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PIXE MULTIELEMENT ANALYSIS OF SERPENTINITE ROCKS FROM LOWER SILESIA (POLAND)

Abstract. The proton-induced X-ray emission method (PIXE) has been applied to multielement analysis of some serpentinite rocks from Lower Silesia (Poland). The major and trace elements with the atomic numbers from 14(Si) to 41(Nb) and Pb have been determined. For some elements (Rb, Sr, Y, Zr, Pb, Br) the obtained data give the first geochemical findings on their abundance in Lower Silesian serpentinites and contribute to general knowledge of geochemistry of ultrabasic rocks. The data were evaluated statistically using simplified graphical method. Some elements (Ca, Fe, Sr, Cr, Mn and Pb) display 2 or 3-modal cumulative frequency distributions but only in very few cases this phenomenon is connected with locality and with the degree of serpentinization of ultrabasites.

INTRODUCTION

Inducing characteristic X-ray emission by charged particles is actually one of the most common methods of X-ray fluorescence analysis. X-ray production cross-sections for charged particles exceed by several orders of magnitude those necessary for excitations by photons, which opens wide possibilities for the determination of trace elements. Another advantage of applying that method is that the charged particles can be strongly focussed, which makes possible the excitation of micro-areas, several mm in diameter. Due to lower intensity and lower energy of bremsstrahlung radiation that forms the background superposing on fluorescence radiation of samples, the utilization of heavy ions is particularly convenient.

The proton beam was first applied for the excitation of X-ray emission in multielement analysis (PIXE) by Johansson *et al.* (1970). The number of works concerning the applications of this method in geology, mineralogy and geochemistry increases /e.g. Kullerud and Steffen 1979, Kullerud *et al.* 1979, Clark *et al.* 1975, Carlsson and Akselsson 1981). A presentation of the applications of that method for solving various scientific problems can be found e.g. in the works of Johansson S.A.E. and Johansson T. B. (1976) and Cahill (1980).

In Poland, the PIXE method has so far been mostly applied in medical and biological research but hardly ever in geology. In this study, the method was applied

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to selected samples of ophiolitic Lower Silesian serpentinites. They were collected from three mafic-ultramafic rock bodies situated in the surroundings of the Sowie Góry (Mt.) Block (Lower Silesia, SW Poland) i.e. from Braszowice—Grochowa, Szklary and Gogółów—Jordanów (Ślęza Mt. Group) massifs (Przybyłowicz 1986). More detailed data on their geological setting and petrology are given among others by Narębski *et al.* (1982).

METHOD

The bombardment of atoms present in a sample (which in this method is called "target") by a beam of protons causes the ejection of inner shell electrons and subsequent emission of characteristic X-rays. The energetic spectrum obtained is composed of characteristic X-ray lines from different elements present in the sample as well as of the background radiation due to proton and secondary electron bremsstrahlung radiations and nuclear gamma emission. X-rays are detected by a semiconductor detector and next analyzed in a multichannel analyzer.

Two main kinds of targets — "thin" and "thick" — are used in this method. In the thin one the effective (mean) X-ray production cross-section $\nu(E)$ is 5% smaller than that for incident proton energy E_0 (Campbell 1977). The specimens which are thin in the case of protons are also thin for X-rays. Therefore, for such targets the attenuation corrections are negligible. Thin targets are generally used in the analysis of biological materials and of all liquids. They require special preparation techniques.

While applying "thick" targets, however, the loss of energy of proton beam and the attenuation of the emitted X-rays there are significant. The target that absorbs the beam completely is called "infinitely thick". The main advantage of using thick targets is a very simple and fast preparation of the sample. Besides, the risk of introducing some contaminants is very small there.

It has been shown that thick targets can be successfully used in quantitative trace element determinations (Willis *et al.* 1977, Johansson S.A.E. and Johansson T.B. 1976). High homogeneity of the target is required in this method because otherwise the analyses of small parts of the target (small amounts of the material, several to 100 mg in weight, are irradiated by proton beam) may be unrepresentative for the whole sample.

In quantitative analysis the comparative method is commonly used. It consists in simultaneously exposing to radiation, in the same configuration, the analyzed samples and analytical standards. Similar chemical composition of both will ensure the same proton stopping power (Clark *et al.* 1975).

