GEOLOGICA CARPATHICA, 42, 2, BRATISLAVA, APRIL 1991,

105–110

URANIUM DISTRIBUTION IN VOLCANIC AND VOLCANOCLASTIC ROCKS OF THE NORTHERN GEMERIC PERMIAN

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(Manuscript received March 19, 1990; accepted in revised form September 7, 1990)

Abstract: Uranium fission tracks indicate the development of uranium distribution in barren volcanics and related tuffs. In rhyolites and their tuffs, most uranium occurs in the matrix whereas in andesite and dacite, this element is bound to Ti oxides which were formed largely as a result of ilmenite and magnetite alterations. Variable uranium distribution in the matrix and Ti oxides reflects processes of remobilization and concentration.

Key words: Permian, Northern Gemericum, fission tracks, uranium distribution.

Volcanic and volcanoclastic rocks of the Gemeric Permian host a U-Mo-Cu mineralization. Barren acid volcanics and related tuffs are considerably enriched in these elements forming ore accumulations (Rojkovič, 1969; Rojkovič et al., 1989).

Acid volcanic and volcanoclastic rocks are regarded as a probable source of U in sedimentary uranium deposits (Dahl and Hagmaier, 1974; Galloway, 1978; Lindroos and Smellie, 1979; Kizis and Runnels, 1984; Walker, 1985). Original U contents in these rocks range from 5 to 40 ppm (Stuart et al., 1983). Uranium distribution in fresh volcanic glasses is homogeneous (Zielinski, 1978; Kizis and Runnels 1984; Walker, 1985). Devitrification, subsequent recrystallization of glass and mainly later alterations, such as argillization and silicification, result in uranium redistribution (Zielinski, 1982; Stuart et al., 1983; Walker, 1985). Uranium can easily be leached from rhyolites and volcanoclastics by acid and oxidizing aqueous solutions (Lindroos and Smellie, 1979; Shmariovich and Modnikov, 1988) and is mobile in the uranyl form, particularly in waters rich in carbonates or phosphates and sulphates (Dahl and Hagmaier, 1974; Lindroos and Smellie, 1979; Goodell, 1985).

To illustrate uranium distribution and migration in volcanic and volcanoclastic rocks of the Gemeric Permian Petrova hora Formation, we have chosen samples of barren rocks, mostly outside the area of ore mineralization. Their location and brief petrographic characteristics are as follows:

1. Psammitic lithic-crystalline rhyolite tuff, Stratená, 3.5 *km* south of the village, Tiesňava valley, 1.2 *km* NW of elevation point Čierna hora 1152 *m*. Macroscopically, the rock is massive, of gray-violet colour. Microscopic study reveals, in addition to crystalloclasts of magmatic-corroded quartz and sericite pseudomorphs after feldspars, also lithoclasts of rhyolite quartz matrix surrounded by predominantly sericite matrix. Chemical composition of fine-grained altered ilmenite, magnetite and biotite ("leucoxene") corresponds largely to TiO_2, whereas Ca and Si have been identified only very rarely. That is why these minerals will be termed Ti oxides in the following text. Disseminated small hematite, pyrite, Ti-magnetite, apatite and titanite grains are abundant.

2. Psammitic crystalline rhyolite metatuff, trench 300 *m* WSW of elev. point 606 *m* Petrova hora, 2 *km* SW of the village Kluknava. Macroscopically light-coloured, gray-green, mildly schistose rock. Its texture is crystalloblastic. Clasts (1–2 *mm* in size) are made up of magmatic-corroded quartz, K-feldspar, plagioclases and sericite pseudomorphs after feldspars. The matrix is microgranoblastic, dominated by small quartz grains (below 0.003 *mm*). The matrix contains dispersed short-prismatic zircons (0.03–0.15 *mm* long with their length/width ratio of 2 : 1) and Ti oxides (prisms and lattices after Fe-Ti oxide alteration). In the separated heavy-mineral fraction, chalcopyrite, tennantite, monazite, titanite and garnet have been identified.

