Fluid/melt – wall rock interaction in the upper mantle beneath the central Pannonian basin

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Antecedents

Upper mantle xenolith-bearing Neogene-Quaternary alkali basalts are found both in the central (Little Hungarian Plain, Bakony-Balaton Highland) and marginal parts (Styrian Basin, Nógrád-Gömör and Transylvanian Basin) of the Carpathian-Pannonian region, providing a unique opportunity for studying the evolution of the lithosphere. The study of ultramafic xenoliths from these localities recognized the effects of numerous mantle processes such as different degrees of partial melting, deformation and mantle metasomatism. Previous studies pointed out that following the extensive depletion of the mantle (~1 Ga, but at least much before than Tertiary, Embey-Isztin et al., 2001) remarkable incompatible trace element and variable Nd-Sr isotopic enrichment affected dominantly the deformed lithospheric mantle. This enrichment was interpreted by Downes et al. (1992) as being due to the host alkaline magmas and (along the Carpathian arc) subduction-related calc-alkaline magmas/fluids traced in the central Pannonian basin.

Most studies dealing with mantle xenoliths from the area focused on peridotites which were not affected by modal metasomatism, with very few dealing with pyroxene-rich and amphibole-bearing peridotites (e.g.: Embey-Isztin, 1976; Embey-Isztin et al., 1989; Downes et al., 1992; Dobosi et al., 2003; Török et al., 2003). Origin of amphibole-enrichment and clinopyroxenites were attributed to metasomatic processes generated by the host alkaline magmatism (Downes et al., 1992; Dobosi et al., 2003). Technical developments in the last decades allow us to study the fine-grained assemblages such as rarely occurring melt pockets, veins and fluid and/or silicate melt inclusions that have been recognized in the mantle materials. Thus, attention has been focused on these clusters (e.g.: Szabó et al., 1995a, 1996; Embey-Isztin & Scharbert, 2000; Bali et al., 2001, 2002) either.

The main aims of this study are:

1. To give detailed textural, major and trace element and isotopic characterization of less studied rock types as orthopyroxene-rich websterites and websterite veins in spinel lherzolitic wall rock, as well as the rarely occurring silicate melt pockets;
2. To determine the conditions of melt/fluid–wall rock interactions and the formation of reaction products in the upper mantle;

3. To give a more comprehensive insight into the complex depletion – refertilization processes affected the lithospheric mantle beneath the central Pannonian basin.

Methodology

50-150 μm thick, double polished thin sections were made of the collected xenoliths. The goal of the double polishing was the study of silicate melt inclusions, on the other hand these thick thin sections are appropriate for further *in situ* analytical analyses. The phases were marked out for chemical analyses following the detailed petrographic study.

Analytical techniques:

Microprobe analyses were carried out using a JEOL Superprobe JXA-8600 WDS at the Department of Earth Sciences, University of Florence and a JEOL Superprobe JXA-8200 WD/ED at the Geocenter Copenhagen. In both laboratories natural and synthetic standards were used for the analyses, and the method of Bence & Albee (1968) was applied for correction. For the determination of average compositions 2 to 5 points were analyzed in each constituent.

For the determination of trace element in the phases of the studied xenoliths laser ablation ICP–MS measurements were carried out using an Elan 6100 ICP-MS equipped with CETAC LSX-200 laser ablation system in the Geocenter Copenhagen. A single line scan or raster method was applied during the measurements. NIST610 and NIST612 synthetic glass standards were used as calibration standards (using the values in Pearce et al. 1997). The CaO contents of the analyzed phases measured on the electron microprobe were used as the internal standard.

