Theses of Ph. D. dissertation

Mineralogical, petrological and geochemical characteristics of Neotethyan advanced rifting stage submarine basaltic volcanism and related hydrothermal processes in NE-Hungary and in some localities of the Dinarides and Hellenides

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Introduction, aims of the study

Re-evaluation of the Mesozoic submarine basaltic suits of the Darnó Unit (NE Hungary) was necessitated on one hand by the new stratigraphic models published for the area (*e.g.,* Haas and Kovács, 2001), on the other hand by the discovery of the peperitic facies[1] in a field trip in 2005, with the help of Prof. Ladislav Palinkaš. Another interesting fact concerning the area is the occurrence of Jurassic submarine basaltic rocks of the Szarvaskő Unit (NE Hungary) in the vicinity of the Triassic Darnó magmatites. Thus, in this area, different stages of the evolution of the Neotethys are represented; *i.e.,* the Triassic, advanced rifting stage (Buda and Kiss, 1980, Haas and Kovács, 2001, Kovács *et al.*, 2008) and the Jurassic, back-arc basin formation (Harangi *et al.*, 1996, Aigner-Torres and Koller, 1999). Among these series, pillow lavas, hyaloclastite breccias and peperitic basalts can be studied together with the related hydrothermal and metamorphic (very low-grade Alpine metamorphism, Árkai, 1983, Sadek Ghabrial *et al.,* 1996) processes.

The volcanic facies analyses of the above given Hungarian occurrences have not been performed before, probably due to the tectonically disturbed situation, where no complete volcanic structure is preserved. In contrast to that, the Hruškovec quarry (Kalnik Mts., Croatia), genetically related to the Darnó Hill (as first suggested by Dimitrijević *et al.,* 2003), luckily preserving the whole structure of a submarine basaltic lava flow, was studied in details (Borojević *et al.,* 2000, Palinkaš *et al.,* 2008). That quarry offered a unique possibility to unveil and distinguish the volcanic facies types in the Hungarian occurrences, so that the research was extended to this outcrop, too.

The model, where both the Kalnik Mts. and the Darnó Unit are representing a Triassic, advanced rifting stage-related volcanism in the Dinaridic-Hellenic zone, required further comparative study in this region. For this comparison the Vareš-Smreka quarry (Bosnia and Herzegovina) and the Avdella Mélange of the Stragopetra Mts. (Greece) localities, representing mostly peperitic facies, were selected. Extending the research to these Dinaridic-Hellenidic areas gave the possibility of large scale geological correlation, too.

The aim of the study was thus to clarify and support the relationship among the pillow lava series of the Darnó Unit, the Kalnik Mts., Vareš-Smreka and the Stragopetra Mts., in order to support the Dinaridic origin of the Bükk Unit, proposed earlier, based on other types of geological evidences. Our methodology covered the determination of the origin of the studied volcanic blocks within the basaltic lava flow (*i.e.,* identification of the volcanic facies), the

[1] Peperite (definition): a genetic term applied to a rock formed essentially in situ by disintegration of magma intruding and mingling with unconsolidated or poorly consolidated, typically wet sediments (White *et al.,* 2000).

description and modelling of the general and specific characteristics of the submarine hydrothermal processes (study extended to the Jurassic basalts, too), and incorporation of all these results into the geological correlation. Detailed studies using that methodology have not been performed in the Hungarian, Bosnian and Herzegovinian, Croatian and Greek occurrences before.

Further on, an important task was to find characteristics that can be successfully used to distinguish (even on the field) the nearby-occurring rifting-related (Triassic) and back arc basin-related (Jurassic) pillow lavas. In this work, comparison of the basalts of the Darnó Unit and the Szarvaskő Unit played an important role too.

All the above mentioned aims contributed to the correlation among the Hungarian Mesozoic volcanic units and their place of origin; moreover, they also contributed to our general knowledge on the submarine hydrothermal processes.

Methods

Fieldwork was done in 5 quarries and several outcrops of the Darnó Unit, complemented with the study of cores from 2 deep drillings in the area. 4 outcrops (both natural and manmade) of the Szarvaskő Unit, 1 operating quarry in both the Kalnik Mt. and Vareš-Smreka, and finally, 7 road cuts and 2 outcrops in the Stragopetra Mts. were included in the study. The main goals of the field work were to distinguish the volcanic facies, prepare sections of the key outcrops (indicating the facies and also the results of hydrothermal alteration) and collect representative samples.

Macroscopic texture analyses and characterisation of the different hydrothermal infillings were done by hand lens observations and stereomicroscopy. Further studies of the hydrothermal minerals and the host rock were done by polarizing microscopy, however, coarser-grained hematite and pyrite were also studied by IR microscopy. Some small opaque grains were identified by reflected light microspectrophotometry, while fine-grained minerals, occurring mainly in the ground mass, were identified by X-ray powder diffraction. The study of the peperitic facies was complemented by the study of dissolution residues of the limestone.

