DETERMINATION OF THE CONCENTRATIONS AND DISTRIBUTIONS
OF RARE-EARTH ELEMENTS IN MINERAL AND ROCK SPECIMENS
USING THE VEPP-4 SYNCHROTRON RADIATION

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Results are presented on X-ray fluorescence determination of the K-series of rare-earth elements (REE) in rocks using synchrotron radiation (SR) from the VEPP-4 storage ring. In a direct, instrumental determination, the detection limit is 5×10^{-5} %. The procedure for chemical preconcentrating which allows the detection limit to be reduced to 10^{-6} % is described. The SRXFA technique has also been employed to study the spatial distribution of REE in rock specimens by scanning with an SR beam.

1. Introduction

Rare-earth elements (REE) play an important role in current geochemical studies since they bear information on the geological processes occurring in the rock-forming period.

The most common method for REE determination in rocks, particularly basic and ultrabasic ones, is neutron activation analysis (NAA) (including its radiochemical version). Its characteristics include high sensitivity, accuracy and reliability as well as offering the possibility of determining any elements [1,2]. Both versions of the technique, instrumental and radiochemical, have some disadvantages: they are time-consuming, expensive and require the extraction of some interfering elements such as Sc, alkalies, alkali-earth elements insofar as their radionuclides, when formed in a reactor, substantially lower the sensitivity. At present, chemists' efforts are directed to the development of sample preparation procedures for NAA that would make it possible to isolate all REE from interfering elements. For this purpose, among the techniques used are ion exchange [3], extractive-chromatographic isolation as well as various procedures based on fluoride, oxalate, etc. depositions [4,5].

X-ray fluorescence analysis (XFA) is basically employed now to control technological materials with a high content of REE. The XFA technique is not at all so time consuming. However, commercial equipment is capable of detecting only the characteristic radiation of the REE L-lines (4.6 eV to 10.1 keV). In addition, the radiation of the K-series of Ti, Fe, Co, Ni, Cu and Zn lie within the indicated range and is, together with the mutual superimposing of L_α, L_β, L_γ lines of different REE, the reason for the low sensitivity and for the impossibility of determining immediately the REE in rocks.

The attractiveness of the XFA technique concerns the fact that some elements, the most difficult for NAA (Sc, Na, Th, U) have in practice no influence on the X-ray fluorescent determination of REE. If the XFA apparatus makes it possible to excite and detect the characteristic radiation from the REE K-series in the 33–63 keV range, any other elements in the rocks do not interfere, in a first approximation, in the analysis. However, as the exciting radiation increases in energy up to 60–70 keV, the quanta path in a silicate base lengthens drastically and, hence, the probability for double Compton scattering processes increases for this radiation and this generate a solid background in the region of the K-lines of the REE to be detected. The double Compton scattering background can be lowered by using this samples whose thickness is many times smaller than the path of a quantum of exciting radiation in the sample material. In this case, the spectral density of the indicated-type background is roughly proportional to the squared mass thickness of the sample. Our experience has shown that in XFA for heavy REE acceptable values of the signal-to-background ratios are achieved at a 10–100 mg/cm² sample thickness. Thus, for a highly-sensitive XFA of the REE K-lines the source is to be tunable with the 40–75 keV range of monochromatized X-radiation and to be capable of providing a luminosity 10^2–10^3 times higher than in the conventional determination of Fe-type elements in a semi-infinite thick sample. An increase in luminosity should compensate for a decrease in the sample thickness, photoeffect cross section and detector efficiency.

