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GEOCHEMICAL CHARACTER OF AMPHIBOLITES FROM TISZA UNIT ON THE BASIS OF INCOMPATIBLE TRACE ELEMENTS

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ABSTRACT

Pre-metamorphic origin of amphibolites and amphibolic gneisses from Kőrös Complex (Eastern Tisza Unit) has been an unsolvable problem for a long time. Last year the trace element (Zr, Y, Nb, Ti, P) composition of almost 100 amphibolite samples were measured and this data base may be useful for determining pre-metamorphic rock types and petrochemical character of amphibolites. Present examinations show that – opposite to the previous results – there were no alkaline magmatites in the area, but the rocks of both tholeiitic and calk-alkaline series were formed. The data also suggest that the original igneous rocks of amphibolic gneisses developed in an island arc, while the amphibolites' either in a fore-arc or in a back-arc basin.

INTRODUCTION

The best and – by numerous drillings – the most densely recovered district of the Tisza Unit's crystalline basement is a part of the Kőrös Complex in the "Tiszántúl" region (previous Kőrös and Szeghalom Formation (SZEDERKÉNYI 1984), or Kőrös–Berettyó Unit (BALÁZS ed. 1984)). This area is approximately bounded by the river Kőrös, the southern boundary of the Szolnok–Máramaros flysch zone, the river Tisza, and the eastern border of Hungary (*Fig. 1.*). Due to the relative many deep drillings this is the most promising district of the whole Tisza Unit from the point of view of modelling metamorphic and pre-metamorphic evolution.

Numerous attempts have been made to explore the paleotectonic position previous to the presumably Variscan metamorphism primarily by examining the mica-schists, gneissose rocks constituting the majority of the crystalline complex and the amphibolites forming thin intrcalations from the point of view of the geochemical nature of their major and partly of their trace elements (e.g. SZEDERKÉNYI 1980, 1983, BEDINI *et al.* 1993.)

Having examined the gneisses and mica-schists the data for the original quality of rock indicate a one-time greywacke-pelitic type sediment (SZEDERKÉNYI 1984). Consequently, a model of sedimentation in eugeosyncline and, in relation, ophiolitic, maybe island arc magmatism seems possible (SZEDERKÉNYI 1981). This theory is not supported undoubtedly by the analysis of the amphibolitic rocks. It is certain only that the majority must have been volcanic rocks, however, the possibilities of the exact type range from comatiite-like rocks to those of calc-alkaline, tholeiite and alkaline affinity. There have also been many attempts made to reconstruct the original tectonic setting.

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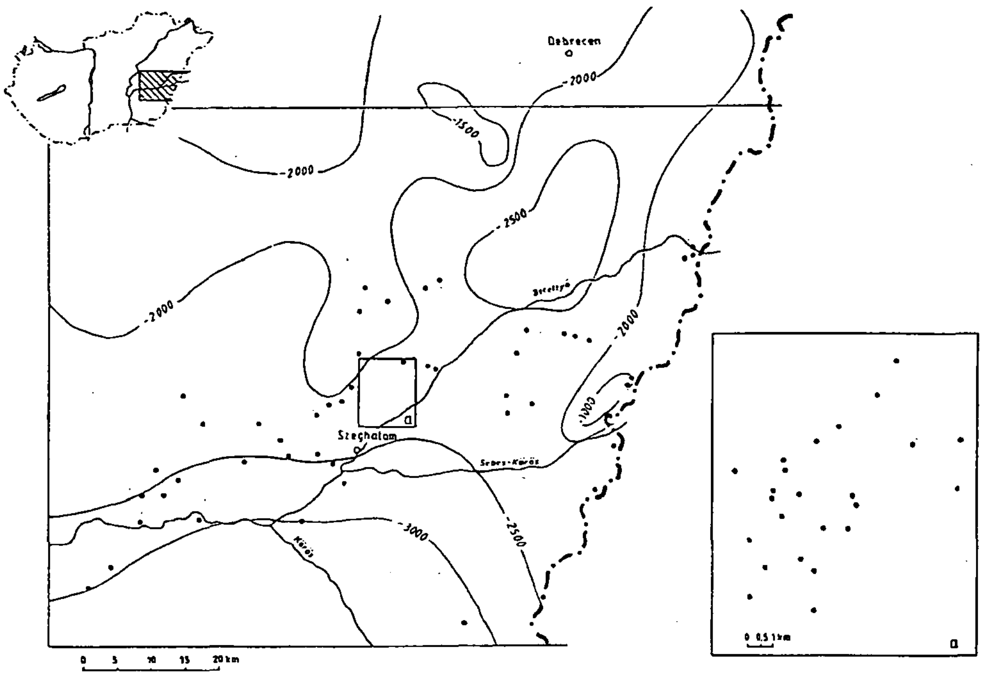