For Pb isotopic measurements samples were analyzed by the Axiom multi-collector ICPMS at the Danish Lithosphere Centre, Copenhagen using the double spike method described in detail by Baker et al. (submitted to Chemical Geology). Sr samples were analyzed automatically in dynamic peak jumping mode by a VG sector 54 TIMS at the Geological Institute, University of Copenhagen. Clinopyroxenes and melt pockets were separated by hand picking under stereomicroscope. Clinopyroxenes were leached in 8N HCl on a hot plate for an hour in teflon beakers (in order to clean the surface contamination). The hand picked melt pockets of 3 samples were not leached. Samples were then dissolved in 7N HNO_3+HF mixture, 7N HNO_3, then 6M HCl.

Following the solution, Pb and Sr were separated in anion and cation exchange resins. Sr samples were loaded onto Re filaments in a mixture of H_3PO_4 and TaF activator whereas Pb was analyzed from solution.

Results

1) Based on petrographic study, three major rock types were distinguished from Bakony-Balaton Highland modally metasomatized suite, turned up mostly from Szentbékkálla, minor from Szigliget. These are: a) orthopyroxene-rich websterites, b) lherzolites containing websterite and clinopyroxenite veins, and c) peridotites and pyroxenites containing silicate melt pockets. Among these rock types, orthopyroxene-rich websterites and websterite veined lherzolites have not been studied before from the Bakony-Balaton Highland ultramafic xenolith suite.

2) The results of detailed major and trace element and isotopic studies confirmed that the orthopyroxene-rich websterites and the websterite veined lherzolites differ from the previously studied peridotitic and pyroxenitic assemblages of the same area, suggesting that they have formed due to processes which have not been studied in details previously. Besides these, the silicate melt pockets appear in variable rock types, of which textures are mostly equigranular and piokilitic (Bali et al., 2001, 2002).

3) Formation of the silicate melt pockets can be attributed to several processes: a) based on trace element compositions, the former presence of amphiboles is essential for the melt pocket formation even in those xenoliths where amphibole was not found during petrographic observations; b) besides the amphiboles, melting of clinopyroxenes (+/-orthopyroxenes) should also be taken into account for modeling the bulk composition of the melt pockets.

4.) In the melt pockets of several xenoliths an external melt/fluid should have also mixed to the *in situ* melts of amphibole and clinopyroxene based on both major and trace element evidences. This external melt/fluid was different from the host alkaline basalt, thus, the melt pockets are the reaction products of metasomatizing melt, migrated in the mantle, and pre-existing amphibole and clinopyroxene. The external melt/fluid could have been released from subducted oceanic crust based on its geochemical character.

5) The melt pockets of some of the xenoliths contained carbonates either. However, the carbonates of the different xenoliths have very similar major element composition a trace element-poor and a trace element-rich type could have been distinguished.

6) In those lherzolites, which contain websteritic and clinopyroxenitic veins the assemblage of veins reached chemical equilibrium with the wall rock lherzolite considering major and trace element and isotopic compositions. Based on high pressure and temperature experiments (e.g.: Gaetani & Grove 1998), it can be assumed that the websterite veins is not direct crystallization product of magmas, but the reaction products of fertile peridotite and H_2O-bearing alkali basaltic magmas. In contradistinction, the clinopyroxenite vein can be direct crystallization product of similar melt.

7) More generations of websterite veins can be distinguished from which the older one (containing pyroxenes with lower Al content) could have gone through deformation and slight partial melting after vein formation, whereas the younger generation with Al-rich pyroxenes have not.

8) The zonation of clinopyroxenes in the websterite and clinopyroxenite veined lherzolites is the results of *in situ* melting, the effect of external melt could have been ruled out. The zonation developed at MOHO depth due to pressure drop and slight temperature rise.

9) The orthopyroxene-rich websterite bodies can rather be considered as the crystallization products of boninitic magma (or reaction product with peridotite) than the reaction product of a strongly depleted peridotite and H_2O-fluid phase, based on their high equilibrium temperature and oxygen fugacity, and the calculated composition of melt keeping equilibrium with the clinopyroxenes.