3. Rhyolite, Novoveská Huta, drillhole 957, 259 *m*. Massive, gray-coloured rock. Its texture is porphyric with quartz and feldspar phenocrysts. Compared to the two preceding samples, feldspars are more intensively replaced by sericite and carbonates. The groundmass contains latticed Ti oxides as well as carbonates and chlorite. The heavy-mineral fraction has been found to contain Ti oxides, chalcopyrite, pyrite and tetrahedrite.

4. Psammitic rhyolite metatuff, Košická Belá, 500 *m* south of the village. Macroscopically the rock is markedly schistose.

Microscopically, it resembles the preceding samples, but quartz and feldspar are deformed and recrystallized. The matrix contains substantial quantities of sericite, which gives rise to its lepidoblastic texture. Apart from Ti oxides, the heavy-mineral fraction also contains chalcopyrite, tetrahedrite and pyrite.

5. Dacite, Vyšný Klátov, confluence of the Vrbica brook, 1400 *m* W of elev. point 559 *m* – Kamenný hrb. Macroscopically the rock is massive, gray-green. The texture of the rock is porphyric and that of the matrix is blastoophitic. Phenocrysts are made up of plagioclases and quartz (0.5 to 1.5 *mm* in size). Spaces between plagioclase laths (0.1 *mm* long), however, are most frequently filled with chlorite. Considerable proportion of quartz is secondary, filling intergranular spaces and veinlets. Sericite replaces plagioclases. Compared to the above-described rhyolites and related tuffs, zircon prisms are smaller (0.01 × 0.004 *m*) and less abundant. Ore minerals are more plentiful than in rhyolites (as much as 2–3 %). Hematite grains (up to 0.7 *mm* large) are disseminated in the rock and are intergrown with Ti oxides. Ti oxides most frequently form elongated grains, sometimes of hexagonal, trapezoidal and square cross-sections which suggest original octahedral shapes of Fe-Ti oxides (Ti-magnetite).

6. Andesite, Závadka, exposure 500 *m* NW of the village. Macroscopically the rock is massive and gray-green, blastoophitic-textured. Plagioclases make up substantial part of the rock (60–70 %). Spaces between feldspars are largely filled with chlorite (30–40 %). Along with ore minerals, it forms pseudomorphs after mafic rock-forming minerals. Chlorite and carbonate replace plagioclases. Quartz is rare. It sometimes fills spaces between plagioclases. Ore minerals are abundant (up to 10 %). Predominant Ti oxides are accompanied by magnetite and ilmenite.

7. Andesite, Krompachy. Outcrop 320 *m* N of the power plant, 445 m above sea level. Both macro- and microscopically, the rock resembles the preceding andesite. Minor sericite replaces plagioclases and accompanies quartz veinlets. Hexagonal cross-sections of Ti-oxide lattices (about 0.1 *mm* in size) occur very frequently.

Rhyolites and related volcanoclastics (No. 1–4) are richer in K, U and Th in comparison with dacites and andesites (Tab. 1, No. 5–7). U contents in rhyolites and their pyroclastics are inhomogeneous, usually ranging around 1–3 and 40 ppm (Rojkovič, 1965, 1969).

Table 1. Results of gammaspectrometric measurements.

No. of sample	K (%)	Th (ppm)	U (ppm)	Th/U
1.	5.6	43.5	10.1	4.3
2.	5.3	20.5	8.7	2.4
3.	3.2	18.4	5.5	3.3
4.	3.1	20.9	3.2	6.6
5.	1.4	8.3	2.4	3.5
6.	0.8	7.6	1.9	4.0
7.	2.0	10.1	2.3	4.4

The above-described seven rock samples have been chosen by us to study uranium distribution in detail by the uranium fission track method. The technique used is as follows: Small rock plates some 3 *mm* thick were mounted by epoxide resin and their surface was polished by a fine polishing powder (grain size 1200). These specimens were then ultrasound-cleaned in alcohol. Rock surfaces were covered with Macrofol (ethylene polycarbonate of the firm Bayer) and firmly fixed. The samples together with the standard glass NBS 962 were irradiated by thermal neutron flux in a reactor of the ÚJV (Institute for Nuclear Research), Prague. The samples were irradiated in position 2, channel TK-12. Macrofol was removed from the samples and was subsequently etched in a 6 N KOH solution at a temperature of 60 °C during 40 minutes. The etched "reprint" of uranium distribution in the samples was thoroughly cleaned and observed in an optical microscope.