Great difficulties arise in distribution measurements of REE in rock specimens. As can be seen from fig. 1,
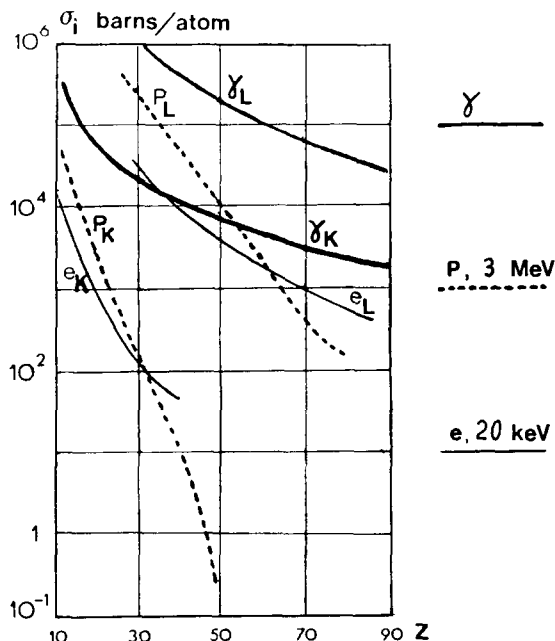
Fig. 1. Ionization cross sections of the K and L shells of elements with atomic number Z from 10 to 90 by electrons (e), protons (p) and X-radiation of optimal energy (γ).

electron-probe analysis or the proton version of the technique with excitation of the K-lines of REE fails here on account of a dramatic reduction of the corresponding ionization cross sections, while an analysis of the REE L-lines encounters the difficulties mentioned above (superimposing of the lines of interfering elements, insufficient resolution of the detector).

Under these conditions the utilization of monochromatized SR for fluorescence excitation allows the XFA technique to be radically enhanced. We recall that electron and positron storage rings with an energy exceeding 4 GeV are the SR sources in the X-ray range we are interested in. In the USSR these are VEPP-3 and VEPP-4 of the Novosibirsk Institute of Nuclear Physics. In 1983 a continually-operating station for XFA was mounted on VEPP-4 [10].

Refs. [8–12] present in detail the quantitative characteristics of SR and describe various aspects of its utilization for analytical purposes. As applied to REE analysis, the following properties of the SR beams are among the most important: the high intensity coupled with sharp directivity (the angular divergence is less than 0.3 mrad); the continuous spectrum enable one to realize monochromatic excitation continuously tunable in a wide energy range (for example, from 30 to 100 keV) using X-ray focusing optics; the natural SR polarization results in a decrease of background from the Compton scattering of the exciting radiation under optimum choice of the detection direction.

The high luminosity of the sample when using focused SR beams has made it possible to create X-ray microprobes with sufficiently high spatial resolution: 2×2 μm^2 for the analysis of light elements (from Na to Ca) [13] and 10×10 μm^2 in the middle part of the Periodic Table (Fe, As, Zr, Mo) [14]. As has already been mentioned, similar devices can also be employed for the analysis of the distribution of REE in undisturbed mineral and rock specimens, with excitation of the K-lines of the elements to be determined.

So far the work has been done using the VEPP-4 XFA station on the determination of Y and Ba in bottom sediments from the Pacific [15]. Though the studies objects are, to a certain extent, natural concentrates of REE (the characteristic contents of light REE: Ln, Ce and Nd, are 50–300 ppm, those of heavy ones, Gd, Dy and Er, are up to 3–10 ppm and larger), the detection limits obtained (0.5 ppm for Eu–Er, 0.7 ppm for Yb at an exposure time of up to 500 s) indicate the applicability of SRXFA technique for the analysis of rocks.

The possibility of using SR for a complex REE determination in rocks, ores and minerals makes urgent the design of a dedicated technique in instrumental and non-instrumental versions as well as an estimation of the metrological characteristics of the technique (precision, reproducibility, sensitivity).

In the present paper the first results are presented on REE determination using the SRXFA technique, to be specific its instrumental version, with a preliminary chemical preparation of rock specimens and artificially manufactured reference samples. The procedure for chemical concentrationing of REE is described. The possibilities are discussed of X-ray microscopy with excitation of the REE K-lines.

2. Description of the experiment

Fig. 2 illustrates the layout of the XFA station which utilizes the SR beam from the storage ring VEPP-4. The SR beam propagates through a vacuum 15 m channel (1) and reaches a box (2) with a one-coordinate focusing LiF monochromator (3). The SR beam is 20×3 mm^2 at the entrance to the monochromator and $\sim 2 \times 3$ mm^2 at its exit, at the focus point. At the monochromator exit the energy E_γ can be smoothly varied from 30 to 90 keV. In the standard operation mode of the storage ring (electron energy $E_e = 5$ GeV, current $I_e = 10$ mA, magnetic field at the irradiation point $H_0 = 0.8$ T) the flux of photons at the monochromator exit, $N(E_\gamma)$, is determined as follows (see ref. [8]):

$$N(E_\gamma) = 2 \times 10^{14} \sqrt{E_\gamma}\, e^{-0.075E_\gamma} \Delta E_\gamma / E_\gamma. \qquad (1)$$