Fluid inclusion microthermometry was completed in samples of 7 representative outcrops in order to clarify the formation conditions of the different hydrothermal infillings. In most cases the measurements were set back not only by the small size of the inclusions, but also by metastable melting (*i.e.,* lack of gaseous phase). The latter may be reduced by the slight *stretching* of the inclusion, but the application of this method to the studied inclusion types needed adjustment and technological development. Identification of the gas phase of some of the inclusions was done by Raman microspectrophotometry.

Electron microprobe analyses of chlorite and datolite were performed in order to obtain information on the pressure-temperature conditions and other characteristics of the hydrothermal and subsequent metamorphic processes. Chlorite chemical composition data were used at the chlorite thermometry calculations. Even if having an uncertainty of approximately 20°C, the use of chlorite thermometry was vital, as it gives information on the formation temperature of the mineral, in contrast to the *minimum* formation temperature retrievable from the homogenisation temperatures of the fluid inclusion microthermometry. On the other hand, with the application of this method, we could obtain formation temperature on minerals that otherwise cannot be studied by microthermometry. The chemical composition of plagioclase and pyroxene crystals was determined by SEM+EDS analyses.

Bulk rock geochemical analyses of 34 representative samples of the studied Hungarian, Croatian, Bosnia and Herzegovinian and Greek outcrops were obtained. The studies were done not only to get more precise information on the formation process of the basalt, but also to trace the hydrothermal alteration (by doing mass transfer calculation) and the effects of the mingling with the wet sediment.

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1. No complete submarine basaltic lava flow structures can be traced in the early Mesozoic submarine volcanics of the Darnó Unit, Vareš-Smreka and Stragopetra Mts., only the characteristic distal (referred to the eruption centre) facies are present, namely, the so-called closely packed pillow, the *in situ* hyaloclastite breccia, the pillow fragmented hyaloclastite breccia and the peperitic facies.

2. The occurrences of the Darnó Unit, the Kalnik Mts., the Vareš area and the Stragopetra Mts. show similarities in the field of volcanic facies, petrological and geochemical characteristics and hydrothermal processes. Thus the earlier suggested connection is complemented by new pieces of evidence.

3. The distal origin (referred to the eruption centre), and the consequent fast cooling, determined substantially the further characteristics of the rock. This can be evidenced in the rock texture (variolitic and sphaerulitic textures are common, though intersertal occurs, too), in the crystal shape of the minerals (skeletal plagioclase crystals are common) and in the results of the fluid inclusion microthermometry (notable temperature decrease can be traced even within a single amygdule).

4. The occurrence of the carbonate peperitic facies at each studied locality is of vital importance, as it reveals a formation depth shallower than the CCD, the rock itself, in the lucky case, may even contain fossils proving the age of the volcanism, and on the other hand, its presence rejects the mid-oceanic ridge-related formation. Moreover, it provides a possibility to clearly distinguish the Triassic (with carbonate peperite) and Jurassic (without carbonate peperite) submarine basalts, *i.e.,* basalts of different Neotethyan stages within the same mélange.

5. Though hydrothermal alteration affected the studied rocks, the most immobile elements (Zr, Nb, Y, Ti) can be used to draw important conclusions from the petrochemical analyses. A genetic relationship among all the studied Triassic rocks is outlined, and the within-plate basalt origin, *i.e.,* the advanced rifting-related formation is supported, confirming the earlier models.

6. On the basis of these results, a belt of Triassic, advanced rifting-related magmatic rocks can be followed, from the displaced fragments of the Dinarides (Hungary), through the Dinarides to the Hellenides. That belt is next to the younger obducted remnants of the real oceanic crust-representing ophiolitic rocks.

7. The most important characteristics of the hydrothermal system of the Triassic, advanced rifting-related pillow lavas are the fast cooling rate (from ~300°C to <50°C), the seawater-related origin of the hydrothermal fluids (the salinity was generally 3−6 NaCl equiv. m%) and the strong dependence on the water/rock ratio.

8. In case of high water/rock ratio (*e.g.,* at the hyaloclastite breccia) the salinity of the hydrothermal fluid was around the seawater salinity. In case of low water/rock ratio (*e.g.,* at the semi-closed systems of the amygdules or cooling cracks) the solution may have got enriched in ions, as a result of the fluid-rock interaction, *i.e.,* the hydration of the rock forming minerals.