Fig. 1. Distribution of the examined area in Hungary and the locality of the boreholes.

It is evident that the given rock types and series can't have developed an the same time in any place. Therefore the creation of a common model from the results is rather complicated, if it is possible at all. The cause of the problem maybe the fact that during the previous studies only the geochemical data of the major elements were available to the authors and even those not in a required number. And an exact result cannot be expected from data of single samples in the case of metamorphic, what is more, polymetamorphic rocks.

Recently trace elements have been measured from more than 100 amphibolite and amphibolic gneiss samples. The measurements were taken by X-ray fluorescence analysis at the Institute of Geosciences of the Johannes Gutenberg University in Mainz, Germany. Due to the large number of analyses of the incompatible trace elements (P, Ti, Y, Zr, Nb) considered also immobile, an opportunity presents itself to reconstruct, more precisely than was done before, the geochemical features of the former magmatic rocks and the tectonic position of their development.

GEOLOGICAL SETTING

The metamorphic body of the Kőrös Complex is formed mainly by medium and high grade metamorphic rocks, first of all by gneiss an mica-schist. In its axial zone lies a migmatite and a narrow granite belt. Into this major crystalline complex thin (maximum 3–4 metres thick) amphibolite and rarely leptinite bodies are intercalated.

The area has developed by the result of a multi-stage metamorphism. The most significant one of those was a Barrow-type amphibolite facies metamorphism, which at places exceeded even the sillimanite isograd. By a K/Ar chronology its age could be estimated to about 320–330 million years. The uplift after the Variscan orogeny was accompanied with considerable erosion and retrogressive processes. The last major metamorphic event was linked with the Alpine orogeny, when mainly different tectonites were developed and in the joint systems hydrothermal mineral association (laumontite, calcite, chlorite, pyrite) was formed due to lateralsecretion.

PETROGRAPHICAL FEATURES OF THE AMPHIBOLITES

Petrologically, the selected samples show a great variety, though the majority consist of the minerals of the general amphibolite paragenesis (e.g. LAIRD and ALBEE 1981). All samples contain acid-intermediate plagioclase, hornblende an quartz. Most samples contain epidote (zoizite, clinozoizite), chlorite, Ti-phase (mainly sphene), biotite and apatite. The chlorites are exclusively of retrograde origin, relics showing a progressive direction cannot be found. Hornblende is occasionally replaced by actinolite and/or bluish-green barroisite type amphibole. In some samples pumpellyite, prehnite and garnet appear indicating the main steps of metamorphic evolution. Rarely scapolite and zircon can be found as relic igneous minerals. The amphibolites do not contain any other relic mineral grains or textural marks suggesting magmatic origin. Although accurate mineral quantification from thin sections has not been taken, on the basis of the quantity of the rock-forming minerals two major groups can be marked out.

The rocks belonging to the first one are massive, greenish-black amphibolites with mainly nematoblastic texture almost entirely made up of amphibole and, in minor part, plagioclase. They often contain sphene, ilmenite, garnet, epidote as accessory minerals. The samples of the other group consisting of less amphibole and more feldspar can be considered as amphibolic gneiss. Here biotite and quartz are also recurrent components. The difference is unexplainable with metamorphic reasons, it may have been caused by the different original rock quality.

GEOCHEMICAL CHARACTER OF THE AMPHIBOLITES

Variables applied

In the course of different metamorphic processes the major elements and a vast majority of the trace elements may mobilize. Therefore however useful these elements could be for classification of fresh igneous rocks and for the identification of their chemical feature, they cannot be applied unboundedly for the geochemical analysis of amphibolites. Ti, Y, Zr, Nb and P however, may suit this requirement.

