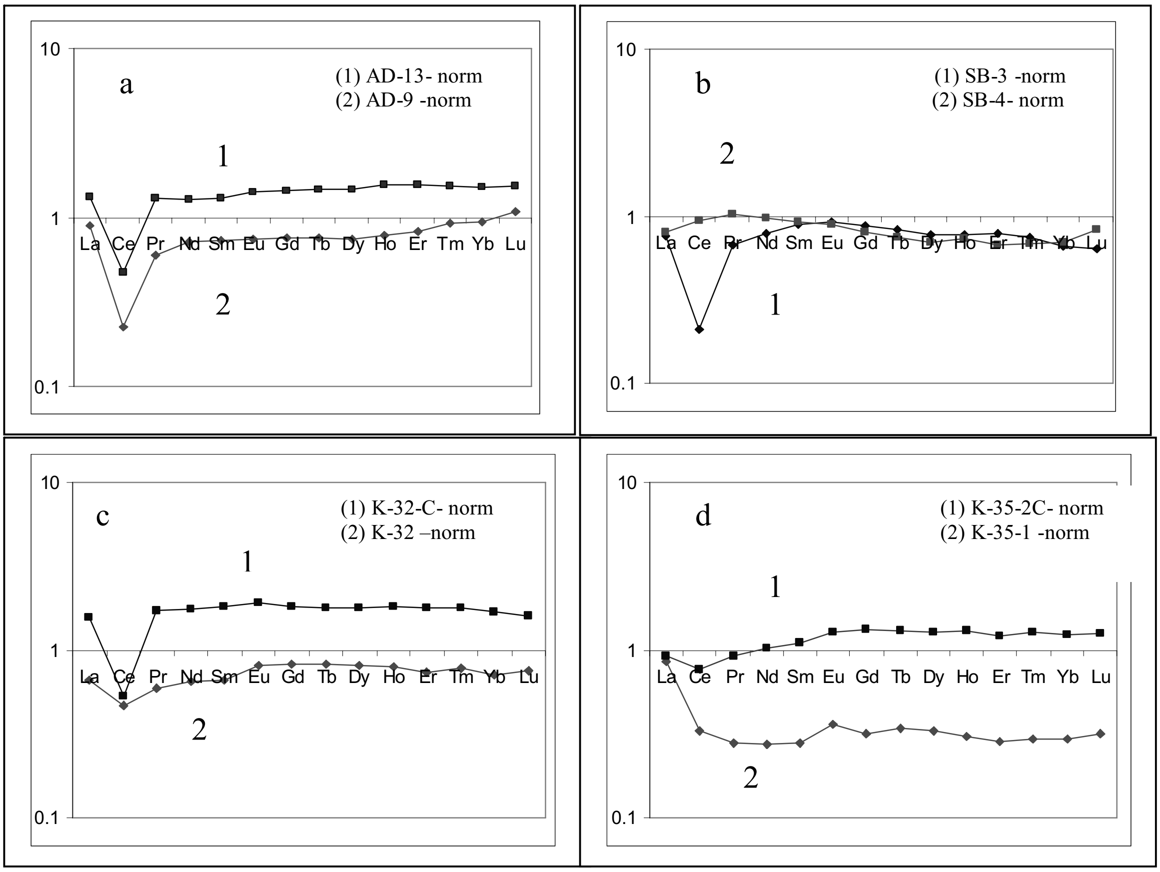


Fig. 5. REE contents in samples from Crimean cross-sections Aksudere (a), Selbukhra (b), and Caucasian cross-sections of Anapo-Agoyskaja zone (c), and Novorossiisk-Lazarevskoye zone (d). Data normalized on the clay of Russian platform.
1 – samples from black shale layers, 2 – limestone samples

As to noble metals (Table 7.2), platinum content in all samples is low and varies from 1 to 9 ng g^{-1}. Gold content in black shale layers varies from 16 to 100 ng g^{-1} and is higher than in carbonaceous ones (5-14 ng g^{-1}). Palladium content in carbonaceous layers fluctuates from 1 to 6 ng g^{-1}; increased concentration was found only in black shale samples AD-13 and K-35-2C (10-14 ng g^{-1}).

