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ZIRCONIUM MINERALIZATION OF YOUNG ALKALINE VOLCANIC ROCKS FROM NORTHERN BOHEMIA

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Abstract: Metasomatized young alkaline volcanic rocks from northern Bohemia contain increased zirconium concentration: ijolites (1246 ppm), pegmatoids (420), and phonolites (2660). Calzirtite (in ijolites and pegmatoids), hainite and its alteration product fluorian eudialyte (in phonolites) are dominant zirconium minerals. The higher Zr content of these rocks resulted from enrichment by postmagmatic low-temperature hydrothermal fluids carrying Na, K, Ca, Al, Fe^{3+}, Si, P, CO_2, F and minor and trace incompatible elements (Sr, Ba, REE, U, Th, Zr, Hf, Ti, Nb, Ta etc.). The influence of fluids is increased in large hypabyssal intrusions (central melilitolite of the Osečná complex) and/or in subvolcanic bodies (phonolite of the Sokol Hill) occurring near regional tectonic zones (Lusatian thrust fault). The accumulation of Zr, REE, U, Th, P, and Ti in basal Cenomanian sediments in the proximity of volcanic intrusions is a common feature and may be explained by the influence of these intrusions on the chemical element redistribution in the sedimentary rocks.

Key words: northern Bohemia, young volcanic rocks, zirconium mineralization.

Introduction

Blumrich's (1983) description of hainite (Na, Ca, Ti, Zr-silicate) from phonolite of the Hradište Hill (Hoher Hain) near Frýdlant iniciated the discussion concerning the bounding of zirconium in young (Neoidic) volcanites of the Bohemian Massif. Hainite, according to him, is a mineral related to rinkite, mosandrite, lavenite, wöhlerite and rosenbuschite. It occurs in two types differing in crystal morphology and optical properties: *1*- acicular crystals in amygdales vugs and bands enriched in aegirine, in places also in the phonolite matrix; Hibsch (1934) introduced the name hainite I for this type; and *2* - thin lobate lamellae in matrix, i.e. hainite II of Hibsch (l.c.). Review of localities of hainite in phonolitic rocks of the České středohoří Mts. was presented by Trenkler (1901), Cornu (1911) and Hibsch (1929). High Zr contents in these rocks, ranging from 960 to 2510 ppm, were reported by Macháček & Shrbený (1970). They determined the approximate chemical composition of a Zr-rich mineral of the phonolite matrix from the type locality of hainite (Hradiště Hill, hainite II) and compared it with similar mineral of phonolites from Olešnice and Rýdeč (České středohoří Mts.). Johan & Čech (1989) investigated the crystal chemistry of hainite I from the type locality using X-ray and electron microprobe methods. Based on the substitution $2 \rightleftarrows Ca\ (Ti, Zr)^{4+} + \square$ they pointed out the similarity of hainite I with götzenite or rosenbuschite, respectively. Slightly increased contents of HREE in ijolites and pegmatoids of the Osečná intrusion are related to zirconium minerals (Pivec et al. 1989). Calzirtite occurs in ijolites and pegmatoids of the Osečná melilitolite body (Ulrych et al. 1990a). A mineral similar to hainite is an accessory phase of phonolites in northern Bohemia (Ulrych et al. 1990b). Kühn (1990) identified three types of hainite by electron microprobe in these phonolites: (1) with Zr, Ti, high Ca and lower Na contents; (2) with Ti, Zr, low Ca and higher Na, REE, Nb contents, and (3) with Zr, Ti, high Mn, Fe, Nb, Na and low Ca contents. A mineral, probably identical with vlasovite, was analyzed by Kühn l.c. in some rims of hainite of the 2nd type. Unfortunately, the fluorine content was not reported in all his chemical analyses. Its amount is supplementary calculated on the stoichiometric base. Fluorine is not considered in the vlasovite chemistry, although the total of all 3 analyses is very low (Σ = 83.5 to 90.0 wt.%).

Zirconium-bearing melanite (ZrO_2 = 1 to 9 wt.%) and perovskite (ZrO_2 = 0.2 wt.%) from melilitolite of the Osečná intrusion represent other zirconium containing minerals (Ulrych et al. 1990a). Kühn (1990) reported Zr in alkali pyroxenes (ZrO_2 = 0.6 to 1.0 wt.%), titanites and REE-bearing minerals (uranmicrolites, rhabdophane and lanthanite) from phonolites of northern Bohemia. All above mentioned occurrences are located in Fig. 1.