Such observation in optical microscope revealed the following forms of uranium distribution in the studied rocks:

1. Dispersed uranium is observed mainly in the matrix of rhyolites and their tuffs, its distribution being irregular. The fission-tracks are more abundant in the sericite aggregates. These places often contain also accumulations of very small grains of ore minerals. No uranium fission tracks can be observed in quartz phenocrysts and crystalloclasts (Figs.

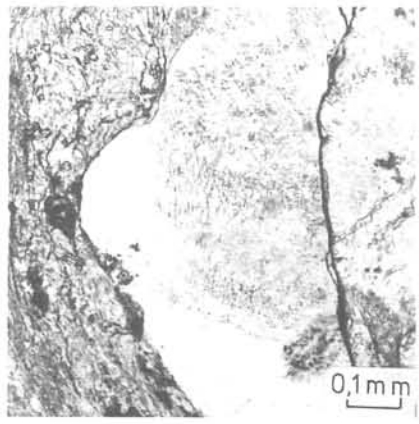

Fig. 1. Rhyolite metatuff with a quartz crystalloclast (white), small zircon grains (gray) and ore minerals (black). Košická Belá, sample No. 4, thin section, magn. 63×, 1 nicol.

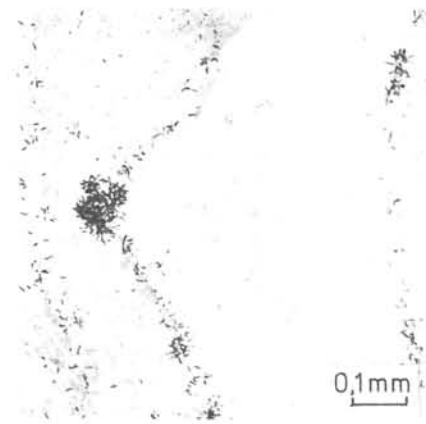

Fig. 2. Fission tracks (FT) reprint of the rock shown in Fig. 1. Distinctly increased fission track concentrations represent zircon grains, slight accumulations forming bands around the crystalloclast are bound to ore minerals and sericite.

1–6), which is in accordance with data by Shatkov et al. (1970), Stuart et al. (1983) and Kizis and Runnels (1984). To determine tracks densities in the matrix we chose planes devoid of their visible accumulations in both microscopic and submicroscopic phases. If we calculate thus determined uranium contentrations in the matrix relative to the content of phenocrysts and quartz veinlets (approximately 20–30 %), FT data and gammaspectrometric measurements confirm a general agreement (Tabs. 2, 3).

2. Increased concentrations of uranium fission tracks can

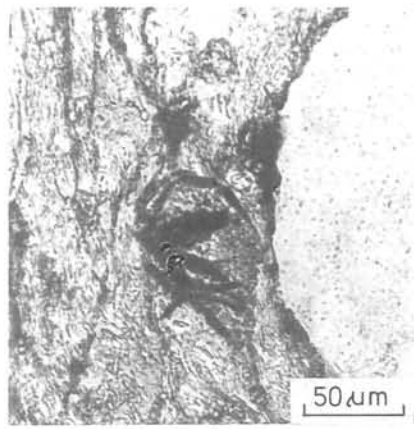

Fig. 3. Close-up view of zircon grains shown in Fig. 1. Thin section, magn. 250 ×.

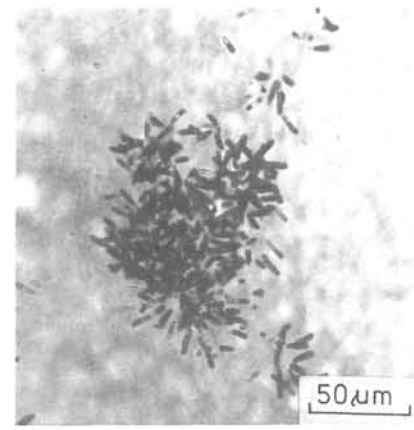

Fig. 4. FT reprint of zircons shown in Fig. 3.