– Because of their high charge/radius ratio they are transported in aqueous fluids only in an exceptional case (e.g. with high F^- activity) (PEARCE and NORRY 1979). As a result they can be regarded immobile also in different metamorphic conditions (e.g. GRAHAM 1976, Pearce 1975, WOOD *et al.* 1976, COISH 1977, WINCHESTER and FLOYD 1984). The incidental mobility of Zr and Ti may be caused by the high CO_2 content of water moving inside the rock (MORRISON 1978), while contact with sea-water could make Ti mobility again (MIYASHIRO 1975). In metamorphic conditions an increase in P-content can often be observed, too.

– On the other hand the change of their quantitative ratios presents each tectonical position conspicuously, and in most cases they characterize precisely the different magma types (PEARCE 1975, PUGLISI *et al.* 1988).

– Finally, in the course of basalt fractionation mainly these elements show incompatible behaviour (COX *et al.* 1979), though in case of a possible crystallization of amphiboles and Fe-Ti oxides the Ti-content of the residual melt decreases suddenly, and so the titanium cannot be regarded incompatible (MIYASHIRO an SHIDO 1975, ALABASTER *et al.* 1982). In the case of clinopyroxene crystallization the distribution coefficient of yttrium might be considered high (0.5–4) (MANN 1983).

Owing to these characteristic features, with proper care, the given element group can be suitable for modelling the pre-metamorphic evolution of metamorphosed basalts and andesites.

Study of immobility

The examination concerning the tectonic setting of rocks must be preceded by proving the immobility of the elements to applied. There are several ways to approach this question. The most obvious one is to set out from the correlation system of elements (EVANS *et al.* 1981). As incompatible elements are in question, it is probable that in the original rocks the correlation coefficient values were significant. These values might decrease considerably in case of mobilization. Therefore a significant correlation would indicate immobility, while the lack of it would indicate mobility. On the other hand, due to similar solutional characteristics, these correlations may last after mobilization processes (RIVALENTI and SIGHINOLFI 1969). Though the values of the correlation coefficient are not high (Table 1.) at the given level (0.99) all values [except r(Nb, Y)] are significant.

TABLE 1.

A correlation matrix of examined elements

	Zr	Y	Nb	Ti	P
Zr		0.59	0.61	0.49	0.64
Y			0.20	0.37	0.57
Nb				0.71	0.62
Ti					0.67

Based on these results the relative immobility of the five elements can be supposed, and they can be used further on for specifying the origin of the amphibolites on the basis of the methods known in igneous geochemistry.

Geochemical features of the samples examined

As the elements examined can be used successfully for solving geochemical problems a number of methods have been set up for their usage. Most of them are discrimination diagrams applying two or three variables. Besides ratio diagrams and spidergrams can also be found. These methods may answer three main problems connected closely with each other: the rock-type, its affinity (e.g.: tholeiitic) and the proper tectonic setting of development (e.g.: **WPB, MORB**). Diagrams generally deal with these questions with some overlapping, very often the same method is expected to define the chemical features of a certain rock and the tectonic setting of its development. On the other hand the complementary categories do not always appear together (e.g.: tholeiitic-calc-alkaline), consequently only a negative result can be accepted with absolute certainty. Because of the same reason a well selected set of methods should be applied, and their correct sequence may result an effective system (SZEDERKÉNYI 1983).

The first task is to determine the type of the rock. The graduation elaborated by FLOYD and WINCHESTER (1977, 1978) uses the today valid IUGS terminology (LE MAITRE 1979) and is easily reconcilable with it. Similar to the **TAS** system a variable responsible for alkalinity (Nb/Y) and one for fractionality (Zr/TiO_2) are used. The importance of the latter is emphasized by ALABASTER *et al.* (1982) and using the Nb/Y ratio as alkalinity index is widespread in literature (for the first time PEARCE and CANN 1973).

