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GEOCHEMISTRY OF SPINELS FROM XENOLITHS OF MANTLE LHERZOLITES (SVERRE VOLCANO, SPITSBERGEN ARCHIPELAGO)

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The paper presents the results of a study (LA-ICP-MS method) of spinel from the collection of mantle xenoliths of lherzolites (seven xenoliths) selected in quaternary alkaline basalts of the Sverre volcano, the Spitsbergen archipelago. The study of two large (more than 15 cm in diameter) xenoliths made it possible to study changes in the composition of minerals in the central, intermediate, and marginal parts of the samples of chromium diopside spinel lherzolites. The sinusoidal character of the REE distribution in spinels, which indicates the manifestation of mantle metasomatism, is established.

The results obtained for the first time on the trace-element composition for spinels from mantle xenoliths in alkaline basalts of the Spitsbergen archipelago are supplemented by data on the geochemistry of spinels of mantle origin published in the world literature.

Key words: spinel, mantle xenoliths, mantle metasomatism, mineral geochemistry, LA-ICP-MS, Spitsbergen archipelago

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Introduction. The study of mantle xenoliths is the only source of information on the deep structure of the Earth. Xenoliths are witnesses and participants in the processes occurring in the mantle, and carry information about the mineralogical and geochemical changes associated with migration and redistribution of matter.

The choice of spinel material for a detailed mineralogical and geochemical analysis of xenoliths and reconstruction of processes occurring in the mantle is not accidental. Spinel is the most stable and resistant to secondary changes in the mineral, which tends to retain its primary composition, which is important in studying the structure of the upper mantle of the Earth [6].

In this paper, we present the results of a spinel study from the collection of mantle xenoliths (seven xenoliths) selected in quaternary alkaline basalts of the Sverre volcano, the Spitsbergen archipelago. At our disposal were two large (more than 15 cm in diameter) xenoliths, which allowed investigating changes in the composition of minerals in the central, intermediate, and marginal parts of the samples of chromium diopside spinel lherzolites.

Mantle xenoliths were extracted on the surface by quaternary alkaline basaltic melts. According to already existing data, spinel lherzolites underwent at least two significant processes: depletion caused by partial melting, and then to the effects of mantle metasomatism [3]. At the mineral level, the latter process is characterized by the appearance of newly formed minerals developing in the primary minerals of xenoliths, in particular, the formation of a new spinel generation should be noted (Fig.1).

Analytical methods. The chemical composition of the minerals at the level of the main elements is determined by the SEM-EDS method at the IPGG of the Russian Academy of Sciences using the scanning electron microscope JEOL JSM-6510LA with the energy dispersing attached device JED-2200. Thin polished plates of rocks were covered with a layer of carbon. Point samples were used to determine the composition of minerals with the help of an electron beam with an accelerating voltage of 20 kV and a current of 1 nA, the beam spot size was 3 μm. The accumulation time of each spectrum is 35 s, natural minerals, pure oxides and metals were used as standards. To correct the matrix effect, the ZAF algorithm was used.

Rare earth and trace elements were measured by the LA-ICP-MS method at the Laboratory of mantle-crust substance and environment of the University of Science and Technology of China.