Here $N(E_\gamma)$ is in s^{-1} and E_γ in keV; the transmission
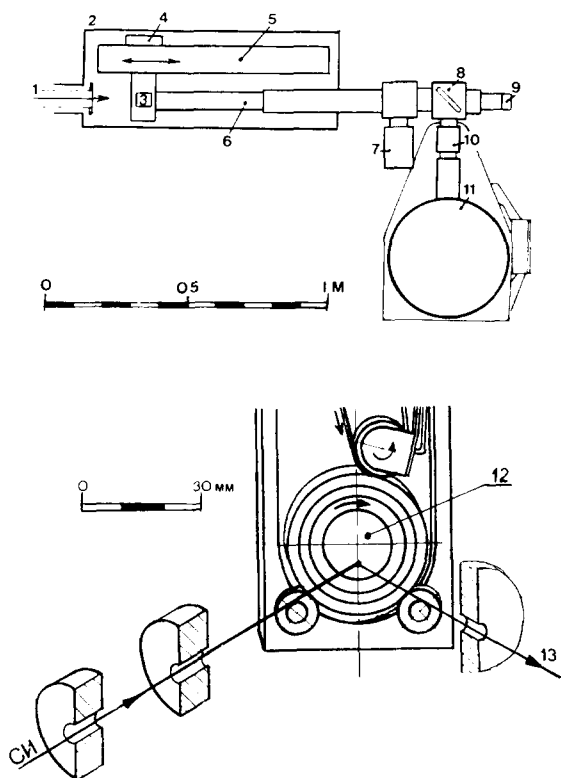
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Fig. 2. General view of the device for SRXFA on the storage ring VEPP-4 (upper); circular scanner (lower). 1: SR transport channel, 2: box, 3: crystal-monochromator, 4: node of crystal rotation, 5: mechanism for the longitudinal movement of a crystal, 6: telescope channel, 7: polarimeter, 8: chamber for analysis, 9: SR beam absorber, 10: collimators and filters, 11: solid state detector, 12: specimen in a cell, 13: detection direction.

band $\Delta E_\gamma/E_\gamma$ is about 2%. In the 40–70 keV range the sample luminosity in the monochromator focus is (8–3) $\times 10^{10}$ photons/s · mm^2.

The monochromatized SR arrives through a telescopic channel (6), at a W chamber (8). In the chamber there is a cell with a sample or a scanner.

XFA spectra are detected by a solid state, super-pure Ge detector "Schlumberger EGPX-50" with an energy resolution of 170 eV on a 5.9 keV line and ~ 300 eV in the region of the K-lines of heavy REE. The solid detection angle is adjusted within $(1-4) \times 10^{-4} \cdot 4\pi$ sr in the regime of highly-sensitive REE concentration measurements and up to $1.6 \times 10^{-3} \cdot 4\pi$ sr in the scanning regime (measurement of the REE distribution in the sample).

The displacements associated with energy variation at the exit from the monochromator, scanning as well as the processes of data gathering and processing are automated using the CAMAC system and an INP micro-

computer "Odryonok". The memory capacity of this microcomputer, being simultaneously a crate-controller, is 65 K 24-bit words at an average speed of 2×10^5 arithmetic operations per second.

2.1. Chemical concentrating of REE

For REE determination in ultrabasic rocks, in the non-instrumental, SRXFA the enrichment procedure was as follows: The rock (0.5–1 g) was mixed in an alund melting pot with 3–6 g of Na_2O_2, and the pot was then placed in a cold box and heated up to 500 ° C. Sintering lasted 5 min at this temperature. The cooled sinter was water leached (200 ml of water in a 400 ml cup), heated to boiling and filtered, in the hot state, through two yellow filters. The precipitate was flushed out 3–5 times with a 0.5% solution of NaOH. The filter with precipitate was placed in the same cup. In the melting pot in which the sintering was carried out, one added 20–30 ml of hot HCl (1 : 1), dissolving the melting residue and the content was transferred to the cup with the precipitate. The cup was heated up to give a complete dissolving of the precipitate and the filter was transformed into homogeneous compound as a result of this.