9. Three main phases of the submarine hydrothermal processes were distinguished: the (1) primary hydrothermal process, occurring at ~300°C (resulting in the albitization of the ground mass plagioclase), the (2) cooling-related hydrothermal processes (causing the chloritization of the ground mass and the formation of the different hydrothermal mineral infillings) and the (3) low-temperature processes (resulting in the appearance of clay minerals and iron oxyhydroxides).

10. Further steps can be distinguished within the (2) cooling-related hydrothermal processes: thin veinlets formed at the highest temperatures, which were followed by the formation of smaller, then larger amygdules and the mineral bands of the pyjamas-type pillow and finally the jig-saw veins. Mineral precipitation sequence can also be established: at higher

temperatures (300−150°C) mainly chlorite, quartz and prehnite precipitated, while calcite and zeolite (laumontite) become dominant at lower temperatures (150−70°C).

11. The abundant vesiculation of the pillows proves the conclusions drawn from the peperitic facies, *i.e.,* the relatively shallow water depth (Skilling *et al.*, 2002). However, in the case of Vareš-Smreka a more precise estimate of 1.5 km is given from the combination of the fluid inclusion microthermometry and the chlorite thermometry. That water depth estimate also supports the idea that the formation of the pillow lava series did not take place in a typical mid-oceanic ridge environment (though the latter could not be ruled out completely, either).

12. The submarine volcanism-related hydrothermal processes can be traced through the geochemical analyses with the help of mass transfer calculation. Based on these calculations, within a single pillow the results of process (1) (described in thesis nr. 9) are dominant, while leading from less to more altered parts of a facies the importance of process (3) is increasing. However, over facies boundaries process (3) can become dominant. The water-saturated sediment of the peperitic facies usually enhanced the alteration processes. The amount of some metals, like Cu, Zn and Co, decreases in the volcanic rock as the alteration process goes on, thus these metals were dissolved into the heated seawater, however, wherever wet limey mud was present, these components could accumulate, causing relatively higher concentrations compared to the average limestone.

13. Based on their main characteristics (*e.g.,* fast cooling, seawater-dominated system), the hydrothermal processes differ significantly from the big fluid circulation systems occurring in the mid-oceanic ridges (Nehlig, 1991, Foustoukos and Seyfried, 2007), supporting the advanced rifting-related origin of these basaltic rocks.

14. The pillow lavas of the Darnó Unit and the Szarvaskő Unit differ significantly in their petrographic and geochemical characteristics. The petrochemical studies indicate that, in contrast to the within-plate basalt origin of the Triassic basalts, the origin of the Jurassic rocks is more likely related to back arc basin or MORB magmatism.

15. The recently discovered siliciclastic peperitic facies in one of the Jurassic basalt localities of the Szarvaskő Unit proves not only the relatively deep formation place (below CCD; chlorite thermometry and fluid inclusion microthermometry indicate 5.6 km formation depth), but also draws attention to the fact that the Jurassic rocks did not originate from typical mid-oceanic ridge realm, either.

16. The submarine basaltic volcanism-related hydrothermal process of the Szarvaskő Unit is in many respects similar to that found in the Triassic pillow lavas: a very rapidly cooling, seawater-dominated, water/rock ratio dependent system was reconstructed. On one hand this

fact emphasises that the rocks of the Szarvaskő Unit were not formed in a typical mid-oceanic ridge environment, either, on the other hand it reveals that these characteristics are common and not geological time dependent properties of non-extended basaltic submarine lava flow-related hydrothermal systems.

17. The datolite-bearing veins of the Jurassic peperitic facies formed after the submarine hydrothermal processes, during the progressive part of the Alpine metamorphism.

Conclusions

The submarine volcanism-related basaltic series of the Hungarian Darnó Hill, the Croatian Kalnik Mts., the Bosnia and Herzegovinian Vareš-Smreka and the Greek Stragopetra Mts. exhibit very similar formation environment and processes on the basis of their volcanological, petrological, mineralogical and geochemical characteristics. These findings support the Neotethyan advanced rifting-related origin of these pillow lava sequences, outlining a Triassic magmatic zone of such volcanics (from the displaced fragments of the Dinarides, in Hungary, extending over the Dinarides to the Hellenides), next to the well-known ophiolitic belt.

Though the Jurassic, most likely back arc basin-related magmatites, occurring in the same mélange, show similar, distal volcanic facies (referred to the submarine eruption centre), they bear definitely different mineralogical, petrological and geochemical characteristics. The most important distinguishing feature (observable even on the field) is the occurrence of the red limestone bearing peperitic facies in the Triassic sequences. In both rock types, hydrothermal processes consisted of three stages and are markedly different from those typical in mid-oceanic ridge-related environments. Their main characteristics are the dominance of seawater, the rapid cooling and the dependence on water/rock ratio. Beside these hydrothermal parageneses, a later one, related to the progressive part of the Alpine metamorphism, was also detected.

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