By assuming that the proton beam is completely stopped in the targets and that the geometry of the recording of emitted X-rays is identical in both the sample and the standard cases, the content of element (Z) in the analyzed sample can be calculated by means of a simple formula:

$$\frac{C}{C'} = \frac{N_z}{N_{z'}}$$

where: C and C' — contents of element (Z) in the analyzed sample and in the analytical standard, respectively (in ppm),

N_z and $N_{z'}$ — numbers of counts of X-ray emission for the line corresponding to the determined element (Z) in the sample and in the analytical standard respectively.

Since geological materials generally consist of several major elements within a narrow range of atomic numbers, their stopping powers are similar (Clark *et al.* 1975). Consequently, by using for comparison analytical rock standards of similar composition, we may neglect corrections because the differences in stopping powers are small.

EXPERIMENTAL

Our analyses were carried out in the Laboratory of Applied Nuclear Spectroscopy, Institute of Nuclear Physics in Cracow. Thick targets were prepared from the powdered sample by pressing in into pellets, 1 cm in diameter and ca. 0.5 mm thick, in a stainless steel vessel. A corundum bottom layer was placed to avoid direct contact of the material with the steel.

The targets so prepared were placed in a target chamber with a 12-position manual target support. For more detailed description of the chamber see Szymczyk *et al.* (1981). Small cyclotron C-48 was used as the source of protons. The proton energy was ca. 2.6 MeV and the beam intensity was up to 5 μ A. The beam diameter on the target was about 5 mm. The X-rays emitted by the target were detected by the ORTEC Si (Li) semiconductor detector, 5.4 mm thick, of the 30 mm² effective area and of the resolution of ca. 180 eV (at 5.9 keV Mn $_{K\alpha}$). The target — detector distance was approx. 25 mm. CAMAC electronics and CIA-70 multichannel analyzer (with a paper tape puncher for off-line processing of the results) were applied. The final processing which involved the least-square fitting of individual peak areas to Gaussian functions was carried out on the ODRA 1305 computer by using three computer codes: "FAFIK", "AZOREK" and "KUBA" (Kajfosz 1976). The beam intensity was found by counting the protons scattered from the aluminium foil placed across the beam path, with a ring-shaped silicon detector. The measurements were normalized to an equal number of scattered protons.

The considerable amounts of iron in the analyzed samples (up to 10% Fe) rendered impossible the estimation in one measurement and with required accuracy of trace elements in the whole range of atomic numbers Z . X-ray emission of this major element caused overloading of the detector. Consequently, the elements showing lower and higher atomic weights were determined in two separate measurements. Shielding of the detector by means of an Al-filter of 45 mg/cm² mass per unit area, allowed the determination of the elements of the atomic numbers higher than 26. This was due to a much better absorption of X-rays coming from the iron atoms, compared with those of higher energy emitted by an element of higher atomic number. Lighter elements ($Z < 26$) were estimated with the detector shielded by a pinhole Al-filter of 18 mg/cm² mass per unit area. Such a technique made possible partial absorption of the disturbing X-rays from the iron and the detection of lower energy radiation emitted by atoms of elements of lower atomic numbers.

Among possible disturbing effects (cf. Dziunikowski 1979), the most essential one is a partial overlapping of radiation peaks of the K_{α} and K_{β} series of the elements with slightly differing atomic numbers. This effect is particularly important for light elements and may sometimes preclude the determination of those occurring in considerably lower amounts than other elements with similar atomic numbers Z . This occurs for scandium (disturbing effects of Ca $_{K\beta}$ and Ti $_{K\alpha}$), vanadium (effect of Ti $_{K\beta}$ and Cr $_{K\alpha}$) and cobalt (effect of Fe $_{K\alpha}$). In other cases of the overlapping of peaks (Br $_{K\beta}$ and Rb $_{K\alpha}$, Rb $_{K\beta}$ and Y $_{K\alpha}$, Sr $_{K\beta}$ and Zr $_{K\alpha}$, Y $_{K\beta}$ and Nb $_{K\alpha}$), deconvolution of interfering peaks was possible but rather difficult, due to the application of filters,