10.) The previously described results suggest that the mantle beneath the Bakony-Balaton Highland Volcanic Field was metasomatized in several fluxes by melts/fluids having different origin. Among these: a) the youngest process could have been the formation of the silicate melt pockets, as their material is not completely crystallized, silicate glass is also present in them. These melt pockets have formed partially due to *in situ* melting of amphibole+clinopyroxene±orthopyroxene and due to metasomatism induced melting of amphibole and clinopyoxene, where the metasomatizing fluid could have been originated from subducting slab. b) The websterite and clinopyroxenite veins (at least the younger ones) are the products of a young process as they have not suffered partial melting and deformation after their formation. The formation of the veins might be attributed to migrating asthenospheric melts released during the asthenosphere upwelling beneath the Pannonian basin. c) The formation of orthopyroxene–rich websterites might be the oldest event. The bodies can be considered either as to the products of fluid metasomatism or boninitic melts, they should have formed in the vicinity of a subducting oceanic plate. The large distance of the Carpathian arc suggests the possibility that these bodies were produced by an older subduction event.

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Published papers and abstracts written in the framework of Ph.D.:

Papers:

Bali, E., Szabó, Cs., Török, K. & Vaselli, O. (2001): The significance of carbonate-bearing and carbonate-free silicate melt pockets in the upper mantle: a case study on Szentbékkálla ultramafic xenoliths, Bakony-Balaton Highland Volcanic Field (in Hungarian with English abstract). Bulletin of the Hungarian Geological Society, 131/3-4, 415-442.

Bali, E., Szabó, Cs., Vaselli, O. & Török, K. (2002): Significance of silicate melt pockets in upper mantle xenoliths from the Bakony-Balaton Highland Volcanic Field, Western Hungary. Lithos, 61, 79-102.

Szabó, Cs., Falus, Gy., Zajacz, Z., Kovács, I., **Bali, E.** (2004): Composition and Evolution of Lithosphere beneath the Carpathian-Pannonian Region: a review. Tectonophysics (in press).

Abstracts:

Bali, E., Falus, Gy., Szabó, Cs., Vaselli, O. & Török, K. (1999): Carbonatite metasomatism in the upper mantle beneath the Bakony-Balaton Highland and Little Hungarian Plain Volcanic Fields, Western Hungary: Evidence from upper mantle xenoliths. Orogenic Lherzolites and Mantle Processes, Pavia, September 12-15. 1999., Abstract volume, Ofioliti, 53-54. *(poster presentation)*

Bali, E. (1999): Geochemical research of melt pockets from upper mantle xenoliths (Bakony-Balaton Highland and Little Hungarian Plain Volcanic Field, Western Hungary). MinWien99, Berichte der Deutschen Mineralogischen Gesellschaft, Beihefte zum European Journal of Mineralogy, 11, MinWien 99, Wien, 1999. August 28.- September 1., Abstract, 67. *(poster presentation)*

Bali, E., Szabó, Cs., Vaselli, O. & Török, K. (2000): Carbonate bearing melt pockets and veins in upper mantle xenoliths from Bakony-Balaton Highlands and Little Hungarian Plain, Hungary. Minerals of the Carpathians International Conference, Miskolc, March 9-10, 2000., Acta Mineralogica-Petrographica, XLI., 13. *(poster presentation)*

Bali, E. (2000): Silicate melt pockets from Szentbékkálla ultramafic xenoliths (Bakony-Balaton Highland). (In Hungarian) Mining - Metallurgy - Geology Conference, Kolozsvár, March 17-19. 2000., 70. *(oral presentation)*

Bali, E., Szabó, Cs., Vaselli, O. & Török, K. (2000): The significance of melt pockets in upper mantle xenoliths from the alkali basalts of the Bakony-Balaton Highland Volcanic Field, Western Hungary. Mantle Dynamic Implications for Tethian Natural Hazard Mitigation, Kovászna, June 16-22. 2000., 3. *(oral presentation)*

Bali, E., Szabó, Cs., Vaselli, O. & Török, K. (2000): Origin of melt pockets in upper mantle xenoliths from the Bakony-Balaton Highland Volcanic Field, Western Hungary. Vijesti 37/3, 18. *(oral presentation)*

Szabó, Cs., Kovács, I., **Bali, E.**, Falus, Gy., Török, K. & Vaselli, O. (2002): Composition and Evolution of Lithosphere beneath the Carpathian-Pannonian Region. Mantle Dynamic Implications for Tethian Natural Hazard Mitigation 58.