Hydroxides were precipitated from a hot solution (100 ml) by a distilled (carbonateless) NH_4OH, adding 20 ml in excess. The cold solution was filtered, washed with water with a few drops of NH_4OH. The filter with the precipitate was then ashed and calcinated in a porcelain melting pot at a temperature of 600 ° C. The calcinated sediment was chlorinated in a quartz "boat" according to the procedure described in ref. [16]. After chlorination, 50 ml of the sediment was transferred to a cup to which was added a 20 ml of tsar's vodka, a few drops of H_2O_2 and evaporated up wet salts. Then, a drop of concentration HCl was added, the cup walls were washed and the volume of the solution was increased to 5 ml. After is, one added 15–20 mg of Ca and 15 ml of oxalic acid mixing the solution with a glass rod. Twelve hours after the solution was filtered through a blue filter, ashed and calcinated for 30 min at a temperature of 800 ° C. The REE concentrate on CaO (filling agent) were pressed into tablets of 5 mm diameter.

2.2. Processing of the spectra

The external-standard method was taken as the basic method for quantitative determination of REE. Fig. 3 illustrates the characteristic shape of the SRXFA spectrum in a complex REE analysis in silicate-based samples. The dominant component in the spectrum is the peak from Compton scattering of the exciting radiation. In XFA using the SR beam, the sample luminosity is not constant because of a gradual reduction of the
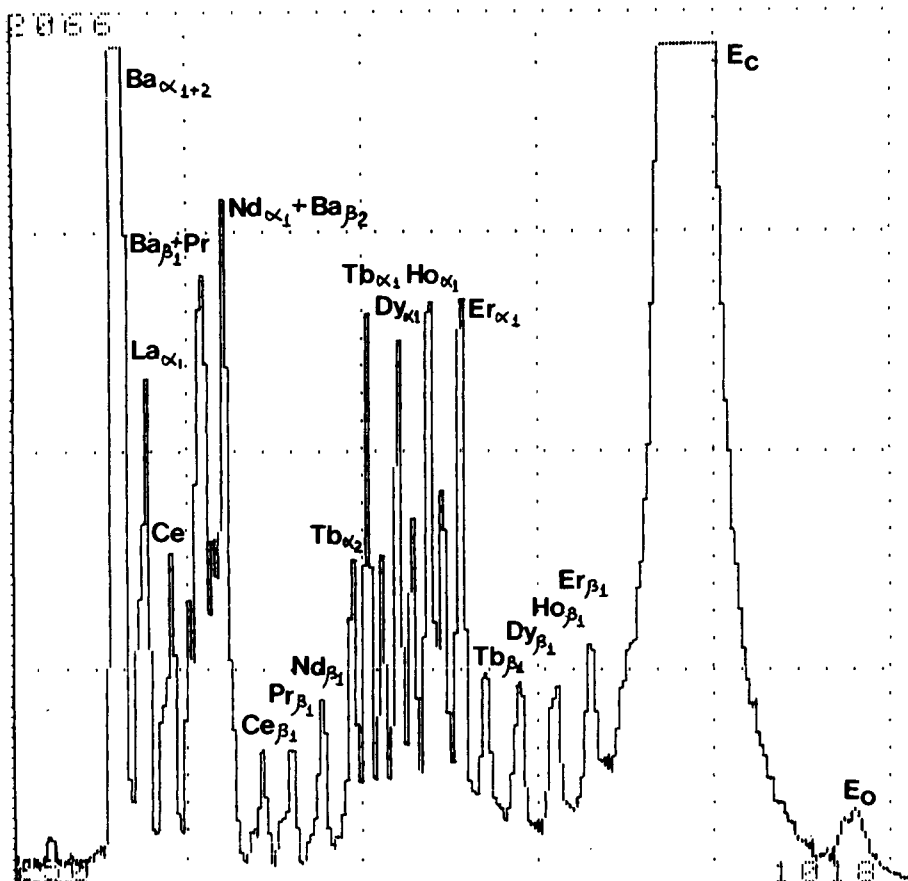
Fig. 3. The spectrum for a sample of rock with REE additives; the concentration of the latter is 10^{-2} %.