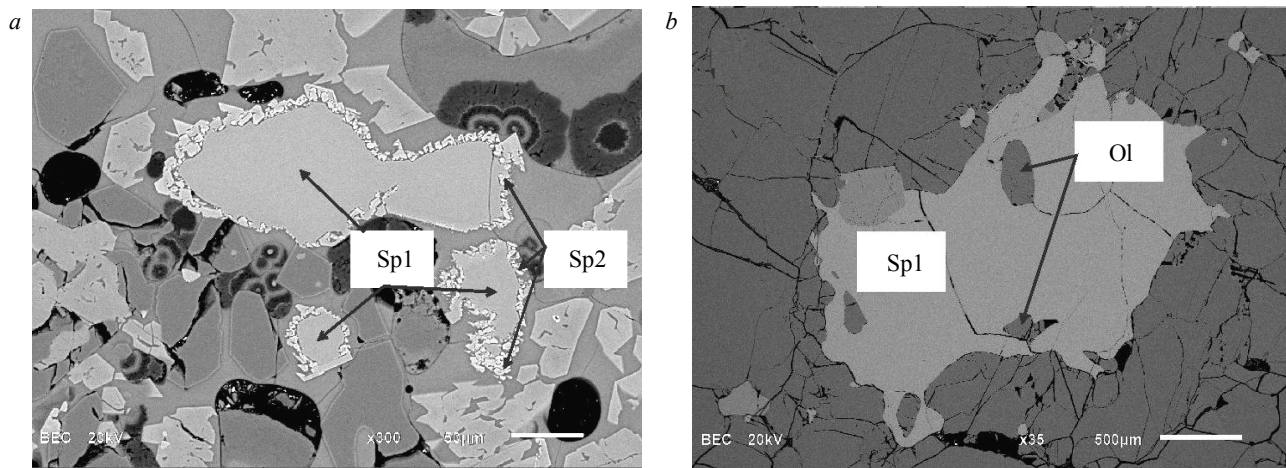


Fig.1. Image in BSE mode of spinels from mantle xenoliths: a - spinel of the first generation of Sp1 become cluttered with crystals of the second generation of Sp2; b - inclusion of olivine Ol in grain of spinel

The detailed conditions of the laser ablation system and the ICP-MS tool and data processing are given in [5]. The GeLAS 2005 laser was 193 nm ArF and the Agilent 7900 ICP-MS mass spectrometer. Helium was used as the carrier gas. Argon was used as an additive gas and mixed with the carrier gas through a T-connector before entering the ICP.

Each analysis consisted of measuring the background (~20-30 s) and analyzing the actual sample (50 s). The content of the elements was calibrated according to the widely accepted standards (BCR-2G, BIR-1G, BHVO-2G and GSE-1G), the NIST 610 standard was used to calibrate the drift of the signal during the analysis. The spot size of the analysis was 32-44 μm . Processing of background and analytical signals, correction of time displacement and quantitative calibration was performed using the ICPMSDataCal program [4, 5]. A signal with a temporal resolution for each analysis was carefully checked for jumps in the content of each element, and in most cases only a «clean» part of the spectrum with a smooth signal intensity was selected. The accuracy and reproducibility of the analysis, based on the repeated analysis of standards, for most trace elements is not worse than $\pm 10\%$ (2σ).

Results and discussion. According to the petrographic composition, xenoliths are represented by spinel lherzolites of the following mineral composition typical of these rocks: olivine (80 %), clinopyroxene (13 %), orthopyroxene (5 %), spinel (2 %). Spinel is divided into two generations: the first – crystals that originated from the original melt, and the second, associated with the process of mantle metasomatism (Fig.1, a).

Spinel of the first generation is represented by xenomorphic crystals located in the intergranular space of olivine and clinopyroxene. The size of the spinel crystals varies from 50 μm to the first millimeters. According to its chemical composition, the first generation of spinel refers to hercynite, the Al_2O_3 content averages 53 %, and Cr_2O_3 is 13 % by mass. Individual grains of spinel are not generally zonal in composition, however, when the composition of different spinel grains is compared, even within a single sample, the variations of the content of the main elements is observed.

Small crystals of the second generation, with an average size of 5 μm , have a more idiomorphic appearance and are cluttered in the form of a fine grain brush of the spinel of the first generation (Fig.1, a). According to the content of the main elements, the spinel of the second generation differs from the first generation by a reduced content of alumina (up to 42 % by mass) and an increase in the Cr_2O_3 content by an average of 20 %. The small size of the crystals of the second generation does not allow us to investigate them by the laser ablation method, therefore, below is discussed the trace-element composition of the spinel of only the first generation.

Representative compositions of first-generation spinels according to LA-ICP-MS are given in the table. The content of oxides of the main elements according to LA-ICP-MS is in good agreement with the results of spinel analysis on an electronic microanalyzer – the average content of alumina according to laser ablation data is also 53.1 % by mass. It should be noted that in the



large xenoliths SH-1 and SH-2 there are noticeable strong fluctuations in the alumina content depending on the region of the sample from which the spinels were selected. Thus, in the central, intermediate and marginal zone, the content of alumina in spinels has the following average values: 55.5, 51.8 and 50.8 % by mass, respectively. The remaining xenoliths are characterized by consistent alumina content (on average 54 %), close to the spinel composition from the central part of the large xenoliths.

