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SPECTROCHEMICAL DETERMINATION OF RARE EARTH ELEMENTS IN SOME MINERALS FROM THE WESTERN CARPATHIANS AND THEIR TYPOMORPHIC EVALUATION

(Tabs. 8)

Abstract: Spectrochemical method of rare earth elements (REE) determination in some minerals after their transformation in insoluble fluorides was worked out. REE in titanites, apatites, amphibolites, epidotites, garnets, scheelites and tourmalines were determined by the above method. The determined REE contents and their distribution enabled to classify the studied scheelites and apatites from the localities of the Western Carpathians in individual genetic types.

Резюме: Был разработан спектрохимический метод определения редкоземельных элементов (р.з.э.) в некоторых минералах после их превращения в нерастворимые флюориды. Этим методом были определены р.з.э. в титанитах, апатитах, амфиболитах, эпидотитах, гранатах, шеелитах и турмалинах. Установленные содержания и распределение р.з.э. позволили присоединить исследованные шеелиты и апатиты местонахождений Западных Карпат к отдельным генетическим типам.

Introduction

Determination of REE contents, as well as determination of their distribution in geological materials are important from the viewpoint of ability of these materials to concentrate REE. This can prove not only enrichment of these elements, but it can serve also for survey of other elements, such as P and W.

Owing to isomorphism of REE with Ca, many minerals containing Ca bear themselves as natural REE concentrators. Among silicates of igneous rocks it is primarily titanite (sphene) which when enriched in REE forms even separate species, e.g. yttrotitanite or keilhaunite containing up to 10—12 % REE. REE are concentrated also in garnets and minerals from the epidote group, especially in allanite.

In addition to silicates, also phosphates which are able to form their own REE minerals, such as monazite or xenotime, have the similar properties. In the case the original system is rich enough in Ca, apatite with high REE content up to 5 % can be formed.

Distinct isomorphism of rare earths with Ca is found in scheelite too. In such case REE content may be used for determination of typomorphic properties and, thus, helps to explain genetic and physical-chemical conditions of its crystallization which affect purity, colour and morphology of resulting

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product. All above-mentioned properties may be used as survey features in evaluation of possibilities of W occurrence.

For the mentioned geochemical considerations a quite rapid and simple analytical method of REE determination in a large number of given monomineral fractions separated from various geological materials is required.

Neutron activation analysis, quite hardly attainable in our conditions and atomic spectroscopy methods summarized by Plško (1986) are used in practice for REE determination.

Spectrochemical analysis (Kubová et al., 1979) was used for solution of the problem under question in our laboratory.

In the case of REE analysis in the above-mentioned minerals containing concentration reaching even several %, a preconcentration is not necessary. Chemical treatment of original samples is proposed more or less for separation of analyzed elements from the original minerals of various macrocomposition (silicates, phosphates, titanites, tungstates) and for their transformation in a common matrix regardless their original macrocomposition. This enables to analyze all samples using the only method. The method in which the samples were transformed in fluorides by hydrofluoric acid was proved the best. Owing to the lowest solubility of REE fluorides, in comparison with their other salts, quantitative separation of the analyzed elements precipitated together practically only with Ca contained in the original sample will be ensured by this method. Thus, the analysis of minerals of various composition will be reduced to REE determination in CaF_2 matrix.

Experimental

The samples were decomposed as follows: 0.5—1 g of sample is treated with HF in the closed PTFE vessel at 180 °C for 2—3 hours for titanites and apatites and for 4—6 hours for tourmalines and epidotes. Garnets are dissolved in aqua regia for 8 hours and the content is dried. Residue is transformed in fluorides by HF in closed vessels at the same temperature. Scheelites are dissolved in HCl in closed vessels for 1—2 hours. Precipitated tungstic acid is separated by filtration and fluorides are obtained by treatment of HF with filtrate in closed pressure vessel. REE fluorides in CaF_2 matrix obtained from each kind of original sample by the described procedures are filtrated, dried at 105—110 °C and weighed in order to establish their enrichment factor. Polyethylene vessels are used.

Various ways of excitation are used for spectrochemical determination of REE, e.g. excitation from solution using plasma burner or in Grimm's glow discharge lamp. Distillation with carrier was applied too. Excitation in direct or alternating current arc is the most used.

Great complexity of REE optical emission spectra containing a large number of very weak spectral lines forms a serious obstacle in general application of spectrochemical method to REE analysis.