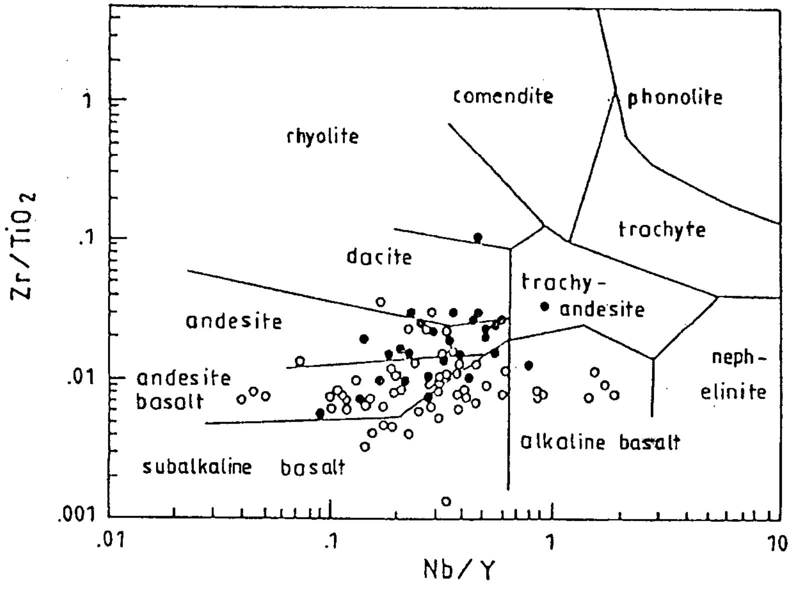

Fig. 2.
Nb/Y vs. Zr/TiO_2 (WINCHESTER and FLOYD, 1977) diagram for determining the rock types of amphibolites

According to the diagram most of the studied amphibolite samples are subalkaline basalts, basaltic andesites and some of them are andesite (*Fig. 2*). The amount of samples in the alkaline basalt field is not significant. On the basis of the two other diagrams (FLOYD and WINCHESTER 1975) used for separating tholeitiic and alkaline basalts it can be taken for certain that the presence of alkaline basalts can be left out of account. (*Fig. 3.*). Owing to the high potassium-content of the amphibolites in some

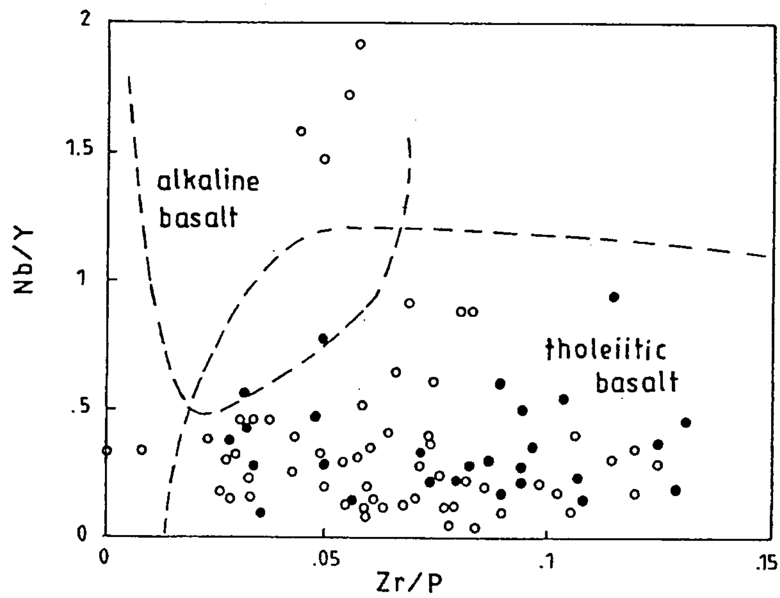

Fig. 3.
Zr/P vs. Nb/Y (FLOYD and WINCHESTER, 1975) diagram for characterizing alkaline and tholeiitic type basalts