Spinel composition by LA-ICP-MS data

Sample	MgO	Al ₂ O ₃	Cr ₂ O ₃	FeO	Ti	V	Mn	Co	Ni	Cu	Zn	Sn	Mg #	Cr #	<i>D_{melt}</i>
	wt %				ppm										
SH-1b-1b-15 (central part of the xenolith SH-1)	21.7	53.3	11.6	11.5	533	399	803	286	3275	2.58	1236	1.11	38.0	40.8	18.94
	21.3	53.5	12.1	11.4	434	405	781	270	3296	2.72	1242	0.98	39.1	42.0	19.43
	22.0	53.0	11.8	11.5	440	397	843	278	3258	3.00	1220	1.04	38.5	41.3	19.14
	21.5	53.5	11.6	11.6	433	410	819	275	3297	3.71	1266	0.94	37.7	40.5	18.79
	21.7	53.3	11.8	11.5	438	407	804	281	3578	3.43	1307	1.16	38.4	41.2	19.11
	21.5	53.3	11.9	11.6	456	404	789	272	3225	3.14	1184	1.02	38.3	41.1	19.04
	21.9	53.7	11.3	11.4	440	431	797	279	3284	2.67	1247	0.74	37.6	40.5	18.78
	21.5	53.2	11.6	11.8	440	400	819	296	3214	3.50	1295	1.02	37.4	40.3	18.69
	21.0	54.9	11.3	11.2	447	390	773	276	3063	3.10	1190	0.60	38.0	40.8	18.91
	21.7	53.7	11.2	11.6	427	391	799	299	3375	2.90	1276	1.08	37.0	39.8	18.50
SH-1b-2b-15 (intermediate part of the xenolith SH-1)	20.6	51.1	14.1	12.3	491	470	829	267	2950	2.48	1176	0.91	41.2	44.1	20.33
	20.6	51.5	13.8	12.4	494	458	811	253	2829	1.93	1080	0.79	40.4	43.3	19.98
	20.3	50.7	14.7	12.4	536	481	846	259	2864	2.54	1240	0.93	41.8	44.7	20.58
	21.1	49.8	14.3	12.9	476	457	842	264	2967	2.38	1144	0.99	40.3	43.2	19.96
	21.0	50.1	14.1	12.9	483	465	880	274	3015	2.60	1223	1.18	40.0	42.8	19.79
SH-1b-3b-15 (marginal part of the xenolith SH-1)	20.8	51.1	13.9	12.3	495	464	847	266	3063	2.04	1218	1.16	40.8	43.7	20.17
	20.4	51.6	14.0	12.1	507	511	841	266	2966	3.01	1151	0.98	41.2	44.1	20.31
	20.6	51.6	13.9	12.1	481	469	857	258	2994	2.89	1133	0.91	41.2	44.1	20.34
	20.4	51.9	13.8	12.1	495	467	831	261	2897	2.28	1183	0.95	41.0	43.9	20.24
SH-2b-1b-15 (central part of the xenolith SH-2)	20.8	51.1	13.9	12.2	486	461	834	261	2958	2.62	1192	1.22	40.8	43.7	20.16
	21.4	55.0	10.1	11.2	390	360	790	276	3257	3.51	1309	1.10	35.5	38.2	17.83
	21.2	56.0	10.1	11.1	401	363	798	280	3330	2.95	1290	1.14	35.7	38.5	17.92
	21.5	55.6	10.0	11.4	352	359	804	285	3309	2.61	1384	0.90	34.9	37.7	17.59
	21.5	55.9	10.0	11.1	352	354	798	277	3258	2.61	1319	0.77	35.4	38.1	17.78
	21.1	56.4	10.3	10.8	439	367	766	264	3097	3.12	1210	0.91	36.6	39.3	18.30
	21.9	55.2	10.4	11.1	417	371	791	278	3251	3.34	1278	0.85	36.3	39.0	18.17
	21.5	55.6	10.4	11.1	423	369	786	279	3228	2.65	1263	0.78	36.2	38.9	18.13
	21.6	55.0	10.4	11.4	440	371	813	288	3433	2.74	1302	1.09	35.8	38.6	17.99
	21.5	55.2	10.3	11.5	445	368	800	281	3280	3.24	1248	0.90	35.3	38.1	17.75
21.7	54.8	10.7	11.3	440	364	811	286	3295	2.79	1241	1.02	36.5	39.3	18.27	
SH-2b-2b-15 (intermediate part of the xenolith SH-2)	20.7	52.0	14.3	11.6	442	443	762	248	2780	2.42	1073	0.41	42.7	45.7	20.99
	21.1	51.3	14.4	11.9	440	442	776	250	2771	2.36	1075	0.25	42.3	45.3	20.82
	21.0	51.1	14.7	11.8	453	448	780	257	2821	2.65	1068	0.45	43.1	46.0	21.15
	21.3	50.4	15.2	11.8	482	455	796	261	2860	2.12	1111	0.44	43.9	46.8	21.47
	21.0	51.5	14.6	11.5	468	441	791	260	2860	2.45	1096	0.44	43.5	46.4	21.31
	21.4	50.6	14.6	11.9	442	446	811	270	3012	2.04	1152	0.39	42.8	45.8	21.04
	21.1	50.9	14.7	11.9	441	442	807	269	3048	2.52	1140	0.24	42.7	45.6	20.98
	21.0	50.9	15.0	11.7	424	437	811	267	2974	2.46	1120	0.59	43.8	46.7	21.44
	21.1	51.1	14.5	11.9	454	444	805	267	3001	2.36	1131	0.38	42.5	45.4	20.89
	21.0	51.4	14.4	11.8	446	444	808	271	3009	2.45	1117	0.31	42.5	45.5	20.90
	20.8	50.1	15.6	12.1	480	455	847	266	2898	2.64	1116	0.28	43.8	46.7	21.44
	20.7	50.0	15.6	12.2	482	460	822	268	2944	2.67	1116	0.51	43.7	46.7	21.42
	20.9	51.0	14.6	12.1	428	445	809	265	2979	2.17	1112	0.42	42.3	45.3	20.82
	20.4	50.4	15.3	12.4	445	456	824	266	2889	2.52	1151	0.45	42.9	45.9	21.07