Bali, E., Szabó, Cs., Vaselli, O. & Török, K. (2002): Carbonate-bearing melt pockets in upper mantle xenoliths from the Pannonian Basin. European carbonatites: implications for the sub-European mantle and their geohazard potential - Abstract volume. 57. *(oral and poster presentations)*

Szabó, Cs., **Bali, E.,** Falus, Gy., Török, K. Vaselli, O. & Downes, H. (2002): Composition and evolution of lithospheric mantle beneath the Pannonian basin: review. Fourth International workshop on Orogenic Lherzolites and Mantle Processes - Abstract volume, 165-166.

Bali, E., Peate, D.W., Zanetti, A. & Szabó, Cs. (2003): Significance of silicate melt pockets in the evolution of the subcontinental lithospheric mantle beneath the central Pannonian basin. EGS-AGU-EUG Joint Assembly, Nice. Geophysical Research Abstracts, 5, EAE 03-A 00654. *(poster presentation)*

Szabó, Cs., Falus, Gy., Kovács, I., Zajacz, Z., **Bali, E.** & Hidas, K. (2003): Composition and evolution of lithospheric mantle beneath the Pannonian basin: a petrographic and geochemical review. Mining - Metallurgy - Geology Conference, Zilah, 85.

Szabó, Cs., Falus, Gy., **Bali, E.,** Kovács, I., Zajacz, Z., Hidas, K. & Peate, D.W. (2003): Composition and evolution of lithospheric mantle beneath the Pannonian basin: a petrographic and geochemical review. The fourth Stephan Müller Conference of the European Geosciences Union, Geodynamic and tectonic evolution of the Carpathian Arc and its foreland: Environmental tectonics and continental topography - Abstract volume, 16. *(oral presentation)*

Szabó, Cs., Falus, Gy., Zajacz, Z., Kovács, I., **Bali, E.** & Hidas, K. (2003): Composition and evolution of the lithosphere beneath the Carpathian Pannonian

region: a review. 2003 Korea-Hungary International Joint seminar on Lithosphere Evolution of the Korean Peninsula and Subcontinental Lithospheric Mantle in the Pannonian Basin, Hungary, Abstract volume, 1-4.

Bali, E., Szabó, Cs & Peate, D.W. (2003): Mantle heterogeneity beneath the central Pannonian Basin. 2003 Korea-Hungary International Joint seminar on Lithosphere Evolution of the Korean Peninsula and Subcontinental Lithospheric Mantle in the Pannonian Basin, Hungary, Abstract volume, 48-53. *(oral presentation)*

Bali, E. (2004): Significance of special orthopyroxene-rich rocks in the upper mantle. 35th Hungarian Young Earth Scientists Conference, Sárospatak, March 19-20. 2004., Programs and abstracts, 23-24. (In Hungarian) *(oral presentation)*

Bali, E., Szabó, Cs., Török, K., Peate, D.W. & Bodnar, R.J. (2004): Significance of orthopyroxene-rich rocks in the upper mantle: a case study on xenoliths from alkali basalts of the Bakony-Balaton Highland Volcanic Field, Western Hungary. 32th IGC, Abstract volume, in press. *(oral presentation)*

References:

Baker, J.A., Waight, T.E. & Meyzen, C. (2004). Pb isotopic analysis of standards and samples using a ^{207}Pb-^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. Chemical Geology, submitted.