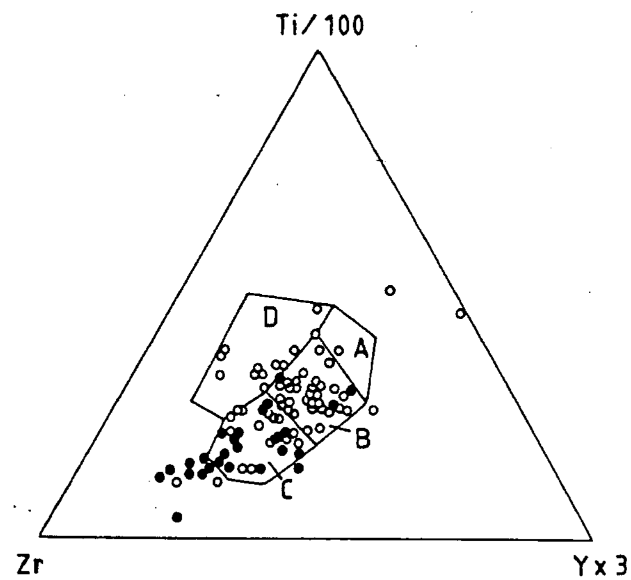

Fig. 4.
Ti-Zr-Y (PEARCE and CANN, 1973) diagram for classifying basalts – **A, B**: low-K tholeiite; **B, C**: calc-alkaline basalt; **B**: ocean-floor basalt; **D**: within-plate basalt

of the samples earlier the alkaline basalt type also seemed possible (SZEDERKÉNYI 1980, M. TÓTH 1993). The high alkaline-content, however, may also be a result of a later, alkaline metasomatic effect, maybe in connection with granitization, which did not influence the trace element composition considerably (SZEPESHÁZY 1971).

In the case of the diagrams above calc-alkaline basalt was not among the offered possibilities. That's why the tholeiitic affinity of the samples is not regarded to be proved for the moment. The problem is just the opposite with the Ti-Zr-Y classification (PEARCE and CANN 1973) where a calc-alkaline field appears at the expense of the tholeiitic one (*Fig. 4.*). Here – as a negative result – island arc (**IAB**) and withinplate (**WPB**) basalt can be excluded though the accuracy of this latter field has been in doubt (ZECK and MORTHOST 1982, HOLM 1982). These statements are verified by the results of the Ti-Zr (PEARCE and CANN 1973) and the Zr/Y-Ti/Y (PEARCE and GALE 1977) diagrams (*Fig. 5., 6.*).

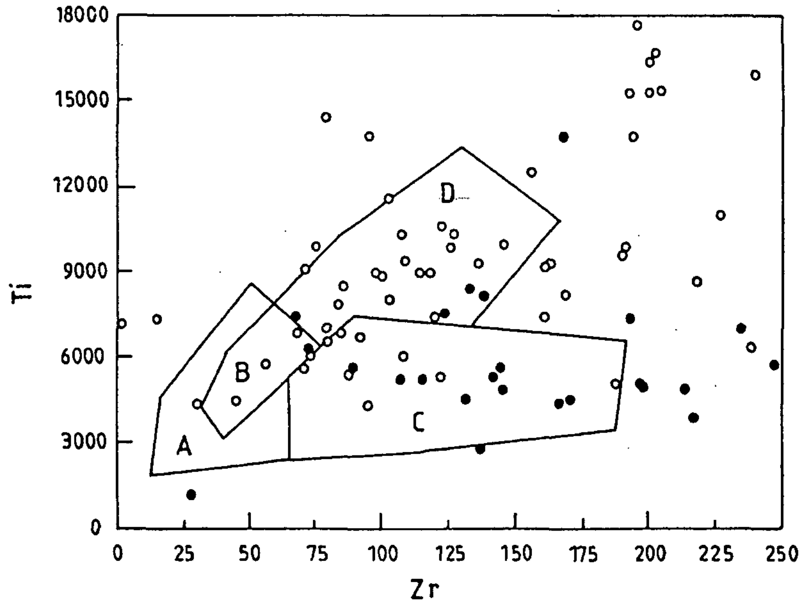

Fig. 5. Ti vs. Zr (PEARCE and CANN, 1973) diagram – **A, B**: low-K tholeiite; **A, C**: calc-alkaline basalt; **B, D**: ocean-floor basalt

PALEOTECTONIC SETTING OF THE ROCKS

Relying upon all that have been said, it can be stated that the parent rocks of amphibolites must have been sea-floor, subalkaline basalts, andesites. To be able to determine whether the samples are from tholeiitic or calc-alkaline series and the tectonic setting of their origin further examinations are needed. According to the diagrams a genetic contact of the rocks with continental or within-plate systems can be excluded and formation of island arc is not possible either. Therefore among the petrotectonic positions the midoceanic ridge seems to be the most possible.