Sample description and analytical procedures

The following samples were used for the study of zirconium mineralization: (1) ijolite POL-71 (metasomatized layer in hypabyssal melilitolite intrusion), Osečná; (2) pegmatoids POL-31, 63, 70, the same locality as (1), and (3) phonolite POL-117,

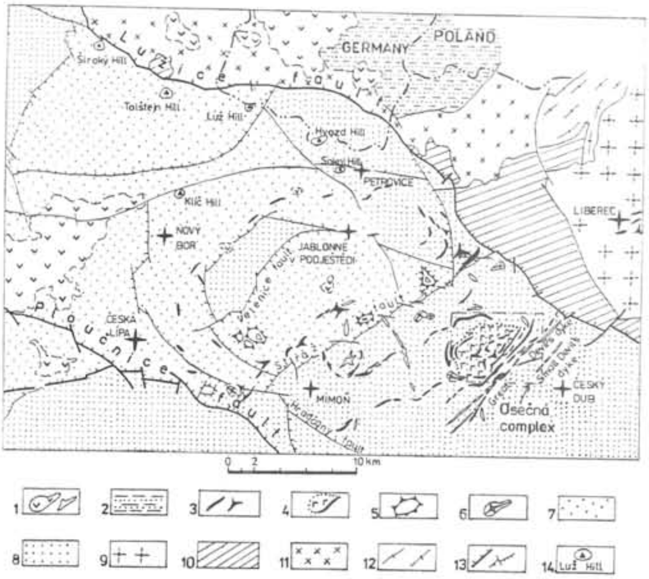

Fig. 1. Geological sketch map of northern Bohemia showing localities of young volcanic rocks with zirconium mineralization.
1 - areas and bodies of Oligocene-Miocene volcanism of the České středohorí Mts. and the Žitava basin; 2 - Miocene sediments of the Žitava basin, 3 - dykes, cone sheets, triplets and volcanic pipes of melilitic and melilite-bearing volcanics; 4 - Osečná melilitolite intrusion; 5 - diatremes of the maar type; 6 diatremes with pipe breccia filling; 7 - Upper Turonian to Coniacian sediments; 8 - Middle Turonian sediments; 9 - granites of the Krkonoše-Jizerský pluton; 110 - Ještěd and Železný Brod crystalline complex; 11 - granitoids of the Lužice pluton; 12 - Jizerské orthogneisses; 13 - important faults (thrust fault - heavy line, fault - thiny line); 14 - phonolite localities with Zr-mineralization.

Klíč Hill, and POL-98, Sokol Hill (both from shallow subvolcanic bodies). Optical determination of Zr-minerals under a petrographic microscope (transmitted light) is difficult due to the small grain size (0.01 to 0.05 *mm*) and the strong alteration of rock matrix. Mineral grains were detected under a microprobe using X-ray area scan in Zr-Lαspectral line. Their shape was studied by back-scattered electron image (BEI) in polished sections (Cam Scan - 4 DV electron microscope).

Chemical analyses were carried out using an electron microprobe JXA-50A with EDAX-711 and Microspec WDX-2A with EDX-analyser Link AN-10 000 for fluorine determination. Experimental conditions for the electron microprobe were as follows: acceleration voltage of 15 or 20 *kV*, beam currents of 30 *nA*, beam diameter of 2 μm and counting time of 30 *sec*. The microprobe operated using the SONDA data-reduction program (Hulínský et al. 1972). Both natural and synthetical standards were applied.

Zirconium minerals

Calzirtite

Calzirtite occurs in the form of subhedral to anhedral, mostly isometric grains, 0.03 to 0.06 *mm* in size, with characteristic cross-section (Fig. 2) and irregular clusters (Fig. 3) in ijolites and pegmatoids of the Osečná melilitolite intrusion (Ulrych et al. 1990a). Crystals are yellowish to brownish in transmitted light, nearly isotropic and without distinct cleavage. Representative analyses of the calzirtite are compiled in Tab. 1. Empirical formula of calzirtite is $(Ca_{1.076}Na_{0.013})_{1.089}Ti(Zr_{2.858}Ti_{0.042}Nb_{0.029}Fe_{0.028}Mg_{0.007}Si_{0.006}Al_{0.005})_{2.972}O_9$. Zirconium distribution in X-ray area scan in Zr-Lα spectral line (of Fig. 2) is given on Fig. 4.