Bali, E., Szabó, Cs., Török, K. & Vaselli, O. (2001): The significance of carbonate-bearing and carbonate-free silicate melt pockets in the upper mantle: a case study on Szentbékkálla ultramafic xenoliths, Bakony-Balaton Highland Volcanic Field (Karbonáttartalmú és karbonátmentes szilikátolvadék-csomók jelentőssége a felsőköpenyben a szentbékkállai köpenyeredetű ultrabázisos zárványok példáján). (in Hungarian with English abstract). Bulletin of the Hungarian Geological Society, 131/3-4, 415-442.

Bali, E., Szabó, Cs., Vaselli, O. and Török, K. (2002): Significance of silicate melt pockets in upper mantle xenoliths from the Bakony-Balaton Highland Volcanic Field, Western Hungary. Lithos, 61, 79-102.

Bence, A., E. and Albee, A., L. (1968): Empirical correction factors for the electron microanalysis of silicates and oxides. Journal of Geology, 76, 382-403.

Dobosi, G. Downes, H., Embey-Isztin, A. and Jenner, G.A. (2003): Origin of megacrysts and pyroxenite xenoliths from the Pliocene alkali basalts of the

Pannonian Basin (Hungary). Neues Jahrbuch für Mineralogie Abhandlungen, 178/3, 217-237.

Downes, H., Embey-Isztin, A. and Thirlwall, M.F. (1992): Petrology and geochemistry of spinel peridotite xenoliths from the western Pannonian Basin (Hungary): evidence for an association between enrichment and texture in the upper mantle. Contributions to Mineralogy and Petrology., 107, 340-354.

Embey- Isztin A. and Scharbert H.G. (2000): Glasses in peridotite xenoliths from the western Pannonian basin. Annales Historico-Naturales Musei Nationalis Hungarici, 92, 5-20.

Embey-Isztin, A. (1976): Amphibolite/lherzolite composite xenolith from Szigliget, north of the Lake Balaton, Hungary. Earth and Planetary Science Letters, 31, 297-304.

Embey-Isztin, A., Dobosi, G. and Downes, H. (2001): Geochemical characterization of the Pannonian Basin mantle lithosphere and asthenosphere: an overview. Acta Geologica Hungarica, 44, 2001 2-3, 259-280.

Embey-Isztin, A., Scharbert, H.G., Dietrich, H. and Poulditis, H. (1989): Petrology and geochemistry of peridotite xenoliths in alkali basalts from the transdanubian volcanic region. Journal of Petrology, 34, 317-343.

Gaetani, G.A. and Grove, T.L. (1998): The influence of water on melting of mantle peridotite. Contributions to Mineralogy and Petrology, 131/4, 323-346.

Kelemen, P.B., Dick, H.J.B. and Quick, J.E. (1992): Formation of harzburgite by pervasive melt/rock reaction in the upper mantle. Nature, 358, 635-644.

Pearce N. J. G., Perkins W. T., Westgate J. A., Gorton M. P., Jackson S. E., Neal C. R. and Chenery S. P. (1997): A compilation of new major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. Journal of Geostandards and Geoanalysis 21, 115-144.

Szabó, Cs., Bodnar, R.J. and Sobolev, A.V. (1996): Metasomatism associated with subduction-related, volatile-rich silicate melt in the upper mantle beneath the Nógrád-Gömör Volcanic Field, Northern Hungary/Southern Slovakia: Evidence for silicate melt inclusions. European Journal of Mineralogy, 8, 881-899.

Szabó, Cs., Vaselli, O., Vannucci, R., Bottazzi, P., Ottolini, L., Coradossi, N. and Kubovics, I. (1995): Ultramafic xenoliths from the Little Hungarian Plain (Western Hungary): a petrologic and geochemical study. Acta Vulcanologica, 7(2), 249-267.

Török, K., **Bali, E.,** Szabó, Cs. and Szakál, J.A. (2003): Sr-barite droplets associated with sulfide blebs in clinopyroxene megacrysts from basaltic tuff (Szentbékkálla, western Hungary). Lithos, 66, 275-289.