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TRACE ELEMENT ABUNDANCES IN RUTILE  
FROM SELECT SUDETIC ECLOGITES AND RELATED ROCKS

**Abstract:** Rutile was separated from eclogites of the Orlica-Śnieżnik Dome (OSD) in the West Sudetes and from eclogites outcropping in the Kamieniec Ząbkowicki metamorphic complex in the Fore-Sudetic Block (FSB). In this rutile, contents of high field strength (Zr, Nb) 3d type transition (Cr, Fe) and other trace elements (Al, Si, Ca) were determined by means of electron microprobe. The OSD rutile is distinctly richer in Cr and, to a lower degree, in Zr but significantly poorer in Nb than FSB rutile. A new Cr-Zr-Nb discrimination diagram for rutile provenance studies has been constructed and tentatively verified. In this diagram, separate fields for Cr-rich rutile from Mg-Al-Cr type OSD eclogites and for Nb-rich rutile from Fe-Ti type FSB eclogites were distinguished.

**Keywords:** niobian rutile, HFSE, 3d type trace transition elements, Cr-Zr-Nb discrimination diagram, rutile provenance study

INTRODUCTION

As the results of recent investigations have shown the feasibility of trace element analysis by electron microprobe (EMP) in geological materials with still growing precision and decreasing detection limits (Brenan et al. 1994; Fialin et al. 1999; Zack et al. 2002; Okrusch et al. 2003) the study of chosen trace element contents in rutile from select Sudetic eclogites has been undertaken. The aim of the study was to estimate a particular trace element preference for rutile and to verify usefulness of select trace element contents for rutile provenance study.

GEOLOGICAL SETTING

Two types of the Sudetic eclogites have been selected for the trace element study in rutile. To the first type belong Mg-Al-Cr eclogites, that underwent UHP metamorphic episode and display the following mineral assemblage: Omp–Grt–Qtz–Rt–Amp–Ky–Phe (Bakun-Czubarow, Kusy 2001). These rocks (M1) outcrop within orthogneisses of the Międzygórze tectonic unit in the eastern part of the core of Orlica-Śnieżnik Dome (OSD). The second type is represented by Fe-Ti eclogites with the following peak metamorphism assemblage: Omp–Grt–Gln–Hbl–Qtz–Zo–Ilm–Rt–Pg–Phe–Ap–Zrn (Bakun-Czubarow 1998). These rocks (KZ2 and

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KZ3) outcrop within mica schists of Kamieniec Ząbkowicki metamorphic complex in the Fore-Sudetic Block (FSB). For comparative investigations the following rutile-bearing rocks were included: 1) microdiamond-bearing gneiss (Erz) from Seidenbach in Erzgebirge, Bohemian Massif (Massonne 2001), 2) kimberlite (Yu2) from Yuzhnaya diatreme in Azov Block of the Ukrainian Shield (Bakun-Czubarow et al. 2001) and 3) UHP eclogite of type A (Dt2) from Datuan in Sulu province, China.

#### METHODS OF INVESTIGATION

From the selected eclogite samples two size fractions of rutile (250-95  $\mu\text{m}$  and <95  $\mu\text{m}$ ) were separated in the Institute of Geology, Academy of Sciences of the Czech Republic. Both fractions were mounted in epoxy on the base glass, then polished with diamond paste.

Microprobe analyses of rutile were performed in the Inter-Institution Laboratory of Microanalyses of Minerals and Synthetic Substances located at the Warsaw University, on a CAMECA SX 100 electron microprobe equipped with three WDS offering combinations of LIF, PET and TAP crystal monochromators. For the trace element measurements in rutile the electron beam with energy of 20 keV, with 150 nA intensity and of 5  $\mu\text{m}$  diameter as well as long counting times were chosen (Tab. 1). For trace element determinations the regular CAMECA software of TR-type was used. Up to 30 trace element point analyses were performed for every fraction of rutile separates.