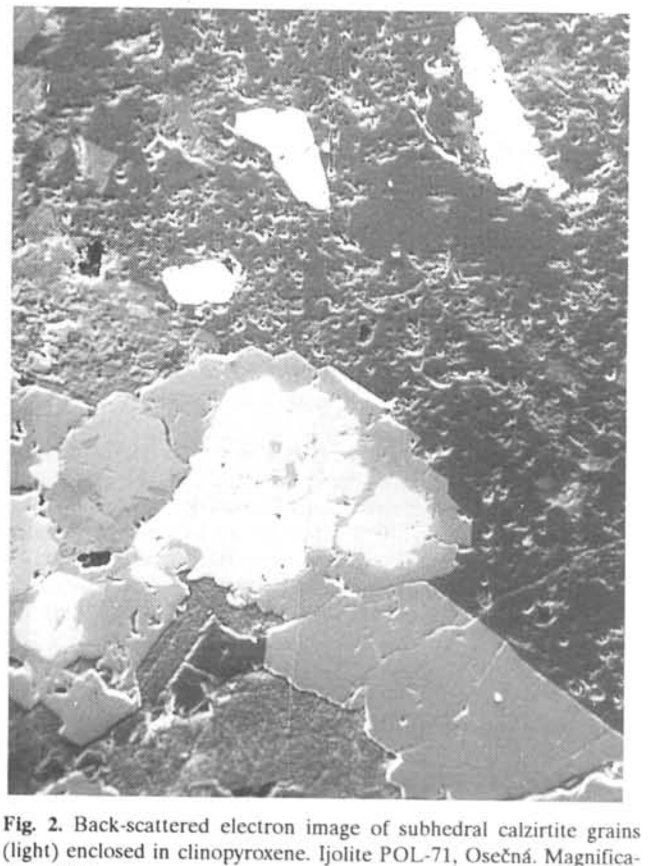

Fig. 2. Back-scattered electron image of subhedral calzirtite grains (light) enclosed in clinopyroxene. Ijolite POL-71, Osečná. Magnification x 200.

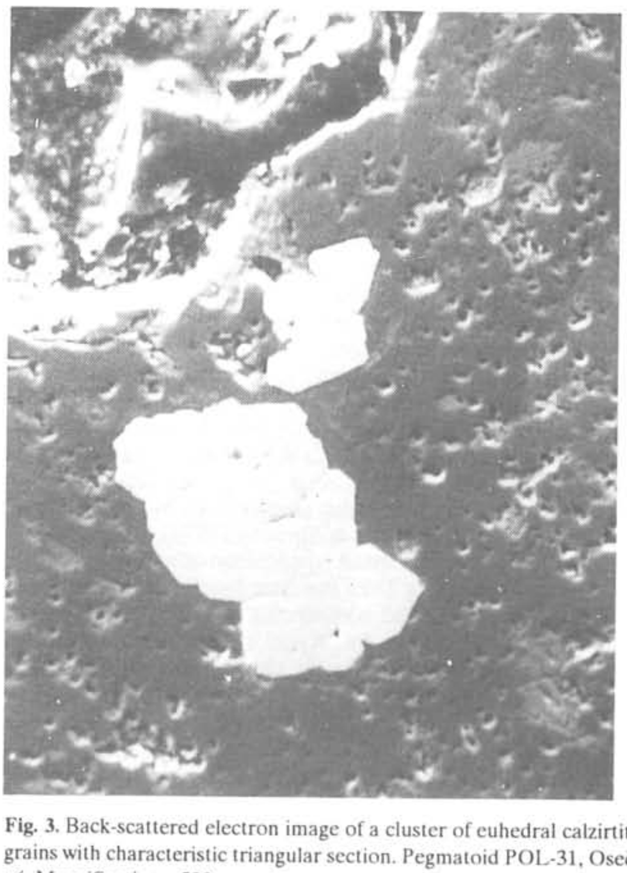

Fig. 3. Back-scattered electron image of a cluster of euhedral calzirtite grains with characteristic triangular section. Pegmatoid POL-31, Osečná. Magnification x 500.

Table 1. Chemical composition of Zr-minerals in young volcanites of northern Bohemia.