Fig. 5. Ore minerals (black) on the periphery of a quartz crystalloclast (white, left) and an elongated zircon prism in rhyolite metatuff (right). Petrova hora, sample No. 2, thin section, magn. 63 ×, 1 nicol.

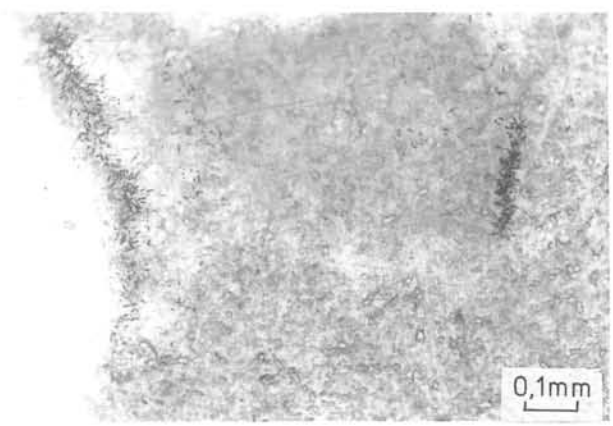

Fig. 6. FT reprint of Fig. 5.

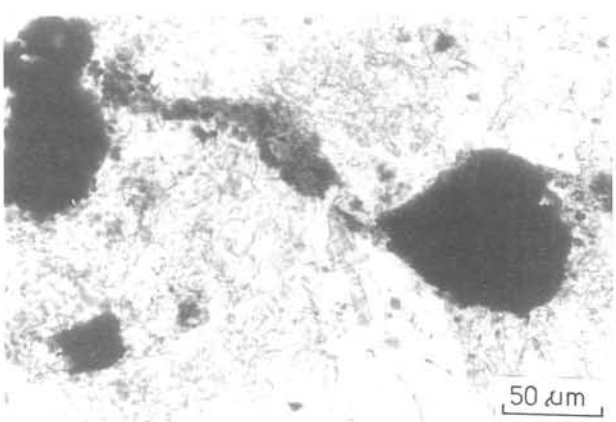

Fig. 7. Fe-Ti oxides (black) in dacite. Nižný Klátov, sample No. 5, thin section, magn. 250 ×, 1 nicol.

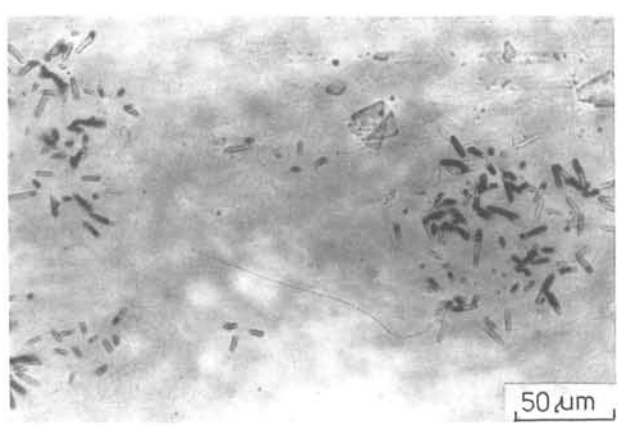

Fig. 8. FT reprint of Fig. 7.

often be observed in zircons of rhyolites, their tuffs and less frequently also in smaller zircon crystals in dacite (Figs. 1–6).

3. Increased concentrations of uranium fission-tracks also occur in Fe-Ti oxides, especially in grains affected by fairly advanced "leucoxenization" (Figs. 7–12). Uranium is adsorbed by Ti oxides. In some intensively "leucoxenized" grains, uranium distribution is irregular. The highest concentrations in the increased background of rutile lattice correspond to uranium oxides and/or U-Ti oxides (Figs. 9–10).