End of the table

Sample	MgO	Al ₂ O ₃	Cr ₂ O ₃	FeO	Ti	V	Mn	Co	Ni	Cu	Zn	Sn	Mg #	Cr #	D _{melt}
	wt %				ppm										
SH-2b-3b-15 (marginal part of the xenolith SH-2)	20.4	51.8	14.5	11.9	453	453	794	259	2925	2.38	1138	0.55	42.5	45.5	20.90
	21.3	50.5	14.3	12.3	444	439	792	259	2891	2.37	1103	0.56	41.4	44.3	20.43
	21.1	50.6	14.7	12.1	455	452	787	259	2816	2.17	1121	0.42	42.4	45.3	20.85
	21.0	51.0	14.4	12.2	450	451	798	257	2876	2.42	1075	0.48	41.6	44.5	20.52
	21.3	51.1	14.2	12.0	442	459	779	257	2849	2.19	1084	0.33	41.9	44.8	20.64
	21.0	50.9	14.9	11.8	465	450	809	254	2810	2.19	1057	0.53	43.5	46.4	21.31
SH-4-15	22.0	54.4	11.7	10.4	432	384	730	255	3096	4.23	1124	0.38	40.5	43.3	20.00
	22.1	54.6	11.4	10.5	428	380	718	250	3018	3.10	1083	0.34	39.8	42.7	19.74
	22.2	54.5	11.5	10.3	491	394	719	254	3158	3.02	1072	0.40	40.4	43.3	19.99
	22.0	54.9	11.4	10.3	461	394	733	255	3141	3.50	1116	0.46	40.2	43.1	19.89
	22.6	55.0	11.1	9.9	461	411	694	245	3004	3.26	1084	0.43	40.4	43.3	19.98
	21.8	55.4	11.5	9.9	484	406	701	250	2998	3.54	1079	0.38	41.3	44.2	20.39
	22.2	55.1	11.5	9.8	488	392	705	251	3125	3.16	1079	0.46	41.7	44.6	20.55
	22.1	54.2	12.0	10.1	514	417	735	269	3167	2.85	1118	0.48	41.8	44.7	20.59
	22.0	54.2	12.2	10.2	429	397	746	256	3182	3.21	1089	0.36	42.2	45.1	20.74
	22.0	55.2	11.5	9.8	450	386	728	262	3180	3.32	1128	0.37	41.7	44.6	20.53
	21.5	55.3	11.8	10.0	456	388	737	260	3218	3.57	1116	0.39	41.7	44.6	20.55
	21.8	54.8	11.8	10.1	511	413	736	261	3142	3.28	1114	0.38	41.4	44.3	20.41
	22.5	54.1	12.0	9.9	446	415	746	269	3141	3.15	1130	0.33	42.4	45.4	20.87
	22.0	54.4	11.7	10.6	479	410	736	265	3151	3.44	1130	0.37	40.2	43.0	19.87
21.7	55.3	11.9	9.7	415	387	731	263	3052	3.16	1140	0.23	42.6	45.6	20.94	
SH-5-15	21.0	53.1	11.9	12.4	471	444	799	266	2846	1.48	1181	0.55	36.7	39.5	18.38