	Calzirtite			Hainite		F- Eudialyte	OH- Eudialyte
	1	2	3	4	5	6	7
Nb_2O_5	0.77	1.08	7.86	2.23	1.38	1.66	0.10
Ta_2O_5			0.53		0.22		
SiO_2	0.07			31.71	32.07	51.90	52.23
TiO_2	16.56	15.90	11.17	8.23	8.06	1.65	1.26
ZrO_2	69.95	69.69	66.95	5.66	6.58	12.68	11.73
ThO_2		0.10					
UO_2		0.10					
Al_2O_3	0.05	0.14			0.03	0.79	0.45
Fe_2O_3					1.25	4.19	0.55
La_2O_3			1.90^x	0.98	0.60		4.85^x
Ce_2O_3				1.27	1.01		
FeO	0.40	0.90	1.68	1.29			
MnO			0.18	2.73	2.06	3.32	1.44
MgO	0.06	0.12					0.28
CaO	12.00	11.00	11.51	31.09	32.05	10.42	11.25
SrO							0.43
BaO							1.16
Na_2O	0.08	0.12		7.51	7.46	4.83	2.29
K_2O				0.11		0.24	
F				11.30	12.09	7.10	
Cl						1.82	1.80
H_2O^+							7.93
H_2O^-							1.53
$\sum$				104.11	104.86	100.60	100.37
-O=2(F, Cl)				-4.76	-5.09	-3.40	-0.41
$\sum$	99.94	98.95	101.88	99.35	99.77	97.20	99.96

Explanations: 1 - calzirtite from ijolite: Osečná; 2 - calzirtite from pegmatoid: Osečná; 3 - calzirtite from carbonatite dyke: Brettel, Kaiserstuhl, Germany (Keller et al. 1990); 4 - hainite from phonolite: Klíč Hill; 5 - hainite I (aver. of 14 analyses) from Hradiště (Hoher Hain) Johan & Čech (1989); 6 - fluorian eudialyte from phonolite: Sokol Hill; 7 - hydroeudialyte from Inagline Massif, South Yakutiya, USSR (Chukhrov ed. 1981) x ΣRE_2O_3.

Carbonatite dykes and breccias of Kaiserstuhl Mts., Germany have been mentioned by Keller et al. (1990) as the only host rocks of calzirtite (in association with zirconolite) in the Neoidic alkaline volcanites of central Europe.

Hainite

Hainite II in the Hibsch' s sense (1934) was found in phonolite (Zr = 1308 ppm) of the Klíč Hill near Svor. It fills small cavities in the matrix forming tiny lamellae (up to 0.02 *mm* in size) and belongs to the younger minerals of the rock. Representative chemical analyses are listed in Table 1. According to Kühn's (1990) description it corresponds to hainite of the 2nd type. Empirical formula of the studied hainite is $Na(Na_{0.77}Ca_{0.212}K_{0.017})_{1.000}(Ca_{3.394}Ce_{0.059}La_{0.044})_{4.067}(Ti_{0.753}Zr_{0.336}Mn_{0.281}Fe_{0.131}Nb_{0.123})_{1.624\ 0.376}(Si_{1.928}O_{6.827}F_{O.173})_2 F_4$