electron current in the storage ring. Therefore, the REE contents in the sample under study and in the reference sample were compared by normalizing the areas of the K_α peaks of these elements over the area of the Compton-scattering peak. Since the thin radiator criterion was satisfied for all the measured samples, the elemental content was defined from the linear expression

$$C = C_{ref} NC/NC_{ref}, \qquad (2)$$

where C_{ref} is the content of the element in the reference sample. NC, NC_{ref} are the normalization coefficient for the sample being measured and the RS:

$$NC = 10^3 N_p / N_{Compt}. \qquad (3)$$

Here N_p and N_{Compt} are the number of detected pulses in the fluorescence peak of the element to be determined and in the peak from Compton scattering and exciting radiation.

Despite the formal simplicity of expression (3), determination of the N_p for the K-lines of REE, particularly at low concentrations, runs into some difficulties. First, this is a mutual superimposing of the spectral

lines $K_{\alpha 1}$, $K_{\alpha 2}$, $K_{\beta 1-3}$ of different elements. The existing procedures of finding N_p under the conditions of non-allowed and partially allowed multiplets are usually based on a multiple successive subtraction of the peak-approximating Gaussians and requires good statistical definiteness of the peaks: $(N_{peak})^{-1/2} \simeq 1-3\%$; this contradicts the desire to measure extremely low concentrations of elements. Second, by then we have not yet found a satisfactory algorithm providing an exact and completely automatic reconstruction of the background lines from the experimental spectrum alone.

To carry out this work, a simplified procedure was designed to indicate, with the help of a computer, a number of reference points needed in background calculations. The spectra were processed as follows. After an automatic search of the peaks and minimuma between them according to the convexity criterion (see ref. [6]), the spectrum with the marked peaks and minima was extracted on a colour graphic display. The program was then translated into the so-called instruction regime in which an operator indicates the position of the peak from Compton scattering and those of the found minima

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which could be considered to be lying on the background level in the spectra of samples of similar content. In addition, the operator indicates the positions and energies of two or more intense peaks (usually the K_α-peaks of Sr, Be, Ce) for scale calibration. A spline based on the indicated minima plus the Compton peak is then taken as the background level.

After "instruction", the program was capable of, in the automatic operating mode, processing a number of spectra of samples and references relatively near in composition. Processing was possible if within the given zones (deviations was no more than 3–5 channels) the Compton peak and the number of minima sufficient to draw the background level were revealed. The exactness of this line was controlled by the operator who watched the images of the spectra and the background on the display screen.

The areas of the peaks were determined by summing the counts in 3–5 channels near their maxima, with the background subtracted. Thus, for quantitative analysis use was made only of the central peaks area whose width was 0.3–0.5 of the total width of the peak at half-height. Narrowing of the integration region worsens the statistical definiteness of the peak, but reduces the influence of errors in the background level and simplifies the procedure of making allowance for the superimposings of the K_α and K_β lines of different elements. Among the peaks found the $K_{\alpha 1}$ lines of the given elements were identified; the areas of the peaks were replaced by the values of NC, calculated according to eq. (3).

Finite values of NC were derived after the correction procedure which is a successive subtraction of the contribution from the $K_{\beta 1}$, $K_{\beta 2}$ and $K_{\beta 3}$ lines of a lighter element in NC for the $K_{\alpha 1}$ line of the next elements. In REE analysis the correction usually started with taking into account the contribution given by the BA lines. The corresponding tabular values were taken as relative values of the $K_{\alpha 1}$ and $K_{\beta 1,2,3}$ lines. During correction, the shape of the lines was assumed to be roughly described by a normal Gaussian distribution; the width was measured experimentally on the 26.4 keV and 59.5 keV lines of the isotope ^{241}Am. After correction the revised values of NC were converted to units of relative weight content of the element according to formula (2).

In this measurement the detection limit ($C_{\min}$) was found from the expression

$$C_{\min} = 3C\sqrt{N_b}/N_p, \tag{4}$$

where C is the relative content of the element in the sample.