Whole rocks were analyzed at the Activation Laboratories Ltd, Canada, with the assistance of the GEOANALIZA Enterprise from Kraków. Major and minor elements were determined by ICP AES method, while the trace elements – by ICP MS one.

Table 1. Conditions of electron microprobe analysis of trace element abundances in rutile.

element	X-ray line	crystal	count time	calibration standard	detection limit
Al	K $\alpha$	TAP	80 s	orthoclase	15 ppm
Si	K $\alpha$	TAP	80 s	diopside	12 ppm
Ca	K $\alpha$	PET	60 s	diopside	25 ppm
Cr	K $\alpha$	PET	60 s	Cr <sub>2</sub> O <sub>3</sub>	50 ppm
Fe	K $\alpha$	LIF	160 s	Fe <sub>2</sub> O <sub>3</sub>	40 ppm
Zr	La	PET	120 s	zircon	65 ppm
Nb	La	PET	120 s	LiNbO <sub>3</sub>	90 ppm

#### RESULTS

Rutile grains from different samples show large variations (1-2 orders of magnitude) for compatible elements Cr (100–6340 ppm), Nb (100–4700 ppm), Zr (70–1580 ppm), and for incompatible ones – Ca (<25–14,000 ppm), Si (<12–6500 ppm), Al (<12–600 ppm) as well as smaller variations (8 times) for Fe (500–4000 ppm).

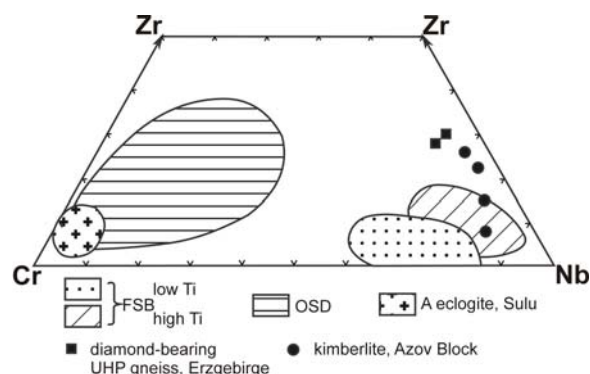


Fig. 1. Cr-Zr-Nb discrimination diagram for rutile from the Sudetic eclogites and related rocks.

Rutile grains from Mg-Al-Cr type M1 eclogite and from Dt2 rock are distinctly richer in Cr and – to a lower degree – in Zr as well as significantly poorer in Nb than rutile grains from Fe-Ti type KZ2 and KZ3 eclogites. From among the analyzed rutiles those from UHP Erz gneiss and from Yu2 kimberlite are the richest in Zr and Fe, but as to Cr and Nb contents they resemble rutile from Fe-Ti eclogites. As far as trace element contents are concerned, most analyzed rutile grains are homogeneous on single grain scale, and less so between the grains in the same rock sample. Trace element enrichment measured by partition coefficients ( $D_i$ ), being the ratio of  $i$  element content in rutile to its value in the host rock, are diversified. For instance,  $D_{Nb}$  being equally high for M1 and Dt2 rutile ( $D_{Nb} \approx 110$ ) is lower ( $D_{Nb} = 45$ ) for rutile from low  $TiO_2 \leq 2.0$  wt%, KZ2 eclogite and even much lower ( $D_{Nb} = 24$ ) for rutile from high  $TiO_2 \geq 4.0$  wt%, KZ3 eclogite.

Table 2. Trace element atoms per  $10^4$  atoms of Ti in rutile and in the Sudetic host eclogites.