	20.3	54.4	11.8	11.8	484	395	768	259	2972	2.10	1127	0.50	37.9	40.7	18.88
	19.9	52.3	14.2	12.0	442	398	826	255	2707	1.52	1147	0.47	41.8	44.7	20.60
	20.1	52.4	13.6	12.1	418	444	824	262	2770	2.54	1121	0.72	40.5	43.4	20.01
	21.0	53.7	10.9	12.6	464	399	789	260	2886	3.99	1178	0.63	34.5	37.2	17.40
	20.6	52.5	11.5	13.6	468	404	843	296	2973	2.10	1177	0.64	34.0	36.7	17.18
	21.3	52.0	13.4	11.6	427	425	762	263	2761	1.79	1114	0.38	41.2	44.1	20.32
	20.7	53.6	11.8	12.3	409	404	821	266	2895	1.69	1181	0.62	36.8	39.6	18.42
	20.5	53.5	11.9	12.4	415	408	831	266	2952	1.50	1186	0.44	36.9	39.7	18.46
	22.5	52.5	11.5	11.9	433	396	794	269	2904	1.99	1181	0.55	36.9	39.8	18.47
	20.8	52.8	13.2	11.6	458	409	748	249	2841	1.63	1179	0.47	40.8	43.7	20.14
	20.9	54.3	10.6	12.4	479	403	776	258	3038	1.60	1156	0.55	34.2	36.9	17.27
	20.9	53.6	11.8	12.0	429	422	829	268	2871	1.86	1224	0.55	37.4	40.2	18.68
	20.4	52.5	13.7	11.8	494	392	751	243	2835	1.67	1116	0.36	41.3	44.2	20.36
20.7	54.0	11.0	12.6	471	401	805	259	2965	2.26	1239	0.47	34.8	37.5	17.52	
SH-6-15	22.3	54.0	11.6	10.7	519	395	738	252	3050	3.11	1054	0.37	39.9	42.8	19.75
	22.0	54.9	11.1	10.5	454	383	706	249	2954	2.92	1085	0.29	39.1	41.9	19.40
	21.7	55.2	11.1	10.6	499	391	707	249	3069	3.13	1076	0.29	38.9	41.7	19.31
	21.6	55.5	11.2	10.3	466	390	703	255	3041	3.14	1042	0.38	39.7	42.5	19.66
	21.6	54.7	11.9	10.5	522	407	736	247	2929	2.97	1091	0.43	40.8	43.6	20.13
SH-7-15	21.0	52.7	11.7	12.6	476	409	848	282	3143	1.92	1247	0.45	36.2	38.9	18.13
	20.7	53.7	11.5	12.2	467	434	825	274	3024	1.80	1270	0.56	36.4	39.1	18.21
	20.6	53.8	11.3	11.9	431	404	803	255	2833	5.51	828	0.61	36.7	39.5	18.35
	20.6	53.4	12.5	11.8	480	397	774	260	3048	2.48	1193	0.50	39.1	42.0	19.41
	21.1	54.3	10.8	12.0	509	411	793	335	3122	2.51	1185	0.43	35.3	38.1	17.76