Since our measurements were performed when the storage ring VEPP-4 operated – owing to other users' demands – at an increased energy ($E_e = 4.3$–4.7 GeV) and the sample luminosity sometimes did not allow a

maximum SSD count rate, we here also present the extrapolated detection limit characterizing the capabilities of the technique at an exposure time of 10^3 s and a 10 kHz counting rate of the detector:

$$C_{\min \text{ extrapol.}} = C_{\min} 10^{-2} \sqrt{f[\text{kHz}] t[\text{s}]}, \tag{5}$$

where f is the detector counting rate in a measurement for which $C_{\min}$ was defined and t is the measurement time.

It is worth noting that spectrometric apparatus with a non-Gaussian (rectangular) pulse forming [17] coupled with an optical feedback SSD has indeed enabled one to work at the indicated counting rates, in practice, without a reduction in energy resolution.

3. Discussion of the results

In order to determine the detection limits ($C_{\min}$) and reproducibility of the results of REE analysis using the instrumental SRXFA technique, among the reference samples of rocks used were ST-1A, SGD-IA and ST-1A with REE additives in concentration of ~ 100 ppm, CaO with introduced La, Pr, Nd and Sm, and pure polystyrene with REE additives in concentration of 10^3, 10^2, 10 and 1 ppm. The characteristic values of the detection limits for a detector counting rate of 10^4 Hz and exposure time of 10^3 s are given in tables 1 and 2 and are 0.13 to 0.33 ppm. At 1 ppm concentration the signal-to-background ratio for the REE lines varies from 0.4 to 0.1 depending on the excitation energy and sample thickness.

The SRXFA technique was used in an analysis (with chemical preconcentrating) of a number of rock specimens and references samples ST-1A and SG-1A, according to the described procedure. The content of REE in the initial samples and concentrates were checked, where possible, by the SRXFA technique and NAA simultaneously. In the concentrating process the chemical yield of REE was 0.8 to 0.7; the mass saturation coefficient K was 20 to 40. It is worth mentioning that a decrease in the relative concent of Ba during concentrating (by a factor K) results in a decrease in background from the spectral $K_{\beta 1,2}$ lines of Ba, in Pr and Nd analysis, and makes possible an X-ray fluorescent determination of these elements in rocks with high content of Ba.

Table 3 gives the characteristics of the analysis of a sample of lherzolite with chemical preconcentrating. The detection limits for REE are 4.4 to 6.8 ppb (4.4–6.8 $\times 10^{-7}$%). At $K = 40$ the detection limit becomes, on average, a factor of 17 lower. The disproportion between the saturation coefficient and the detection limit is accounted for first by the fact that the chemical yield of REE is other than unity and, second, by a certain worsening of background conditions in the detection

Table 1

Results of REE determination in the samples on the basis of CaO with La, Pr, Nd and Sm additives; (excitation energy = 69 keV, detector counting rate 1.3 kHz, exposure time 200 s, sample thickness 125 mg/cm^2)

Element	C [ppm]	NC (for 1 ppm)	N_p	N_b	C_{min} [a] [ppm]	$C_{min\,extrap}$ [b] [ppm]
La	29.2	0.62	468	60	1.45	0.23
Pr	32.1	0.97	797	65	0.97	0.15
Nd	32.0	0.84	695	65	1.11	0.17
Sm	24.1	0.79	491	70	1.23	0.20

[a] C_{min} is the detection limit in the given measurement.

[b] $C_{min\,extrap.}$ is the extrapolated detection limit for a detector counting rate of 10 kHz and exposure time of 10^3 s.

Table 2

Results of REE determination in reference samples on the basis of polystyrene with La, Pr, Nd, Ho and Er additives (excitation energy 62 keV, detector counting rate 0.3 kHz, exposure time 200 s, sample thickness 15 mg/cm^2)

Element	C [ppm]	NC (for 1 ppm)	N_p	N_b	C_{min} [ppm]	$C_{min\,extrap}$ [ppm]
La	10	0.27	66	15	1.76	0.14
Pr	10	0.29	69	15	1.68	0.13
Nd	10	0.28	67	15	1.73	0.134
Ho	10	0.40	93	97	3.18	0.25
Er	10	0.43	101	70	4.31	0.33

region due to a simultaneous increase in intensity of a great number of spectral lines.