	OSD			FSB					
			M1 wh rock	low Ti			high Ti		
	Rt 1			Rt 2		KZ2 wh rock	Rt 3		KZ3 wh rock
	a	b		a	b		a	b	
Al	3.4	3.9		1.3	4.8		3.4	1.5	
Si	1.8	2.5		1.3	1.5		1.2	1.8	
Ca	0.5	4.8		0.7	9.4		0.1	9.8	
Ti	$10^4$	$10^4$	$10^4$	$10^4$	$10^4$	$10^4$	$10^4$	$10^4$	$10^4$
Cr	20.3	27.4	484.0	8.6	10.6	133.0	2.5	3.1	<7.6
Fe	13.8	22.2		36.4	31.0		23.5	22.5	
Zr	2.6	2.9	84.0	1.2	1.2	172.0	0.9	1.0	57.3
Nb	2.2	2.8	3.2	18.3	19.4	19.6	9.8	9.1	9.5

a– 250-95 $\mu$ m; b– < 95 $\mu$ m

Cr has similar enrichment in rutile from all the studied eclogites ( $D_{Cr} = 4-7$ ), whereas Zr in rutile shows significant differences in relation to the host eclogite: rutile from OSD and Dt2 rocks is distinctly enriched in Zr ( $D_{Zr} = 4.5-14.0$ ) while

rutile from FSB eclogites is depleted ( $D_{Zr} = 0.33 - 0.45$ ). On one hand, the behaviour of Zr in rutile from the Sudetic eclogites confirms the observations made by Zack et al. (2002) on Trescolmen eclogites (Central Alps), where on the basis of HFSE mass balance the following element order of decreasing preference for rutile  $Nb > Ti > Cr > Zr$  has been established. On the other hand, Zr behaviour reflects the differences in mineral parageneses between the OSD and FSB eclogites. In the FSB eclogites to the stable paragenesis belongs also ilmenite, that according to Jang & Naslund (2003) has partition coefficient  $D_{Zr}$  almost one order of magnitude higher than rutile. Trace element contents in rutile and its host rocks were also expressed in atoms per  $10^4$  atoms of Ti (Table 2). In all the investigated rutile separates the fine fraction, as compared to the coarse one, is distinctly enriched in Ca and, to a lower degree, in Cr. The enrichment in Ca may be caused by contamination of rutile with Ca silicate phases. With decreasing *mg* number of eclogites and simultaneous increase of Ti content in the rocks the preference of Cr and Zr for rutile decreases. In all the studied samples Nb shows similar atomic ratios per  $10^4$  Ti atoms in rutile and host rocks, but varying between the rock samples. As the content of Ti in the other eclogitic minerals (except rutile and ilmenite) is negligible, the above mentioned similarity indicates that rutile is the main Nb carrier, controlling Nb contents in whole rocks. Cr shows slight preference for rutile, but this accessory mineral does not control Cr budget in whole rocks. Nevertheless, Cr contents in rutile are positively correlated with the numbers of Cr atoms per  $10^4$  Ti atoms in host rocks, in spite of the differences in the eclogite mineral parageneses. The only exception among the analyzed samples is kimberlite Yu2, in which chromian spinel is present and rutile shows depletion in Cr ( $D_{Cr} = 0.4$ ).

The analyzed trace transition and HFS elements are significant for the rutile provenance study. The Nb vs Cr discrimination diagram suggested by Zack et al. (2002) is not applicable for the Sudetic eclogites, as the rutiles from Fe-Ti eclogites plot there into the field of metapelites. A new Cr-Zr-Nb discrimination diagram for rutile, with distinguished fields of high Cr rutile from Mg-Al-Cr eclogites (M1 and Dt2) and of high Nb, low Zr rutile from Fe-Ti eclogites (KZ2 and KZ3), has been constructed (Fig. 1).

#### CONCLUDING REMARKS

1. Rutile is strongly dominant carrier of Nb in eclogites.
2. Cr shows slight preference for rutile, independent on an eclogite paragenesis.
3. Zr content in eclogitic rutile is strongly dependent upon the presence of stable ilmenite, that shows one order of magnitude higher than rutile preference for Zr.
4. The usefulness of the newly constructed Cr-Zr-Mg discrimination diagram for rutile provenance studies has been tentatively verified.

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