Mg # = Mg / (Mg × Fe_{tot}) × 100 % in the studied samples of spinels varies, a difference is observed in this index even within one sample (see table). In large xenoliths, the magnesia of spinels is of a consistent variation, but only in its own zone. Thus, in the SH-1 and SH-2 xenoliths in the central part, the average magnesia value is 35.8, in the intermediate region – 40.7, and in the mar-

ginal zone – 38.0. This character of zoning can be explained by the presence in the intermediate part of large xenoliths of microinclusions of olivine in spinel according to electron microscopy. Further interaction of fluids with olivine microinclusions leads to a redistribution of part of magnesium to the host olivine spinel [3].

$Cr\# = Cr / (Cr \times Fe_{tot}) \times 100$ % of studied spinel varies from 36.7 to 46.8 without certain regularities. So, in one sample this indicator can vary from 38.1 to 42.0 (see table). In large xenoliths there is a marked increase in chromium content from the center to the edge. Most likely, this is due to mantle metasomatism, manifested in the form of partial melting processes, which manifested itself in the investigated xenoliths [7]. The degree of partial melting can be estimated using the regression equation [1]:

$$D_{melt} = 0.426 \times Cr\# + 1.538.$$

where D_{melt} – degree of partial melting, %; $Cr\#$ – chromium content index for spinels, %.

The degree of partial melting averages about 20 %, not exceeding 21.5 % (see table). The degree of partial melting is most strongly represented in the intermediate part of the large xenoliths, and not in the marginal xenoliths. This pattern is most likely associated with a temperature gradient in large xenoliths during processes of mantle metasomatism, in which the fluid unevenly affects the entire volume of a large xenolith.

By the ratio of the principal elements, a regular inverse correlation of the content in spinels MgO and FeO (Fig.2, a) and Al_2O_3 and Cr_2O_3 is observed (Fig.2, b), due to isomorphous substitutions of these pairs of elements. With respect to the correlation of chromium with other elements, it is worth noting the dependences associated with manganese (Fig.2, c). The chart clearly shows two trends, fundamentally different in the nature of the correlation of the content in the spinels Cr_2O_3