Present determination of all REE in geological materials, especially in some minerals representing their collectors (concentrators) puts heavy demands on spectral lines choice, particularly from the point of view of their coincidences.

Table 1

Wavelengths of used spectral lines in nm

Element	wavelength (nm)	element	wavelength (nm)
Sc I	391.181	Gd II	342.247
Y II	437.494	Tb II	332.440
La II	433.374	Dy I	421.172
Ce II	395.254	Ho II	345.600
Pr II	390.844	Er II	390.631
Nd II	430.358	Tm II	313.126
Sm II	388.529	Yb I	398.799
Eu II	420.505	Lu I	328.174

Table 2

Experimental conditions

Spectrograph	PGS—2
Illumination	three-lens with intermediate stop
Spectral range	270—440 nm
Intermediate diaphragm	3.2 mm
Slit width	0.012 mm
Sample bearing electrode	SU—308
Counter electrode	SU—359
Electrode gap	4 mm
Excitation	A. C. arc
Current	6 A
Exposure time	90 s
Sample treatment	sample: (graphite powder with 0.3 % Pd) = 1 : 1

Differences in matrix were eliminated by the above-mentioned method, i.e. by the transformation in fluorides by HF treatment of the samples. REE are separated in this way and, at the same time, enriched in a uniform CaF_2 matrix. Therefore, attention was paid to the choice of spectral lines displaying as low as possible coincidences at simultaneous spectrochemical determination of all natural REE in CaF_2 matrix.

In detailed study of the problem of possible interferences in the used spectral range, intensive spectral lines with the lowest number of interferences were chosen. As far as final choice of lines is concerned, it should be pointed out that Pr line is obviously interfered by Ce content over 0.1 %, La line — over 0.3 % Pr and Gd line by Dy content over 0.3 %. All other lines do not show any interferences with other elements present in concentrations up to 1 %, nor with Ca which is present in a high concentration.

Wavelengths of the chosen spectral lines are presented in Tab. 1.

Experimental conditions of determination are given in Tab. 2.

Table 3

Standard deviation values ($\bar{s}_r$ %) for determined elements

	$\bar{s}_r$ %		$\bar{s}_r$ %		$\bar{s}_r$ %
Sc	10.5	Nd	9.3	Ho	7.4
Y	6.0	Sm	17.3	Er	12.0
La	9.4	Eu	17.5	Tm	12.4
Ce	8.9	Gd	8.7	Yb	11.2
Pr	8.8	Tb	12.2	Lu	10.0
		Dy	16.8		

Table 4

Concentration ranges of REE determination

	Δc(ppm)	c*		Δc(ppm)	c*
Sc	20—10 000	2	Gd	30—10 000	6
Y	60—20 000	25	Tb	30—10 000	19
La	100—20 000	35	Dy	30—10 000	6
Ce	30—20 000	16	Ho	30—10 000	8
Pr	30—20 000	12	Er	30—10 000	6
Nd	100—20 000	30	Tm	30—10 000	6
Sm	100—10 000	46	Yb	20—10 000	6
Eu	30—10 000	5	Lu	30—10 000	6

Explanatary notes: c* — the lowest concentrations determined in real samples accounting the preconcentration factor.

Table 5

Verification of accuracy of the results

Element	theor. value μg/g	exper. value μg/g
La	300	281
	3 000	2 535
Ce	300	286
	3 000	3 069
Pr	300	250
	3 000	3 396
Tb	3 000	2 829
Dy	300	314
Er	300	297
Tm	3 000	3 062
Yb	300	284
Lu	3 000	3 048

Overwhelming part of the studied spectral range with presence of the most sensitive REE spectral lines is overlapped by intensive cyanogen bands. In order to repress them, CO_2 protective atmosphere in Schöntag's quartz cell was used. In spite of this, when determining Dy and Eu, background of the used spectral lines had to be corrected on residual CN band components and the spectral Nd line — on the influence of Ca content using the method described by Plško (1987).

Precision of the described method characterized by standard deviation of geometric average $\overline{S_r}$ ($^0/_0$) from 2 parallel measurements performed on each sample is given in Tab. 3.

Analyzable range of REE concentrations is listed in Tab. 4.

Accuracy of the method was checked by complete analysis of model samples of known composition, including the chemical procedure. It has been established that preconcentration does not affect the result obtained by synthetic calibration standards in a considerable extent.