Table 10. Substantial composition of samples from Crimean (AD, SB) and Caucasian (K) cross-sections

10.1. Rock-forming elements, %

	AD-8	AD-9	AD-10	AD-11	AD-12	AD-13	AD-14	AD-15	AD-16
Al_2O_3	3.82	3.76	4.56	3.6	4.48	8.88	5.37	4.6	3.6
Cbulk	28.3	38.5	33.8	34.1	28.8	14.4	22.5	23.9	19.7
TOC	8.7	19.8	15.6	15.5	12.4	9.2	3.4	6.6	0.29
CO_2	27.0	25.8	25.1	25.7	22.6	7.2	26.2	23.8	29.7
CaO	34.1	31.7	36.6	30.6	27.4	9.4	35.3	28.4	31.4
MgO	0.78	0.75	0.93	0.75	0.89	1.67	1.12	0.88	0.72
Fe_2O_3	1.77	1.48	1.78	1.75	1.77	6.75	2.22	2.07	1.36
TiO_2	0.19	0.19	0.25	0.18	0.24	0.49	0.26	0.39	0.21
Na_2O	0.58	0.52	0.55	0.44	0.44	0.44	0.41	0.6	0.7
MnO_2	0.03	0.03	0.04	0.03	0.03	0.06	0.36	0.03	0.06
P_2O_5	0.11	0.12	0.18	0.13	0.17	0.18	0.15	0.11	0.14
S	0.29	1.01	0.68	1.17	0.57	0.96	0.28	0.24	0.13
N	0.29	0.7	0.54	0.54	0.41	1.04	0.14	0.24	0.04
H	1.17	2.35	1.84	1.88	1.61	10.97	0.8	1.07	0.52

	SB-2	SB-3	SB-4	SB13	SB-14	SB-15
Al_2O_3	1.5	0.70	2.90	2.93	3.47	2.88
Cbulk	11.4	27.3	22.1	21.5	16.6	22.8
TOC	0.17	10.9	0.27	0.35	1.05	0.54
CO_2	15.5	22.5	30.0	29.1	29.3	30.6
CaO	18.6	27.8	35.0	35.7	33.9	34.7
MgO	1,54	0,82	0,59	0,65	0,75	0,65
Fe_2O_3	2,52	2,2	0,9	1,14	1,4	0,99
TiO_2	0,44	0,28	0,19	0,15	0,17	0,15
Na_2O	0,27	0,1	0,6	0,5	0,47	0,45
MnO_2	0,03	0,02	0,1	0,12	0,09	0,1
P_2O_5	0,66	0,18	0,1	0,11	0,14	0,1
S	0,03	0,27	0,015	0,022	0,33	0,027
N	0,04	0,38	0,04	0,05	0,06	0,06
H	0,56	1,48	0,47	0,44	0,54	0,5

	K-35-1	**K-35-2C**	**K-35-4**	**K-32**	**K-32C**
Al_2O_3	1.30	5.03	2.30	3.04	3.40
Cbulk	26.1	10.2	17.9	10.4	0.64
TOC	0.95	10.2	0.35	0.15	0.64
CO_2	34.6	< 0.1	24.3	14.1	<0.1
CaO	40.6	0.59	28.1	16.8	0.5
MgO	0,4	0,67	0,74	0,49	0,9
Fe_2O_3	0,54	6,9	1,8	1,8	2,4
TiO_2	0,1	0,35	0,24	0,29	0,57
Na_2O	0,8	1.0	1,2	0,6	0,2
MnO_2	0,12	0,01	0,41	0,25	0,008
P_2O_5	0,05	0,2	0,14	0,07	0,11
S	0,028	1,82	0,15	0,007	0,014
N	0,07	0,3	0,02	0,03	0,07
H	0,3	1,1	0,14	0,13	0,33

10.2. Microelements ($\mu g\ g^{-1}$)

	AD-8	**AD-9**	**AD-10**	**AD-11**	**AD-12**	**AD-13**	**AD-14**	**AD-15**	**AD-16**
Ag	0.53	0.3	0.3	0.9	0.5	1.4	1.1	2.1	0.16
As	13.1	8.7	6.6	8.9	10.1	41.7	9.4	6.9	7.6
Ba	3170	3440	3900	3950	4120	3460	3120	4790	5090
Co	6.2	8.1	4.2	8.9	4.1	33	4.4	8.0	8.6
Cr	95	85	91	89	112	159	206	216	49
Cu	98	83	94	85	106	200	155	176	72
Li	185	46	148	46	54	90	61	216	204
Mo	6.4	10.4	6.8	8.6	6.0	11.2	2.6	4.4	1.4
Ni	69	97	94	93	122	99	44	66	30
Sc	4.3	3.9	4.1	3.9	4.8	9.5	5.5	5.8	4.9
Sr	1204	1165	581	1192	1115	501	1060	739	689
V	270	259	270	200	324	259	221	385	48
Y	27	26	29	27	34	43	27	26	32
Zn	94	155	153	168	207	526	353	417	68
Se	0.1	1.1	0.2	1.2	0.5	0.1	0.1	0.6	0.4
W	6.4	4.6	4.5	4.9	4.7	10.9	8.2	9.8	5.9
Pb	26	20	15	22	15	28	16	24	32
Pt		0.006	0.005			0.006		0.0025	
Au		0.007	0.025			0.1		0.014	
Pd		0.003	0.004			0.014		0.01	