variously absorbing K_{α} and K_{β} radiations of various elements. Therefore, the ratios of intensities of K_{α} and K_{β} lines were estimated experimentally by adding known amounts of determined elements to the sample of typical chemical composition for the rocks studied (serpentinite of Grochowa). The correct K_{β}/K_{α} ratio was computed from the difference of measurements between the primary sample and that containing known amounts of one of the element of overlapping peaks. Moreover, measurements of the contents of individual elements were performed for 10 targets of the same sample of Grochowa serpentinite and, subsequently, the average (mean) values of numbers of counts and their standard deviations were computed. It was found that errors due to method differed for the different elements. The lowest relative standard deviations found were for Fe, Br, Ni and Pb (4–6%) and a little higher — for Sr (ca. 8%). The largest errors are characteristic for determinations of Rb and Zn (relative standard deviations 16 and 15%). Besides, relative standard deviation values tell if the homogeneity of the analyzed material is sufficient, which is necessary for obtaining representative results.

Quantitative analysis was made from the sensitivity calibration curves showing the relation between the number of counts of detector per 1 ppm content of individual

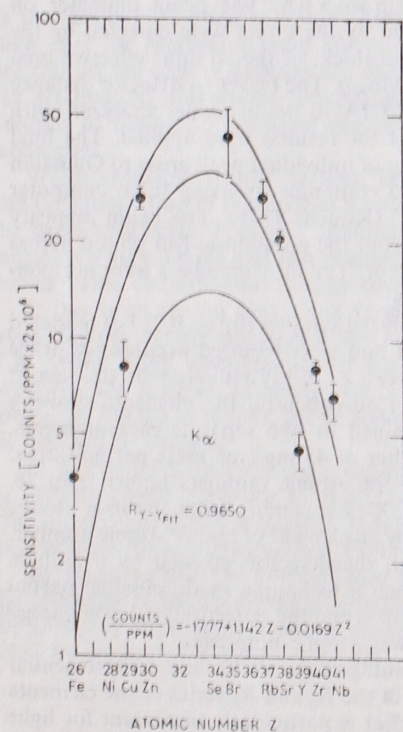


Fig. 1. Sensitivity calibration curve for K_{α} -lines ($Z \geq 26$)

Detector shielded by an Al-filter of 45 mg/cm² mass per unit area. Number of scattered protons $2 \cdot 10^6$. R — multiple correlation coefficient. Confidence interval estimates computed for $1-\alpha=0.95$

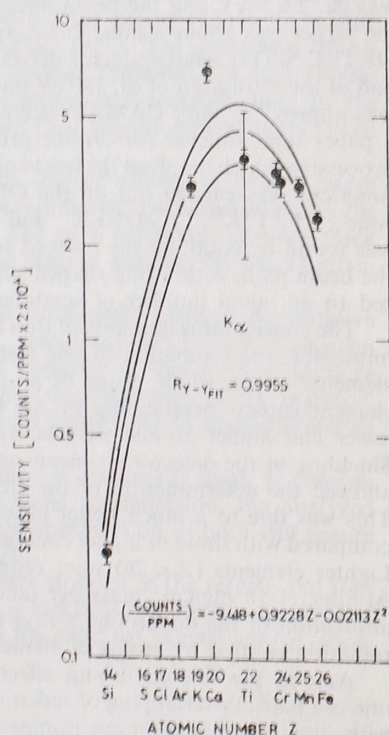


Fig. 2. Sensitivity calibration curve for K_{α} -lines ($Z \leq 26$)

Detector shielded by a pinhole Al-filter of 18 mg/cm² mass per unit area. Number of scattered protons $2 \cdot 10^4$. R — multiple correlation coefficient. Confidence interval estimates computed for $1-\alpha=0.95$

elements and their atomic numbers Z (Fig. 1 and 2). These curves were obtained from the results of 10 measurements performed for the two targets of multielement standards, one made by International Atomic Energy Agency (lake sediment SL-1, Dybczyński and Suschny 1979) and the other made by the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Academy of Sciences of USSR in Moscow (peridotite PIM-1). The error of the quotient of the number of counts by the content of an element (in ppm) is computed by using the error propagation law while taking into account the standard deviation of mean count numbers and the determination error given by producers of analytical standards. Calibration curves are plotted in a semi-logarithmic system. Experimental points were estimated by means of the 2nd order polynomial, with the inverse squares of errors taken as statistical weights of these points.