Verification of accuracy was carried out also by analysis of a mixture of REE oxides with declared content (SPEX, Industries, INC, U.S.A.). Results of determination of the selected elements are listed in Tab. 5.

Results and discussion

45 monomineral fractions of scheelites were analyzed. Scheelites from the following genetic types are represented in the analyzed set:

a) veiny (v), (Sb-W, Sn-W, Au-W, W, W-Mo associations),
b) strata bound and scheelites from migmatites (m),
c) skarn (s).

Average values of the obtained results are presented in Tab. 6. The highest concentrations of Y, light REE (LREE — Ce, Pr, Nd, Sm, Eu, Gd), heavy REE (HREE — Tb, Dy, Ho, Er, Tm, Yb, Lu,) in scheelites from the veiny types are evident from the table. Lower contents are in scheelites bound to stratified types of mineralization and to scheelites in migmatites. The lowest contents are in scheelites from skarns. The presented results verify and make more accurate those obtained by photoluminiscent and X-ray spectral analysis (Nauchitel et al., 1977).

REE contents in scheelites from some of the localities of the Western Carpathians are listed in Tab. 7.

REE contents in scheelites from the first three localities are close to m values. REE content in scheelites from Sb deposit Dúbrava is typical of the veiny types.

REE distribution in scheelites depends probably on genetic type of deposit where scheelite occurs. This can be used in classification of the scheelites found during heavy panning. Such testing based on typochemical properties of scheelite should enable to distinguish perspective anomalies from the less perspective ones.

Similarly as in scheelite, rare earths are concentrated also in apatite. They may be used in elucidation of its genesis. For the above-mentioned reasons, REE content has been analyzed so far in monomineral fractions of accessory apatites from granitoids of the Veporic crystalline complex and in monomi-

Table 6

REE contents (in ppm) in scheelites of various genetic types (veiny — v, strata bound — m, skarn — s)

	n	Y	LREE	HREE	REE	(REE + Y)
v	7	360	1 029	254	1 283	1 645
m	8	88	313	85	399	487
s	2	15	105	25	131	146

n — number of samples

Table 7

REE contents (in ppm) in scheelites from some Western Carpathians localities

type	locality	Y	LREE	HREE	REE	(REE + Y)
m	Klenovec	50	265	22	287	337
		98	208	149	357	455
m	Kokava n. R.	278	290	116	406	684
m	Jasenie	986	58	51	109	1 095
		532	151	44	195	727
		150	367	45	412	562
v	Dúbrava	380	917	448	1 365	1 745

Table 8

REE contents (in ppm) in apatites from granitoids (a), carbonatites (b) and carbonates from carbonatites (c)

type	n	Y	LREE	HREE	REE	(REE + Y)
a	2	1 418	1 007	377	1 384	2 802
b	8	296	2 624	6	2 630	2 926
c	9	103	707	118	825	928

n — number of samples

neral fractions of apatites from the deposit Evate (Mozambique) of carbonatite type. Results are given in Tab. 8.

Results presented in Tab. 8 display characteristic representation of REE in apatites from granitoids and carbonatites. LREE/HREE ratio in apatites from granitoids is 2.7, in apatites from carbonatites it is quite high — 437 what corresponds with Marchenko's et al. (1975) data. In the case of the minerals separated from carbonatites, LREE/HREE ratio is considerably higher in apatites than in carbonates — 6. This indicates tendency of REE to be concentrated in the final mineralization phases.

Conclusions

The proposed spectrochemical method of simultaneous determination of REE in minerals enables to obtain the results applicable in determination of their typomorphic properties. This can be applied with advantage in determination of genetic characteristics, as well as in survey and prognosis as shown on the example of scheelites and apatites.

It has been established that in the studied set of scheelites where three genetic types are represented there are significant differences in REE contents and distribution. The highest contents (1640 ppm in average) are in the veiny types which comprise scheelite from the analyzed Carpathian localities. Average REE contents of scheelites from the strata bound and migmatite types are about 500 ppm. From the studied localities of the Western Carpathians, scheelites from the localities Klenovec, Kokava nad Rimavicou and Jasenie belong to this type. The lowest REE contents (ca. 150 ppm) have been established in scheelites of the skarn type. Scheelite occurs rarely in skarn deposits of the Western Carpathians. The above-mentioned value was therefore obtained from the samples of other regions.

Similarly as in scheelite, REE content may be used for testing of the genetic type also in apatite. It is important mainly in heavy panning where testing of isolated apatite grains allows to indicate character of its primary source.

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