	SB-2	SB-3	SB-4	SB13	SB-14	SB-15
Ag	1.18	0.9	3.8	1.21	0.13	0.09
As	14.7	11.3	<2.5	8.9	5.5	4.3
Ba	1260	817	218	257	123	192
Co	8.2	9.6	14.1	25.4	16.6	6.9
Cr	87	87	31	49	63	51
Cu	76	157	30	90	113	66
Li	217	86	186	204	203	50
Mo	1.3	6.2	1.9	2.1	2.1	1.3
Ni	50	140	24	42	57	25
Sc	10.4	5.7	3.9	3.6	4.1	3.7
Sr	392	630	653	964	915	913
V	103	312	25	32	39	29
Y	73	33	27	24	24	21
Zn	76	132	31	83	110	55
Se	0.4	0.4	0.4	0.03	0.01	0.1
W	8.5	6.0	7.2	4.3	4.5	6.2
Pb	19	9.3	11	27	22	28
Pt	0.002	0.003			<0.0025	0.009
Au	0.014	0.016			0.018	0.011
Pd	0.002	0.006			0.005	0.004

	K-35-1	K-35-2C	K-35-4	AD-8	AD-9
Ag	<0.1	1.45	<0.1	0.1	0.1
As	2.5	45.6	<2.5	<2.5	7.6
Ba	369	400	536	1130	1810
Co	4.1	28.1	8.3	5.2	8.3
Cr	19	85	42	32	113
Cu	17	249	11	16	93
Li	32	90	46	128	78
Mo	0.6	27.6	<0.1	<0.1	0.1
Ni	14.5	183	20	17	21
Sc	2.9	10.2	6.5	4.3	13.6
Sr	1321	523	598	479	208
V	19	409	28	28	163
Y	12	14	25	25	42
Zn	41	89	83	38	77
Se	0.3	2.5	0.3	0.4	0.4
W	8.1	5.1	9.3	5.9	8.9
Pb	10	57	18	9.1	31
Pt	<0.0025	0.003		<0.0025	<0.0025
Au	0.006	0.02		0.005	0.006
Pd	0.001	0.01		0.001	0.002

10.3. Rare earth elements (μg g^{-1})

	AD-9	**AD-13**	**SB-3**	**SB-4**	**SB-14**	**SB-15**	**K-35-1**	**K-35-2C**	**K-32**	**K-32C**
La	33.5	49.9	28.6	29.8	28.4	26.5	32.1	34.8	25.0	58.9
Ce	16.7	35.4	15.7	70.5	54.3	10.1	24.8	57.8	35.1	39.7
Pr	5.2	11.2	5.8	8.9	7.8	5.9	2.4	8.0	5.1	14.8
Nd	23.1	41.4	25.5	31.6	27.2	22.2	8.8	33.1	21.1	56.2
Sm	4.53	8.08	5.5	5.7	4.9	4.26	1.74	6.9	4.13	11.3
Eu	0.96	1.85	1.2	1.16	1.1	0.91	0.47	1.68	1.06	2.5
Gd	4.0	7.5	4.6	4.2	4.0	3.5	1.8	6.9	4.3	9.4
Tb	0.59	1.15	0.65	0,59	0.82	0,70	0.35	1,28	0.80	1,41
Dy	3.6	7.1	3.8	3.4	3.6	3.0	1.5	5.4	3.3	8.7
Ho	0.7	1.5	0.7	0.7	0.9	0.7	0.3	1.3	0.8	1.8
Er	2.3	4.3	2.2	1.9	2.4	1.9	0.8	3.4	2.0	5.0
Tm	0.38	0.63	0.31	0.28	0.41	0.30	0.12	0.53	0.32	0.73
Yb	2.6	4.1	1.8	1.9	2.3	1.7	0.8	3.0	1.8	4.6
Lu	0.44	0.63	0.26	0.34	0.39	0.34	0.13	0.52	0.31	0.66

Data on the content of elements and their ratios lead to geochemical conclusions on the origin of objects investigated. In particular, results of Q-mode factor analysis revealed 5 main factors related to: 1) carbonate sedimentation; 2) fine siliciclastic matter; 3) diagenesis; 4) anoxic and 5) oxic environment. Such proxy as the ratio Mo/Mn [12] points to variable oxic/dis(an)oxic environment in the cross-sections Aksudere and Selbukhra. The ratio TOC/Norg [13] gave evidence of OM of different genesis: from marine to terrestrial. The so-called excess concentrations are highest for such elements as Ba, Cr, Cu, Ni, V, Zn.

According to the results of comparative analysis, there are no direct analogies between sediments of such Quaternary stagnant basins as the Black Sea and Eastern Mediterranean. Geochemical backgrounds for Crimea and Great Caucasus sediments were shown to be strongly different ones. Moreover, based on available geochemical, sedimentological and paleontological [14, 15] data we assume that Crimean OAE2 sediments formed in the environment of carbonate inner shelf and irregular local upwelling. For Great Caucasian black shales the environment of rather deep-water basin with layer of oxygen minimum looks as more preferable one.

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