Table 1
PIXE sensitivity as a function of the atomic number ($Z \geq 26$) for K_{α} -lines. Detector shielded by an Al-filter of 45 mg/cm² mass per unit area. Number of scattered protons $2 \cdot 10^6$

Atomic number Z	Element	Sensitivity [counts/ppm $\cdot 2 \cdot 10^6$]			Detection limit L_D	Determination limit L_Q
		measured for standard SL-1	estimated from the curve	estimation error for $1-\alpha=0.95$		
26	Fe	3.63 ± 0.10	3.22	2.58	50	150
28	Ni	—	9.05	5.21	9	27
29	Cu	8.1 ± 1.6	14.00	7.70	8	24
30	Zn	17.7 ± 1.6	19.54	10.84	4	12
31	Ga	—	24.61	14.16	4	12
34	Se	—	33.24	19.12	1.5	5
35	Br	43 ± 11	32.36	18.77	1.2	4
37	Rb	27.5 ± 3.3	22.91	11.67	1.2	4
38	Sr	20.3 ± 1.1	17.18	8.26	2.2	7
39	Y	4.5 ± 0.6	11.91	5.78	3.3	10
40	Zr	8.1 ± 0.6	7.64	4.17	4	12
41	Nb	6.6 ± 1.0	4.53	3.04	4.5	14
82	Pb ¹	39.2 ± 7.8	—	—	1.7	5

¹ For L_{α} -line

Apart from experimental data and the obtained results, Tables 1 and 2 contain estimation errors (confidence intervals) calculated for confidence level $(1-\alpha)=0.95$, which answer the question of type (1) (Natrella 1966)¹. For the atomic numbers, for which no experimental data were obtained, the mean estimation error accepted was computed for the whole calibration curve. Detection (L_D) and determination (L_Q) limits presented in these tables were calculated on the basis of Currie's (1968) proposal by assuming a well known background value for confidence level equal 0.95.

Detection and determination limits (in ppm) of individual elements were expressed in terms of the sensitivity defined as the number of counts (peak area after background subtraction) for 1 ppm of a given element for a given number of scattered

¹ In that interval, for a given confidence level, there is a true value of dependent variable (sensitivity) corresponding to a definite value of an independent variable (atomic number).

Table 2
PIXE sensitivity as a function of the atomic number ($Z \leq 26$) for K_{α} -lines. Detector shielded by a pinhole Al-filter of 18 mg/cm² mass per unit area. Number of scattered protons $2 \cdot 10^4$

Atomic number <i>Z</i>	Element	Sensitivity [counts/ppm · 2 · 10 ⁴]			Detection limit <i>L_D</i>	Determination limit <i>L_Q</i>
		measured for standard: (1) — SL-1; (2) — PIM-1	estimated from the curve	estimation error for $1-\alpha=0.95$		
14	Si	0.213 ± 0.003 ⁽²⁾	0.23	0.06	900	2740
16	S	—	0.87	0.20	170	520
17	Cl	—	1.46	0.33	90	270
19	K	3.0 ± 0.2 ⁽¹⁾	3.08	0.69	50	150
20	Ca	6.9 ± 0.4 ⁽¹⁾	3.87	0.87	45	140
22	Ti	3.7 ± 0.3 ⁽¹⁾	4.55	1.00	30	90
		3.4 ± 1.7 ⁽²⁾				
24	Cr	3.1 ± 0.3 ⁽¹⁾	3.63	0.79	45	140
		3.3 ± 0.3 ⁽²⁾				
25	Mn	3.0 ± 0.2 ⁽¹⁾	2.80	0.63	65	200
26	Fe	2.39 ± 0.06 ⁽¹⁾	1.96	0.46	130	400

protons. The detection limits obtained are close (for some elements slightly lower) to those reported by Carlsson and Akselsson (1981) for geological standards.