To determine uranium distribution in more detail, we calculated uranium concentration on the basis of uranium fission tracks. Fission track densities in the individual phases were calculated to be up to 2×10^7 tracks/cm^2. Uranium contentrations in the individual samples were calculated after Wagner's formula (1973):

$$C_{(g/g)} = \frac{A \,.\, P_i}{\varrho \,.\, L \,.\, g_p \,.\, g_r \,.\, I \,.\, \varphi \,.\, \sigma \,.\, f}$$

where: $C_{(g/g)}$ = uranium contentration, A = uranium atomic weight, P_i = density of induced tracks per cm^2, ϱ = density of investigated material, L = Avogadro number, $g_p = 1$, $g_r = 1$, I = $^{235}U/^{238}U$ in the isotopic mixture – 7.26×10^{-3}, φ = dose of thermic neutrons 1.3×10^{14}, σ = $580 \times 10^{-24} \times cm^{-2}$, $f = 4\ \mu m$.

The thermal neutron dose was calculated by the comparison of the density of induced tracks on Macrofol and corresponding tracks densities in glasses, as well as by the comparison of the density in NBS glasses irradiated in the reactor NBS.

The calculated uranium contents suggest that the highest U contents in andesite and dacite can be observed in Ti oxides where their contents average 52–280 ppm U (Tab. 2). The distribution character is bimodal, depending on the "leucoxenization" degree of Fe-Ti oxides. In some grains, trace density exceeded 2×10^7 tracks/cm^2, which corresponds to contents over 800 ppm U (Fig. 13). In the relatively best preserved andesite with Fe-Ti oxides (No. 6), measured values range only within a narrow interval from 28 to 75 ppm, whereas in clearly silicified andesite (No. 7) and dacite (No.

Table 2. Uranium contents (in ppm) calculated from fission tracks.

No. of sample	Matrix	Ti-(Fe) oxides	zircons
	$\bar{x}$	$\bar{x}$	$\bar{x}$
1.	18.0	208	313
2.	11.0	300	328
3.	7.1	408	247
4.	3.6	358	385
5.	1.2	270	307
6.	1.4	52	
7.	1.5	280	

Note: Error of the above contents calculated only from the number of fission tracks counted does not exceed ± 15 %.

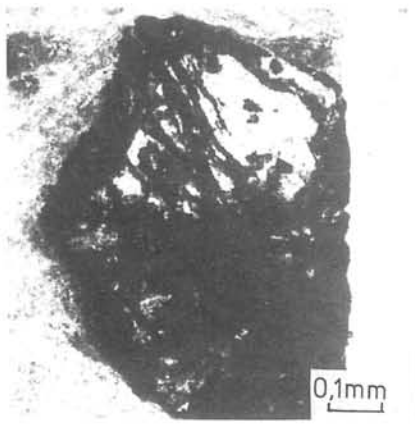

Fig. 9. Lattice of Ti oxides (black) in rhyolite. Novoveská Huta, sample No. 3, thin section, magn. 63 ×, 1 nicol.

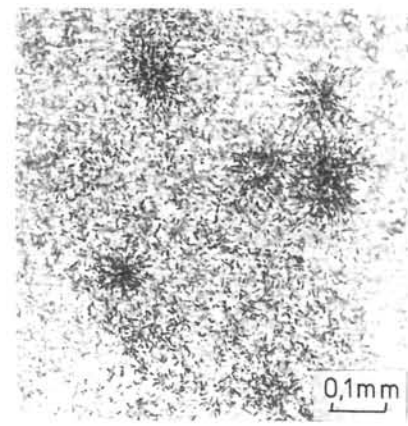

Fig. 10. FT reprint of Fig. 9.

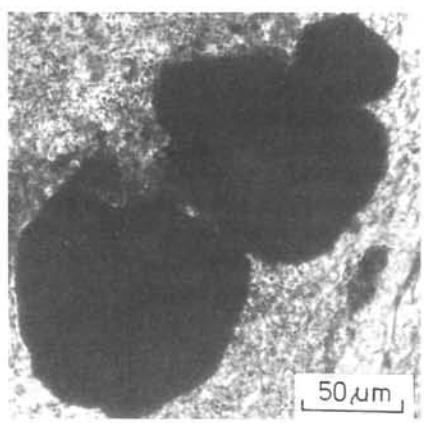

Fig. 11. U-Ti oxides (black) in rhyolite. Novoveská Huta, sample No. 3, thin section, magn. 250 ×, 1 nicol.