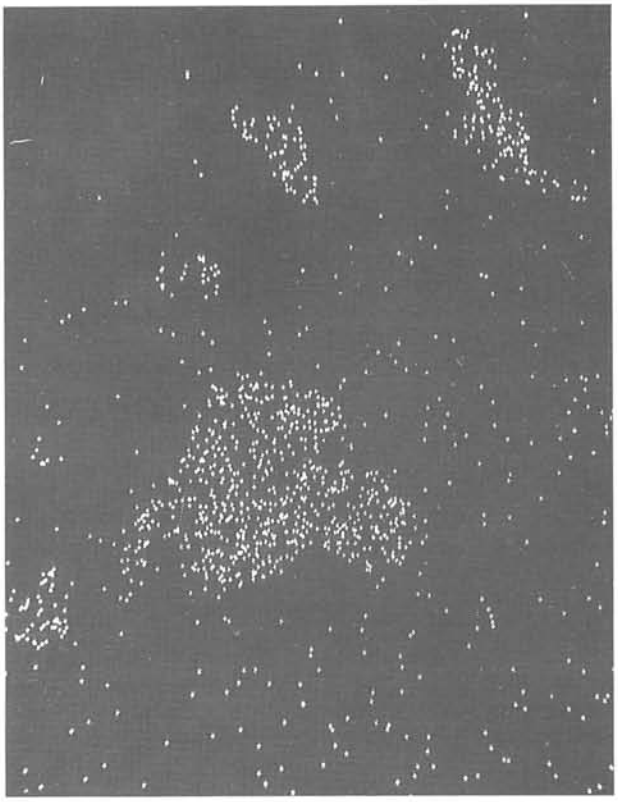

Fig. 4. X-ray area scan in Zr-Lα line of calzirtite (see Fig. 2).

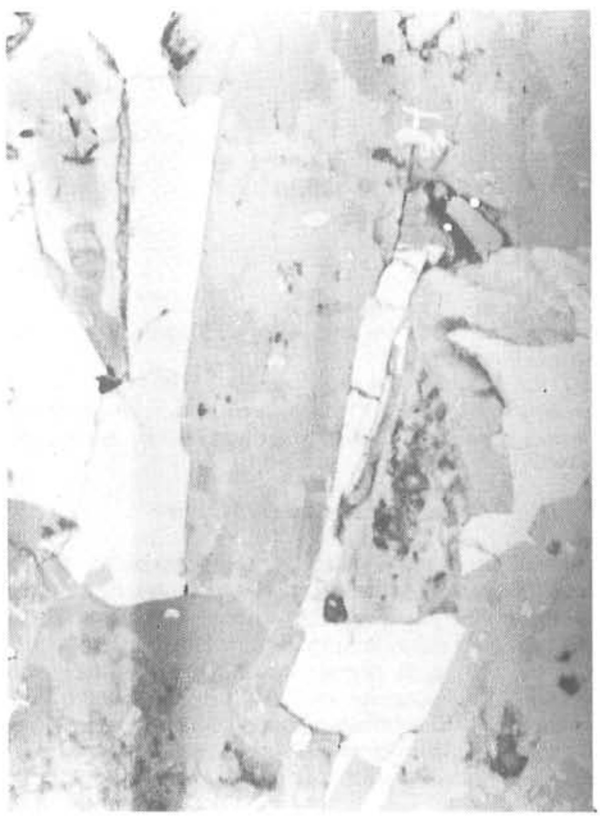

Fig. 5. Back-scattered electron image of subhedral laths (light) of fluorian eudialyte. Phonolite POL-98, Sokol Hill. Scale bar 30 μm.

Fluorian eudialyte

The only zirconium mineral chemically related to fluorian eudialyte was identified in the phonolite of the Sokol Hill near Petrovice. This rock represents phonolite with the highest Zr-enrichment in the Bohemian Massif (Zr = 2650 ppm). The mode of the fluorian eudialyte occurrence is similar to hainite II of the Klíč Hill (Fig. 5), but the colour of eudialyte is deeper brown and it is more frequent (0.5 to 1.0 vol.%).

Chemical analyses of the supposed vlasovite (in spite of absence of fluorine determination) from phonolite of the Luž Hill (Kühn 1990) are similar to fluorian eudialyte analyses. Mentioned vlasovite forms distinct dark rims around hainite II and spots within hainite II grains. Metasomatic origin of hydroeudialyte after eudialyte was described in Chukhrov ed. (1981) and similar process may be accepted for the origin of our fluorian eudialyte by replacement of original hainite II.

High variable fluorine contents (5.6 to 9.1 wt.%) and even impregnations of fluorine around fluorian eudialyte and the shape of trigonal fluorian eudialyte support an assumption of the metasomatic origin after monoclinic hainite II. Empirical formula of the fluorian eudialyte is:

$(Ca_{1.438}Na_{1.207}Fe_{0.406}Mn_{0.351}Al_{0.120}K_{0.039})_{3.561}$
$\square_{2.439}(Zr_{0.799}Ti_{0.160}Nb_{0.096})_{1.053}(Si_{3.344}O_{7.855}F_{1.145})_2(F_{0.603}Cl_{0.397})$.

Götzenite with high REE content (7.8 wt.%) (Czygan 1973; Albrecht 1981) is the only Zr-bearing rock-forming silicate which has been reported in phonolites of the central European alkaline province.