Lead was the only element determined from the L_{α} line. For all the other elements the K_{α} lines were used. The application of this calibration curve is possible on the assumption that for each element the effect has a linear character i.e. that the dependence of number of counts for a given line of X-ray emission on the content of the element emitting it is a straight line. The correctness of this assumption was confirmed by the results of measurements for analytical standards, containing different amounts of trace elements. The standards used in our work were prepared in the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM), Academy of Sciences of USSR in Moscow (peridotite PIM-1), Institute of Geochemistry, Siberian Branch of Academy of Sciences of USSR in Irkutsk (plateau-basalt ST-1A and essexite gabbro SGD-1A) and by International Atomic Energy Agency (lake sediment SL-1).

RESULTS

The geochemical data obtained were statistically evaluated using simplified graphical method (Narebski 1983). The results and data on cumulative frequency distribution types, means and standard deviations are presented in Table 3. Some comments on geochemical regularities in individual groups of the elements determined using the PIXE method are given below.

Major elements: silicon, calcium and iron

All these elements display normal cumulative frequency distributions but only in the case of Si it is unimodal in character. Calcium frequency distribution is 3-modal

and that of iron — bimodal. In general, the data obtained on the abundances of these elements in Lower Silesian serpentinites are similar to those reported by other authors (e.g. Kubicz 1966, Bakun-Czubarow 1966).

Trace alkali and alkaline-earth elements: rubidium and strontium

In the serpentinites analyzed Rb shows a unimodal normal frequency distribution. Its average content — 13.8 ppm — is rather high when compared with the data for two Canadian serpentinites (1.036 and 7.75 ppm respectively — Stueber and Murthy 1966) and clark value proposed by Turekian and Wedepohl (1961) for ultramafic rocks — 0.2 ppm.

Strontium displays bimodal normal frequency distribution, and the arithmetic means for two populations amount to 10 and 22 ppm. Because of small number of data no standard deviations were calculated for them. The mean of the first population is close to those reported for the Canadian serpentinites (8.36 and 5.85) and to Turekian-Wedepohl's range of Sr contents in ultramafic rocks (1–10 ppm).

Trace transition elements of 3d group

In the rocks analyzed titanium shows a unimodal normal cumulative frequency distribution. Its mean content in them amounts to 106 ppm and so it is approximately three times lower than the clark value for ultramafic rocks (300 ppm — Turekian and Wedepohl 1961). Higher contents of Ti are also reported by Bakun-Czubarow (1966) for Bielice ultramafites, Klodzko region, Lower Silesia (average abundance 293 ppm) and for serpentinites of ultrabasic massif Belvidere Mountain, Vermont, USA (0.02–0.05% — Labotka and Albee 1979). Similar data are given by Wicks and Plant (1979). It should be mentioned that Ti occurs in these rocks mainly within accessory chromites and magnetites and also, in very small amounts, in serpentine minerals.

Chromium

This element generally concentrated in ultrabasic rocks is usually connected with chromite and magnetite, though Cr-rich chlorites (containing up to 2% Cr₂O₃) were also reported. In Lower Silesian serpentinites studied the bimodal frequency distribution of chromium is shown by different slopes of straight lines corresponding to the two populations. Their computed means are 1570 and 2320 ppm. These data are close to those reported by Bakun-Czubarow (1966) for Bielice serpentinites and by Kubicz (1966) for ultrabasites of Grochowa.

Manganese

This transition trace element also concentrates mainly in accessory chromite and magnetite (Labotka and Albee 1979). In the analyzed serpentinites Mn shows a 3-modal normal cumulative frequency distribution. The mean values for 2nd and 3rd population (750 and 1330 ppm) are higher than the average Mn contents in Bielice serpentinites (Bakun-Czubarow 1966 — 457 ppm) and the values (480 and 540 ppm) reported by Zeissink (1971) for nonweathered serpentinites from laterites of Greenvale and Rockhampton, Australia.