The reproducibility of SRXFA results is reflected in table 4. In REE reanalysis of the same element, the r.m.s. deviation is 3–5% at 40–70 ppm content and 8–10% at a 10–20 ppm content. When repeating the concentrating with subsequent analysis using the SRXFA technique, reproducibility of the results is ± 8% at a content of REE in the original sample of 3 ppm higher, and ± 30% for 0.5–2.0 ppm contents (see table 5).

Thus, the possibility has been shown of an instrumental determination of some REE with their content

Table 3

Results of REE determination in a sample of lherzolite and its concentrate (excitation energy 55 keV, time of analysis 200 s)

REE	K [a]	C [ppm]	N_R	N_b	C_{min} [ppm]	$C_{min\,extrap}$ [ppm]
La	1	1.85	30	21	0.85	0.076
La	39.9	1.85 K	277	9	0.06	0.0044
Ce	1	4.0	52	24	1.13	0.10
Ce	39.9	4K	516	12	0.08	0.0059
Nd	1	2.3	30	36	1.38	0.12
Nd	39.9	2.3 K	259	12	0.09	0.0068

[a] K is the mass enrichment coefficient equal to the ratio of the masses of the initial sample and the final product after concentrationing; the detector counting rate is 0.4 kHz for $K = 1$ and 0.27 kHz for $K = 39.9$.

Table 4

Reproducibility of the results on REE determination in the concentrate from the reference sample ST-1A (enrichment coefficient $K = 28.9$, excitation energy $E = 77$ keV)

	Normalization coefficients (NC)							
	La	Ce	Pr	Nd	Dy	Er	Yb	Eu
1	36.3	64.7	21.3	42.4	17.4	12.4	20.3	–
2	32.9	65.7	18.3	40.1	17.3	12.5	17.4	–
3	35.5	70.9	–	37.9	17.3	11.2	17.5	17.7
4	33.0	69.6	17.4	41.2	17.1	11.3	18.1	17.0

Table 5

Reproducibility of the results on REE determination using concentrationing in the sample of lherzolite 1/81

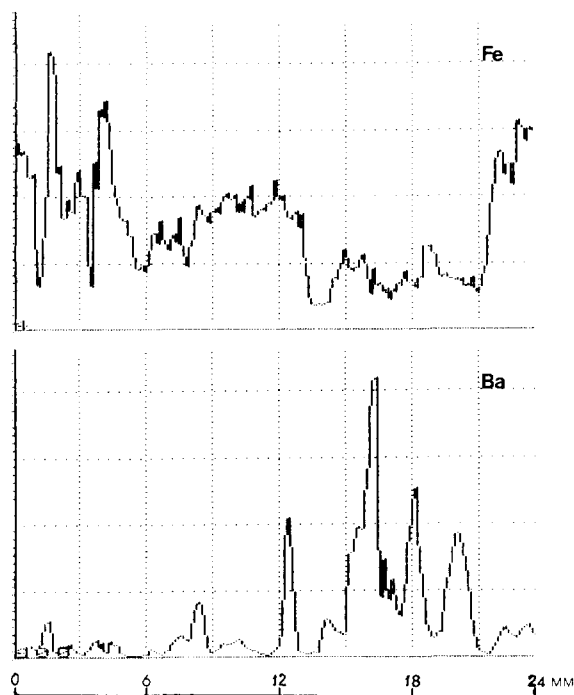| No. of the sample	Energy [keV]	K	Sample weight (mg)	Measured content (ppm)					
				La	Ce	Nd	Dy	Er	Yb
1/81(2)	77	30.2	16.90	3.1	12.3	6.4	1.1	0.78	1.5
1/81(3)	77	39.9	12.8	3.0	10.9	6.1	1.0	0.68	1.2
1/81(5)	75	18.9	27.1	3.0	11.4	6.9	0.9	1.0	1.9

Fig. 4. The profilograph of a sample of xenolite from the kimberlite pipe.

in rocks of 0.5 ppm or higher using the SRXFA technique. Chemical preconcentrating enables one to determine practically any REE in most rocks.