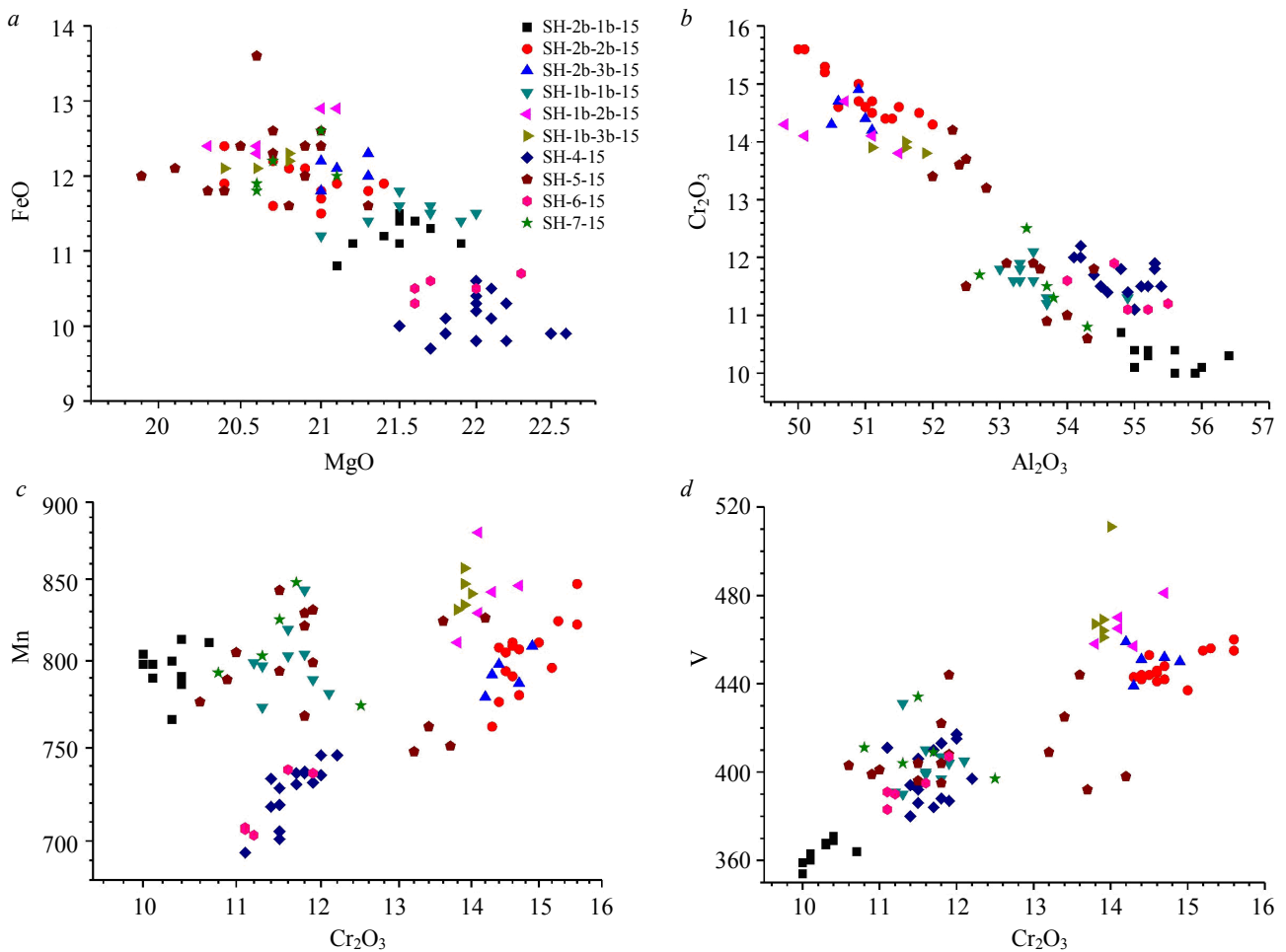


Fig.2. Composition of spinels from mantle xenoliths of Sverre volcano

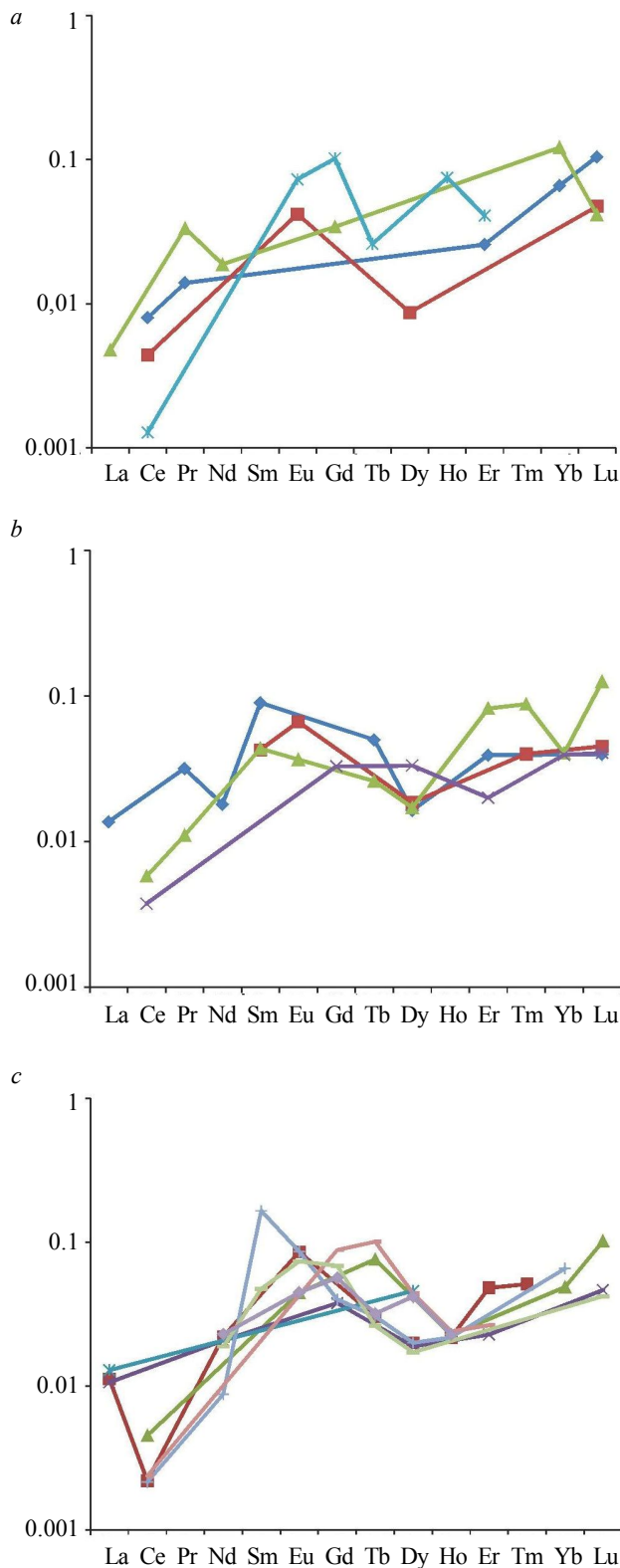


Fig.3. Distribution spectra normalized to chondrite composition CI, rare-earth elements in spinels from xenolith SH-1: a – central part, b – intermediate part, c – marginal part

entire representative sample of spinels increases from La to Eu and further to Gd. In some spinels, the content of La and Ce is below the sensitivity threshold of the LA-ICP-MS method. Eu-anomaly in a number of samples has an implicitly pronounced positive character (Fig.3). The content of heavy REE is sharply differentiated, from Gd to Dy, the normalized contents decrease, and the min-

and Mn. For large xenoliths in the central and intermediate parts, as well as in smaller xenoliths (SH-4-15, SH-6-15), there is a positive correlation of these elements, for marginal parts and xenoliths of smaller size (SH-5-15, SH-7-15) is a less significant negative correlation. Such an ambiguous distribution is difficult to interpret. We can note the direct dependence for all the samples of spinels between the contents of Cr_2O_3 and V (Fig.2, d), which is typical for xenoliths of the upper mantle.

The average iron content in the spinels under consideration is 11.5 %, with a minimum of 9.8 % and a maximum of 13.6 %. In large xenoliths, the FeO content is sufficiently sustained in each zone, while in small xenoliths variations in the iron content are rather significant (see table).