Nickel

This characteristic trace element of ultramafic rocks displays unimodal normal cumulative frequency distribution and mean content 3200 ppm. This value is a little higher than the average Ni content in Bielice ultrabasic rocks (2607 ppm — Bakun-Czubarow 1966) while Kubicz's (1966) data for serpentinites of Grochowa—

Characteristics of frequency distribution of some

Element Frequency distribution type, modality	Number of samples	Number of data above detection limit
Si normal, 1-modal	11	11
Ca normal, 3-modal		
1) 260—710 ppm	9	9
2) 1880—3450 ppm	7	7
3) 7300—11900 ppm	9	9
Fe normal, 2-modal		
1) 3.6—6.9%	20	20
2) 8.3—11.3%	6	6
Rb normal, 1-modal ¹	28	22
Sr normal, 2-modal		
1) <2.7—22 ¹	23	17
2) 22—23 ³	4	4
Ti normal, 1-modal ²	23	21
Cr normal, 2-modal		
1) 830—1980 ppm	13	13
2) 2110—2620 ppm	12	12
Mn normal, 3-modal		
1) 51—260 ppm ³	3	3
2) 560—870 ppm	10	10
3) 1070—1940 ppm	13	13
Ni normal, 1-modal	26	26
Zn lognormal, 1-modal	27	27
Pb ⁵ normal, 2-modal		
1) <1.7—6.1 ppm ¹	14	9
2) 8.5—9.4 ppm ²	5	5
Y ³	26	7
Zr lognormal, 1-modal (E < 0) ⁴	28	13
S lognormal, 1-modal ¹	26	22
Cl lognormal, 1-modal ¹	26	18
Br normal, 2-modal? ³	28	11

¹ Not well defined due to high detection limit.

² Result for one sample from Jordanów (710) ppm has been excluded.

³ Insufficient amount of data.

elements in serpentinites from Lower Silesia

Table 3

Mean value: arithmetic mean \bar{x} (geometric mean \tilde{x}) [ppm]	Standard deviation $S_{\bar{x}}$ ($S_{1\pm x}$) *Range R [ppm]	Variation coefficient $V_{\bar{x}}$ ($V_{1\pm x}$) [%]
18,2%	0,7%	3,8
460	50	11
2600	200	7,7
9100	450	4,9
5,4%	0,2%	3,1
9,5%	0,5%	5,1
13,8	1,8	13
10,4	2,5	25
22,4		
106	10	9,4
1570	100	6,4
2320	50	2,1
150	51—260*	
750	30	4,0
1330	70	5,3
3200	150	4,7
(78)	(0,34)	(~ 100)
2,5	<1,7—6,1*	
8,9	8,5—9,4*	
	<3,3—26,4*	
(3,3)	<4—40*	~ 150
(460)	(0,38)	(~ 100)
(120)	(0,49)	(~ 150)
	<1,2—9,7*	

⁴ Negative excess (too flat frequency distribution curve).

⁵ Much higher 6 results as evident geochemical anomalies rejected.

Brasowice massif are distinctly lower, except for strongly altered rocks. It should be, however, mentioned that in the former case the samples were analyzed using the spectrochemical method and in the latter by means of classical chemical procedure, without the use of international analytical standards.

Zinc

This rather chalcophilic, but in these rocks distinctly lithophilic, element, connected crystallochemically with Fe^{2+} in chromites and magnetites, displays unimodal lognormal distribution. Its average content (geometric mean) in these rocks amounts to 78 ppm, approximately corresponding to the clark value of Wedepohl (56 ppm). Much higher Zn concentrations were reported from chromite deposit-bearing serpentinites of Maryland, Pennsylvania, USA — 200 to 5000 ppm (Pearre and Heyl 1960).

Lead

This element shows a bimodal normal frequency distribution. Arithmetic means for these populations are 2.5 and 8.9 ppm. Very similar data were reported for two fresh serpentinites from laterite profiles Greenvale and Rockhampton, Australia — 6 and 9 ppm (Zeissink 1971).

Yttrium and zirconium

These two typically incompatible elements occur in ultrabasic rocks in fairly low amounts. The clark value for yttrium is 2.3 ppm (Polański and Smulikowski 1969) and that for zirconium ranges from 30 to 45 ppm (Turekian and Wedepohl 1961). Because of a comparatively high detection limit for Y (3.3 ppm), establishing the presence of this element with the use of the PIXE method was possible only for 7 out of 26 samples and therefore these data could not be evaluated. A similar detection limit for Zr (4 ppm) allowed us to determine the content of this element in more than half of the samples studied. Its frequency distribution is unimodal and lognormal, showing negative excess (a too flat frequency distribution curve when compared with Gaussian one). Geometric mean of this truncated distribution amounts to 3.3 ppm.