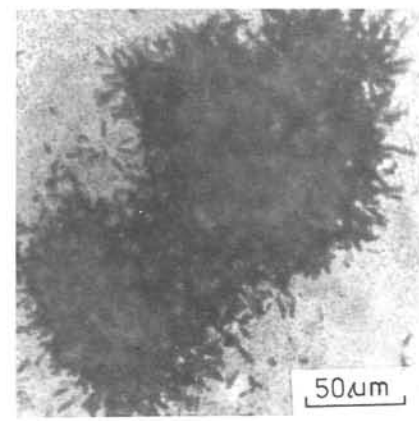

Fig. 12. FT reprint of Fig. 11.

5), U contents in Ti-oxides vary from 81 to 647 ppm and from 21 to 785 ppm U, respectively. In contrast, U contents in zircons are less variable (188–417 ppm). The highest U contents in the andesite and dacite groundmass, including undifferentiated small ore mineral grains, did not exceed 50 ppm.

The matrix of the rhyolites and their tuffs is characterized by higher and more variable U contents in comparison with more mafic volcanics (Fig. 13). In general, average U contents in the rhyolite matrix are higher (except for sample 3) than

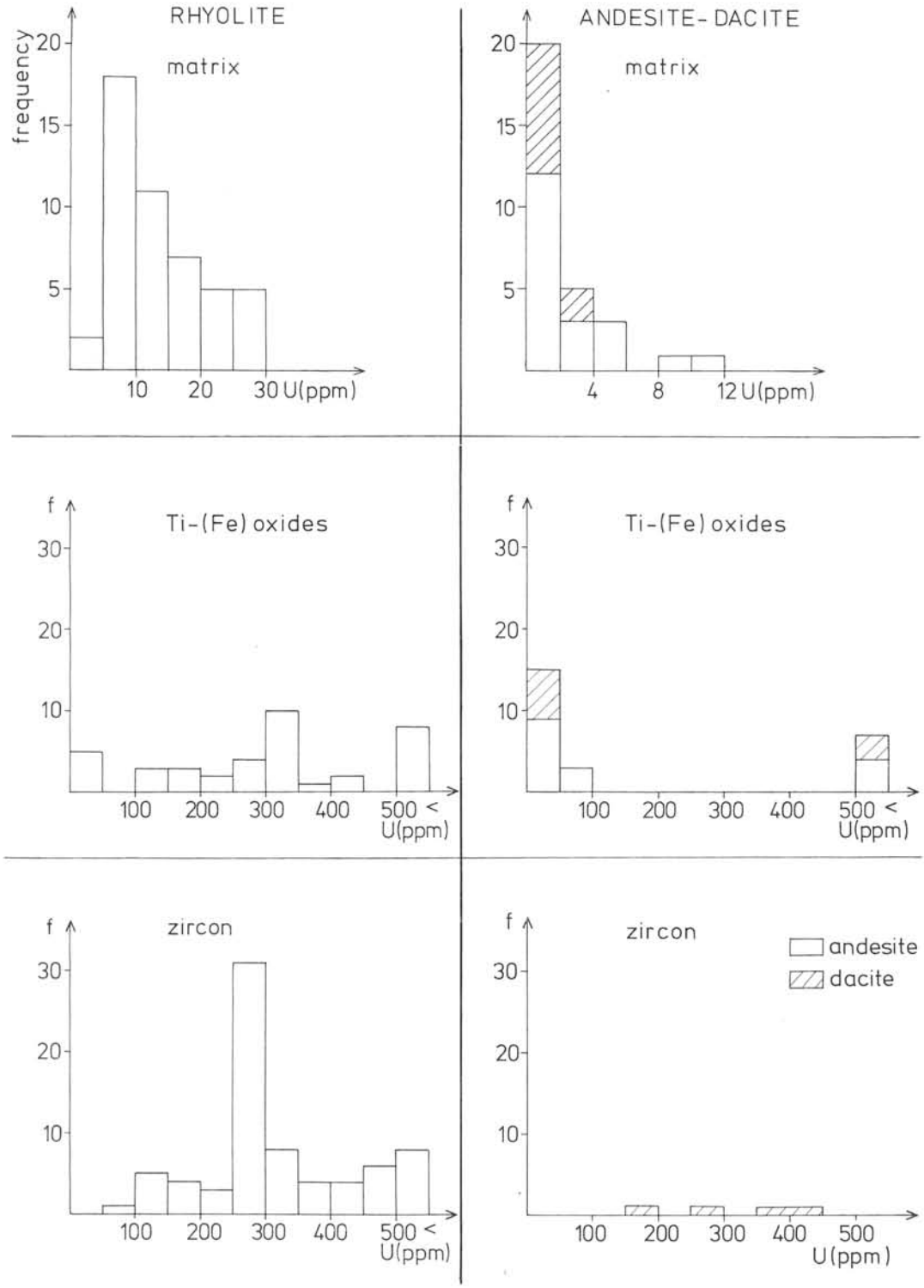

Fig. 13. Abundance of U contents measured by FT method.
On the left in rhyolite and rhyolite tuff, on the right in andesite and dacite. Up is matrix, in the centre Ti-(Fe) oxides and down is zircon.

Table 3. Uranium distribution in the rock.

No. of sample	U (ppm) in rock	U (ppm) in matrix	%	U (ppm) in Ti-(Fe) oxides	%	U (ppm) in zircon	%
1.	10.1	9.6	95.3	0.4	3.8	0.09	0.9
2.	8.7	8.4	96.3	0.3	3.2	0.04	0.5
3.	5.5	5.2	93.8	0.3	4.9	0.07	1.3
4.	3.2	2.5	78.4	0.5	16.6	0.16	5.0
5.	2.4	0.8	32.9	1.5	63.0	0.10	4.0
6.	1.9	1.0	52.1	0.9	47.9		
7.	2.3	0.9	41.5	1.4	58.5		

maximum contents observed in intermediate volcanics. U contents in Ti and Fe-Ti oxides are also very variable, which is probably caused, like in dacites and andesites, by the degree of "leucoxenization" of Fe-Ti oxides and the formation of U as well as U-Ti oxides. The highest content and greatest dispersion of U contents in Ti oxides (25 to 727 ppm) occur in the sample 3 which is also characterized by the lowest U content in the matrix. This suggests that U was redistributed from the matrix and was adsorbed in Ti oxides. U contents in rhyolite zircons most frequently lie within the interval of 250–300 ppm, their average contents in the investigated samples attaining 247 to 385 ppm U.