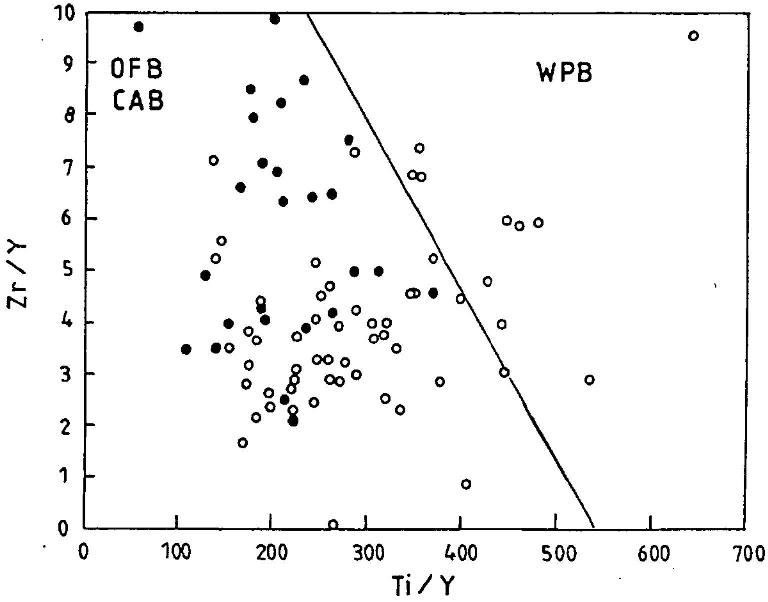

Fig. 6. Zr/Y vs Ti/Y (PEARCE and GALE, 1977) diagram

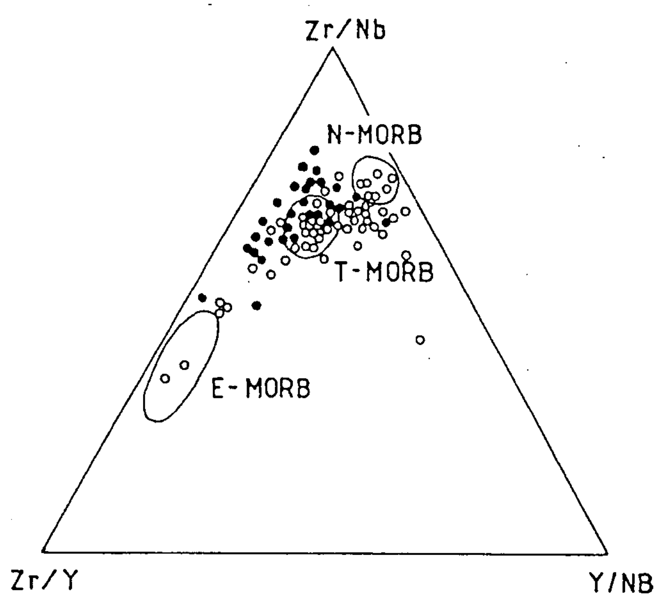

Fig. 7. Zr/Y-Y/Nb-Zr/Nb (FODOR and VETTER, 1984) diagram for distinguishing **MORB** basalts

The fact that in case of partial melting to various extent the five elements studied appear in the melt in different quantities (HESS 1989) makes the classification of **MORB**-type basalts possible and the conditions of development more exact. Especially the increase of Nb-quantity indicate well the enrichement (**E-MORB**) of the original substance (**N-MORB**) (LE ROEX *et al.* 1983). The development of transitional magma (**T-MORB**) can be explained by hybridization of the two previous types (LE ROEX *et al.* 1983). This change is shown clearly by the alteration of the Zr/Nb ratio, as Zr-content is not reactive to the changes above (WEAVER *et al.* 1979, SAUNDERS *et al.* 1988). On the basis of average value of the Zr/Nb ratio (18.6) in our case **T-MORB** type is possible (ERLANK and KABLE 1976).