Sulphur

The frequency distribution of this element in serpentinites of the region studied is unimodal and lognormal with geometric mean 460 ppm, which is slightly more than the clark values (100–300 ppm) after Turekian and Wedepohl (1961) for ultrabasic rocks.

Chlorine and bromine

These two highly electronegative elements are supposed to enter ultrabasic bodies during serpentinization. A positive correlation between Cl contents and degree of alteration of ultrabasites has been observed (Stueber *et al.* 1968). Microprobe analyses have shown that chlorine concentrates in serpentine veins (0.2–0.8 wt %), where brucite can be its parent mineral (Rucklidge 1972).

Chlorine was detected, using the PIXE method, in the majority of analyzed samples, showing in these rocks unimodal, lognormal frequency distribution with geometric mean 120 ppm which slightly exceeds the clark value for ultrabasic rocks after Turekian and Wedepohl (1961), amounting to 85 ppm.

The presence of bromine was established, using the method applied, in 11 out of 28 analyzed samples. Its frequency distribution is bimodal and normal but the

amount of data in both populations is insufficient to calculate the mean values. Since the detection limit in the PIXE method for Br amounts to 1.2 ppm, the contents of this element in Lower Silesian serpentinites slightly exceeds the clark value proposed by Turekian and Wedepohl (1961) i.e. 0.5–1 ppm.

Some trace elements were detected, using PIXE method, only in some of the rock samples analyzed.

Distinctly anomalous copper contents were established in two serpentinite samples of Grochowa (75 and 320 ppm) which considerably exceed average clark value of this element for ultrabasic rocks as proposed by Turekian and Wedepohl (10–20 ppm). This anomaly is consistent with a recently discovered occurrence of native copper in Grochowa ultrabasic body (Gunia P., in press).

In two samples of Grochowa and one of Nasławice (Gogołów—Jordanów ultrabasic massif) some enrichment in selenium was found, slightly exceeding the detection limit of this element using the PIXE method (1.5 ppm). The data obtained amounted to 1.6, 1.7 and 2.3 ppm Se, which considerably exceeds the average content of this element in basic and ultrabasic rocks (0.13 ppm) as proposed by Sindeeva (1964).

Only one sample of altered serpentinite from Jordanów contained a distinctly anomalous amount of gallium (46 ppm) whilst in all the other serpentinites analyzed the contents of this element were lower than its detection limit (4 ppm). It should be noted that Waleńczak and Pendias (1958) determined gallium spectrochemically in the serpentinites of Wolibórz near Nowa Ruda (7.5 ppm) and of Grochowa (2 ppm). The average content of Ga in ultrabasic rocks is, after Turekian and Wedepohl, 1.5 ppm.

Similarly, only one sample of slightly altered serpentinite of Grochowa was found to contain an anomalously high amount of niobium (17 ppm) whilst the detection limit of this element, using the applied PIXE method, was 4 ppm. It should be remembered that, after Turekian and Wedepohl (1961), an average niobium content in ultrabasic rocks was assumed to be 16 ppm but numerous recent determinations of this element with the help of modern instrumental methods have shown that its content is by one order of magnitude lower and amounts to 1.5 ppm for ultramafic rocks of the upper mantle origin (Wedepohl 1969). This improved value is consistent with our results when the detection limit for niobium taken is 4.5 ppm.

CONCLUSIONS

1. Proton-induced X-ray emission makes possible simultaneous determinations of numerous major and trace elements in serpentinites. Among the obvious advantages of this method are relatively low detection limits for some petrogenetically important trace elements, as well as simple and rapid preparation of so called "thick targets", whose application ensures a sufficient accuracy of the estimation of those elements. Only in the case of Cu and Zn some disturbances were observed due to the attenuation of their X-rays by iron.

2. The data obtained for some elements (Rb, Sr, Y, Zr, Pb, Br) gave the first geochemical findings on their abundance in Lower Silesian serpentinites and contribute to the knowledge of geochemistry of ultrabasic rocks.