The knowledge of U contents in the individual mineral phases of the studied rocks has allowed us to calculate their share in the total U content in the rock (Tab. 3). These shares indicate that, despite fairly high U contents in zircons, U in rhyolites and related tuffs is bound predominantly to the matrix. A similar relationship in rhyolites of the West Carpathian neovolcanic mountains has been observed by Forgáč (1975). In contrast, U in andesites and dacite studied by us is bound mainly to Ti oxides.

Summary

Uranium fission track study suggests that the development of U distribution i.e. its remobilization and contentration can also be observed in unmineralized volcanic rocks. The original homogeneous U distribution was preserved in resistant zircon. The irregular distribution in the matrix as well as in Ti and Fe-Ti oxides reflects remobilization and concentration processes. Devitrification and subsequent alterations of the matrix resulted in the mobilization and accumulation of U in parts rich in clay minerals (at present altered to sericite). "Leucoxenization" and removal of Fe from Fe-Ti oxides gave rise to subsequent adsorbtion of U in Ti oxides. Low-grade uranium ores were thus formed in the Upper Permian. Later, during the Alpine orogenic processes, further U remobilization took place and economic concentrations of this element were formed.

Acknowledgements: We wish to thank RNDr. J. Šindlerová and E. Škripeňová for their assistance in sample treatment.

Translated by Ľ. Böhmer

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