To analyse the peculiarities of REE and iron distributions as well as those in the samples of rocks and mineral grains, polished plates of rocks of ~ 0.1 mm thickness were scanned by a monochromatic SR beam. As samples, use was made of xenolite and a large (~ 20 mm diameter) garnet grain from Kazakhstan. A circular scanner enabled the concentrations of elements to be detected along circles of radii 2, 4, 6, and 8 mm. The excited area on the sample was 0.8 mm^2, and the measurement time at each point was 1–3 s. The scanning step was taken within 0.06–0.25 mm. The program allows a simultaneous detection of 7 elements (Fe, Sr, Y, Zr, Ba, La and Ce).

The profilographs obtained for a sample of xenolite are illustrated in fig. 4.

The studies are assumed to continue, with higher spatial resolution, using a two-coordinate scanner with 10×10 μm^2 step of scanning. The results show that one can obtain maps of the REE distributions with a statistical error of about 30% for 2 ppm contents and about 10% for 20 ppm, for a measurement time of 1 s per point.

4. Basic conclusions

(1) The possibility has been shown of instrumental determination of REE in basic and ultrabasic rocks by the SRXFA technique at 5×10^{-5} % content.

(2) Chemical preconcentrating of REE with subsequent SRXFA enables the REE to be determined at 10^{-6} % content.

(3) Scanning with a collimated SR beam offers the possibility of studying the REE distribution in samples of rocks and some mineral grains.

References

[1] E.V. Smirnova, S.V. Lontsih and A.I. Sidorovsky, Ah. Anal. Khimii 39 N(10) (1984) 1804, in Russian.
[2] E.J. Cortes, Radioanal and Nucl. Chem. Art. 84(1) (1984) 157.
[3] J. Bishop and T.C. Hughes, J. Rad and Nucl. Chem. Art 84(2) (1984) 213.
[4] G.M. Kolesov, J. of Radioanal. Chem. 30 (1976) 553.
[5] S. Meloni, M. Oddone and A. Cecchi, Poliv. J. Radianal. Chem., 71 (1,2) (1981) 429.
[6] V.B. Baryshev, Yu.P. Kolmogorov, G.N. Kulipanov and A.N. Skrinsky, Preprint INP 83-142, Novosibirsk (1983), in Russian.
[7] V.B. Baryshev, Yu.P. Kolmogorov, G.N. Kulipanov and A.N. Skrinsky, Zh. Anal. Khimii 41(3) (1986) 389, in Russian.
[8] G.N. Kulipanov and A.N Skrinsky, Usp. Fiz. Nauk 122 (1977) 369 [English translation: Sov. Phys. Usp. 20 (1977) 559].
[9] C.J. Sparks, in Synchrotron Radiation Research, eds., H. Winick and S. Doniach (Plenum, New York, 1980) p. 459.
[10] J.V. Gilfrich, E.F. Skelton, S.B. Quadrl, J.P. Kirkland and D.J. Nagel, Anal. Chem. 55 (1983) 187.
[11] V.B. Baryshev, Yu.P. Kolmogorov, G.N. Kulipanov and A.N. Skrinsky, in Proc. 6th Nat. Conf., SR-84, Novosibirsk (1984) in Russian.
[12] V.B. Baryshev, G.N. Kulipanov and A.N. Skrinsky, Proc. Conf. on Synchrotron Radiation Instrumentation, Stanford, 1985. Nucl. Instr. and Meth. A246 (1986) 739.
[13] P. Horowitz and J. Howell, Science 178 (1972) 608.
[14] W. Petersen, P. Ketelsen, A. Knochel and R. Pausch, In Proc. Conf on Synchrotron Radiation Instrumentation, Stanford (1985) Nucl. Instr. and Meth. A246 (1986) 731.
[15] A.V. Dubinin, I.I. Volkov, V.B. Baryshev and G.N. Kulipanov, Geokhimia 1 (1986) 70, in Russian.
[16] N. Yordanov and H. Daiev, Zh. Anal. Khimii 17 (1962) p. 429, in Russian.
[17] O. Ignatyev, A. Lysenko, A. Pulin, U. Shevchenko and N. Shkola, Proc. 6th Nat. Conf. on Synchrotron Radiation SR-84, Novosibirsk (1984) in Russian.