3. Simplified statistical evaluation of data have shown that some elements (Ca, Fe, Sr, Cr, Mn and Pb) display 2- or even 3-modal frequency distributions but only in very few cases this phenomenon is connected with a localization or degree of alteration of analyzed serpentinites. This refers to usually lower Ca and Mn contents in serpentinites of the Jordanów—Nasławice region and of Bystrzyca Górna and to anomalously high Pb abundances in some more altered ultrabasic rocks.

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ZASTOSOWANIE METODY PIXE W WIELOPIERWIASTKOWEJ ANALIZIE SKAŁ SERPENTYNITOWYCH Z DOLNEGO ŚLĄSKA (POLSKA)

Streszczenie

Metoda wzbudzenia charakterystycznego promieniowania X przy pomocy protonów (PIXE) została zastosowana w wielopierwiastkowej analizie wybranych serpentynitów dolnośląskich. Oznaczono pierwiastki główne i śladowe o liczbach atomowych od 14 (Si) do 41 (Nb), a ponadto Pb. Dla pewnych pierwiastków (Rb, Sr, Y, Zr, Pb, Br) uzyskane wyniki są pierwszą informacją na temat ich zawartości w serpentynitach dolnośląskich. Otrzymane zbiory wyników opracowano statystycznie stosując uproszczoną metodę graficzną. W kilku przypadkach stwierdzono 2 lub 3-modalne rozkłady częstości (dla Ca, Fe, Sr, Cr, Mn i Pb). Podziały na populacje nie są jednak na ogół związane ani z różnym stopniem zserpentynizowania skał ani z lokalizacją.

OBJAŚNIENIA FIGUR

Fig. 1. Krzywa wydajności dla linii K_{α} ($Z \geq 26$)

Detektor osłonięty filtrem z Al o masie powierzchniowej równej 45 mg/cm^2 . Liczba rozproszonych protonów równa $2 \cdot 10^6$. R — wielowymiarowy współczynnik korelacji. Przedział ufności obliczono dla $1-\alpha=0,95$

Fig. 2. Krzywa wydajności dla linii K_{α} ($Z \leq 26$)

Detektor osłonięty filtrem z Al o masie powierzchniowej równej 18 mg/cm^2 , z otworem w środku. Liczba rozproszonych protonów równa $2 \cdot 10^4$. R — wielowymiarowy współczynnik korelacji. Przedział ufności obliczono dla $1-\alpha=0,95$

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ПРИМЕНЕНИЕ МЕТОДА PIXE В МНОГОЭЛЕМЕНТНОМ АНАЛИЗЕ СЕРПЕНТИНИТОВЫХ ПОРОД ИЗ НИЖНЕЙ СИЛЕЗИИ (ПОЛЬША)

Резюме

Протонный метод возбуждения характерного X-излучения (PIXE) был применен в многоэлементном анализе некоторых нижнесилезских serpentinitов. Определялись главные элементы и элементы-примеси с атомными

числами от 14 (Si) до 41 (Nb), а кроме того Pb. Полученные результаты впервые характеризуют содержание некоторых элементов (Rb, Sr, Y, Zr, Pb, Cr) в нижнесилезских серпентинитах. Полученные множества результатов обработано статистически, применяя упрощенный графический метод. В нескольких случаях обнаружено 2 либо 3-модальное распределение частот (для Ca, Fe, Sr, Cr, Mn и Pb). Однако выделенные совокупности вообще не связаны ни с различной степенью серпентинизации пород, ни с их местоположением.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Кривая эффективности для линии $K_a(Z \geq 26)$

Детектор закрыт Al фильтром с площадью массой 45 мг/см². Количество рассеянных протонов равно $2 \cdot 10^6$. R — многомерный коэффициент корреляции. Доверительный предел рассчитан для $1-\alpha = 0,95$

Фиг. 2. Кривая эффективности для линии $K_a(Z \leq 26)$

Детектор закрыт Al фильтром с площадью массой равной 18 мг/см² и со щелью по середине. Количество рассеянных протонов равно $2 \cdot 10^4$. R — многомерный коэффициент корреляции. Доверительный предел рассчитан для $1-\alpha = 0,95$