The enrichment of the original melt can be followed if not a usual discriminating diagram but a ratio diagram is used. The elements applied are incompatible during both tholeiitic and calc-alkaline differentiation and their immobility can also be proved. Therefore it is probable that the value of their ratios will be close to constant, for by measuring the ratios the often disturbing effect of magmatic differentiation could be excluded (MYERS and BREITKOPF 1989). In this way on the Zr/Nb-Zr/Y-Y/Nb diagram the hybridization trend of rift basalts can be seen (*Fig. 7*) (FODOR and VETTER 1984). As the figure shows most sample are of **T-MORB** type and only some of them are of **N-MORB**. The number of rocks enriched with Nb (**E-MORB**) is subservient. The majority of the samples shows **T-MORB** character also on the Nb-normalized spidergram (MYERS and BREITKOPF 1989) (*Fig. 8*). All things considered it can be stated that the original magma went through a slight Nb-enrichment.

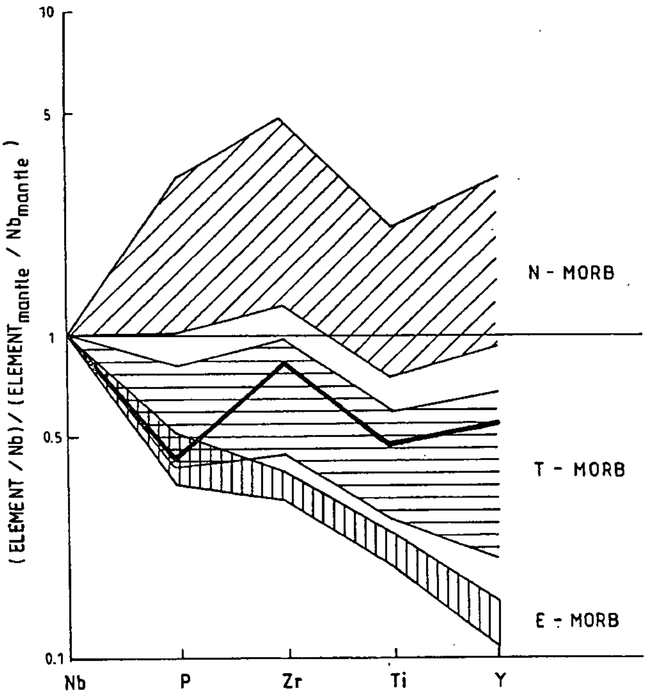

Fig. 8. Nb-normalized spidergram (MYERS and BREITKOPF, 1989; modified). Solid line represents the examined amphibolites

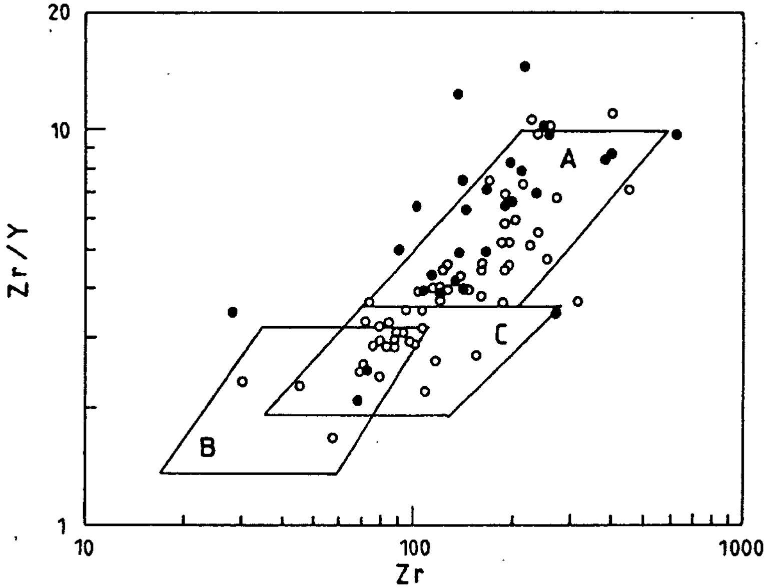

Fig. 9.
Zr vs. Zr/Y (Pearce and Norry, 1979) diagram for distinguishing basalts of the main tectonic setting – **A:** Within-plate basalt; **B:** Island-arc basalt; **C:** Mid-ocean ridge basalt

Mineralogically the main difference between the two subalkaline trends is that in the calc-alkaline one the crystallization of magnetite (generally Fe-Ti-oxides) and amphiboles plays an ipmortant part too (Miyashiro and Shido 1975, Hess 1989). As in these minerals the distribution coefficient is large (1.5; 7.5) (Pearce and Norry 1979), the Ti-content increasing together with Zr indicates a tholeiitic, while the decreasing one a calc-alkaline differentiation trend (Beccaluva *et al.* 1977). Using this figure (*Fig. 5*) – in accordance with other diagrams – suggests that rocks of both series were present on the examined territory.