The distribution of rare-earth elements (REE) in spinels is a rather complex issue, since it has not been established to date exactly what position the REE ions occupy in the crystal lattice of the mineral. However, it is worth noting, that the work of F.P.Lesnov [2] suggests that the most likely candidates, the position of which in the spinels is occupied by trivalent HREE ions, are the ions VIII Fe^{2+} and VIII Mg^{2+} . Data on the content of REE in spinels are very limited and mainly affect chrome spinels (reviewed in [2]).

We provide representative analyzes of the REE content in spinels. The average total content of rare-earth elements in the studied grains does not exceed 0.12 ppm, and the REE distribution spectra have a pronounced sinusoidal appearance with inflection points, corresponding to Dy and, in some cases, Ho (Fig.3). Such a distribution of rare-earth elements is atypical for spinels, since in the literature analysis (review in [2]) it was established that typical REE spectra in spinels show a gradual decrease from light to heavy REE. It was previously established that the sinusoidal character of the REE distribution spectra in minerals, in particular in mantle garnets, along with other features of the composition is an indicator of mantle metasomatism [8].

The normalized content of light REE in the



imum value among the HREEs is Ho, which is the inflection point with the subsequent increase in the normalized contents of the elements from Er to Lu.

Thus, for the first time the results (method LA-ICP-MS) were obtained for the sparse composition of spinels from mantle xenoliths of lherzolites in alkaline basalts of the Spitsbergen archipelago, supplementing the data on the geochemistry of spinels of mantle origin published in the world literature.

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