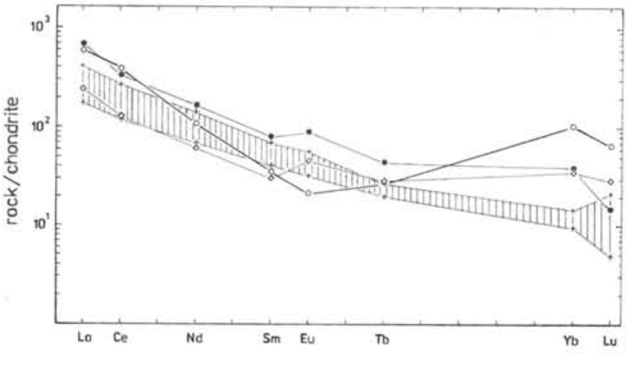

Fig. 6. Chondrite normalized REE pattern of Zr-rich young volcanites of northern Bohemia.
Ijolite POL-71, Osečná - full circle, pegmatoid POL-31, Osečná - square, phonolite POL-98, Sokol Hill - open circle; vertically shaded area with crosses corresponds to melilitic rocks of northern Bohemia (Ulrych 1990b).

Discussion and conlusions

Increased zirconium contents are characteristic for Neoidic, especially metasomatized alkaline volcanites of northern Bohemia. Following average zirconium contents in polzenite-phonolite bimodal association are reported by Ulrych et al. (1990b): melilitolites - 291 ppm, pegmatoid - 391, ijolite - 1246, micromelilitolite - 316, polzenite s.s. - 242, melanephelinite - 225, phonolite - 976 and anomalous phonolite - 1904 ppm. Comparable data for Neoidic volcanites from the same region were reported by Shrbený & Macháček (1973), Shrbený (1989) and Kühn(1990).

Zirconium oxides and silicates of studied alkaline volcanites crystallized from postmagmatic low-temperature hydrothermal phase (Boctor & Yoder 1986). Host rocks are hydrothermally enriched in Na, K, Ca, Al, Fe^{3+}, Si P, CO_2, F and trace incompatible elements as Sr, Ba, REE, U, Th, Zr, Hf, Ti, Nb, Ta, P etc. (Ulrych et al. 1988). Calzirtite in metasomatic products of melilitolite, i.e. ijolite and pegmatoids, belongs to the mineral paragenesis: (Ti, Ba)-bearing-phlogopite II, (F, OH)-bearing titanian andradite, perovskite III, titanomagnetite, apatite III, wollastonite, pectolite, sodalite, carbonates and zeolites (Ulrych et al. 1990a). Hainite and fluorian eudialyte in phonolites is a member of similar association, with aegirinaugite, titanomagnetite, titanite, apatite, REE-minerals, carbonates, analcime and zeolites.

Slightly increased HREE concentrations are especially characteristic for volcanites of the polzenite-phonolite association affected by low-temperature hydrothermal fluids enriched in incompatible elements, including Zr and REE (Fig. 6). According to Jones & Larsen (1985) eudialyte shows generally LREE-enrichment but also has a kinked pattern due to some HREE concentration. Slight enrichment in HREE of studied volcanites is proportional to the contents of Zr-minerals: phonolites (0.5 to 1.0 vol.%) → ijolites >(0.2 vol.%) → pegmatoids (~0.1 vol.%). Fig. 6 summarizes plot of chondrite normalized REE-distribution in studied rocks with Zr mineralization.

The influence of low temperature phase on the concentration of zirconium was more intensive in large hypabyssal intrusion (e.g. central melilitolite intrusion) and/or in shallow subvolcanic bodies (Sokol Hill) occurring in the neighbourhood of regional tectonic faults (Lusatian thrust fault). Tectonic zones served as a feeding channel of the hydrothermal fluids concentrating incompatible elements including Zr. Scharm et al. (1984) documented such concentrations along the Stráž fault (in Fig. 5). Transport of zirconium is in contradiction to their supposed low mobility in natural systems. Majer & Čadek (1979) have demonstrated that higher fluorine concentrations may have favourable influence on the transport of zirconium in low acid solutions. The other ligands e.g. CO_3^{2-}, SO_4^{2-} and Cl. are not important for Zr migration. The favourable role of young volcanites in redistribution of Zr, REE, U, Th, P and Ti mineralization in basal Cenomanian sediments is known (Rutšek 1982; Scharm ed. 1986).

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