The simultaneous presence of both series – crossing what has been said – suggests an island arc development (Miyashiro 1975). This supposition seems to be supported by some other facts too which contradict development of rocks in a rift:

– the large (nearly 50 percent) ratio of rocks of andesitic composition connected almost exclusively with island arcs (Bailey 1981);

– the greywacke type composition of original sediments;

– the absence of any trace suggesting ophiolite association;

– the little width and quantity of amphibolite bodies.

CONCLUSIONS

Why is it that all the geochemical methods applied up to this point unanimously reject the possibility of island-arc development?

With regard to the elements studied from the point of view of the island arcs the most characteristic features are negative Nb-anomaly (Emmet 1987, Saunders *et al.*

1988) and low Zr-content (PEARCE 1975). The amphibolites in the vicinity of Szeghalom, however, show positive anomaly in the instances of both elements especially Zr, which can be regarded as a fact excluding the possibility of subduction. Therefore geochemically the origin connected with rift seems provable and that connected with island arc seems improvable, while relying upon the stratigraphic and geochemical character of the rocks nearby the former can be excluded categorically.

The elucidation of this contradiction is possible in several ways. The most apparent possibility is to assume the opening of a brack-arc basin parallel with the agency of the island arc. In this case the development of the new basin is characterized by the formation of rift-type tholeiites, while that of the island arc by the development of calc-alkaline rocks.

In sedimentary environment referring to the island arc rift type basalt may also appear in the territory of the fore-arc. Here the andesites having high content of Mg, Cr and Ni are of boninite type (JAKEŠ and MIYAKE 1984). Among the samples examined by us for three basaltic andesites Cr>800 ppm, Ni>400 ppm could be seen and the previous examinations have also shown samples with extremely high Mg content (SZEDERKÉNYI 1984).

As on every diagrams the main argument against formation on island arc was the significant positive Zr-anomaly, the explanation of it must be very important. It may arise that Zr became mobile independently from the other elements due to alteration of examined rocks. However this supposition is opposed to the results of the examination on immobility. Therefore already the original volcanics and also the magma may have shown positive anomaly. In case of continental subduction Zr often appears relatively high content far higher than that characteristic of the island arcs (JAKEŠ and WHITE 1972), and the Zr/Y ratio may be higher as well (BAILY 1981). This may be the reason why most samples in Zr-Zr/Y discrimination have proved to be of within plate origin. (*Fig. 9*)

Whether the oceanic side of the sontinental island arc is considered to be the place of volcanism or the existence of a back-arc basin is assumed, the majority of contradictions arising seems to be solvable. The final answer, however, can be given by the accurate examination of further trace elements and the rare earths of the amphibolites. The detailed geochemical analysis of the leptinites of acid volcanic origin reaching the quantity of the amphibolites in some places (SZEDERKÉNYI 1984) is also needed.

SUMMARY

Geochemical features and tectonic setting of development of the amphibolites and amphibole gneisses in the Kőrös Complex of the Tisza Unit has been a problematic question for a long time in the literature of the subject. Some, so far open, questions could be answered by the geochemical analyses of the basis of incompatible trace elements.

- Probably, pre-metamorphic volcanics of alkaline affinity cannot appear in the territory, the alkaline character of the rocks can be the result of an alteration effect.
- Relying upon subalkaline basalts and andesites the existence of both tholeiitic and calc-alkaline trends is proved, therefore volcanism on destructive plate margin is possible. On the basis of the thorough examinations development on continental margin is probable. The question is, however, whether the development of the tholeiitic basalts links with fore-arc or back-arc basin.
- The explanation to the significant Zr and less Nb anomaly is still not satisfactory.
- As, apart from some exceptions, the pre-metamorphic rock type of amphibolites has proved to be tholeiitic basalt, and that of the amphibole gneisses to be calc-alkaline andesite, it can be stated that the main reason for the petrological differences present among the examined metamorphites described before is the original quality of rock.

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