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Origin of amphibole megacrysts in the Pliocene-Pleistocene basalts of the Carpathian-Pannonian region

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Abstract: Major and trace element compositions, stable H and O isotope compositions and Fe^{3+} contents of amphibole megacrysts of Pliocene-Pleistocene alkaline basalts have been investigated to obtain information on the origin of mantle fluids beneath the Carpathian-Pannonian region. The megacrysts have been regarded as igneous cumulates formed in the mantle and brought to the surface by the basaltic magma. The studied amphiboles have oxygen isotope compositions (5.4±0.2 ‰, 1 σ), supporting their primary mantle origin. Even within the small $\delta^{18}O$ variation observed, correlations with major and trace elements are detected. The negative $\delta^{18}O$-MgO and the positive $\delta^{18}O$-La/Sm(N) correlations are interpreted to have resulted from varying degrees of partial melting. The halogen (F, Cl) contents are very low (<0.1 wt. %), however, a firm negative (F+Cl)-MgO correlation ($R^2 = 0.84$) can be related to the Mg-Cl avoidance in the amphibole structure. The relationships between water contents, H isotope compositions and Fe^{3+} contents of the amphibole megacrysts revealed degassing. Selected undegassed amphibole megacrysts show a wide δD range from −80 to −20 ‰. The low δD value is characteristic of the normal mantle, whereas the high δD values may indicate the influence of fluids released from subducted oceanic crust. The chemical and isotopic evidence collectively suggest that formation of the amphibole megacrysts is related to fluid metasomatism, whereas direct melt addition is insignificant.

Key words: Carpathian-Pannonian region, mantle metasomatism, amphibole megacrysts, degassing, trace elements, stable isotopes.

Introduction

Megacrysts hosted in alkaline basalts are frequently studied in order to obtain information on the chemical characteristics of the mantle source. Among the usual megacryst assemblage (olivine, pyroxene, spinel, amphibole), amphibole is potentially the most important mineral due to the amount of information it can provide. Amphiboles are usually enriched in trace elements compared to other megacryst minerals (e.g. Witt-Eikschen & Harte 1994; Johnson et al. 1996), making trace element analyses relatively easy and accurate. Oxygen isotope compositions of amphiboles have long been studied with high precision due to the reactivity with the commonly used BrF_5 reagent in contrast to other megacryst minerals like olivine or spinel. Being a hydrous mineral, amphiboles may also be analysed for H isotope composition, thus yielding important constraints on metasomatic processes in the mantle. These features may make amphibole an excellent subject of mantle geochemistry studies. However, there are a number of factors that must be taken into account in interpreting the chemical and isotopic compositions. First, megacryst amphiboles are usually formed by metasomatic processes in the mantle, thus their co-existence with other megacryst minerals can be questionable. Second, trace element contents may be strongly fractionated due to crystallochemical variations in the amphiboles and its parent magma (H_2O activity, fO_2, etc., e.g. Ionov & Hofmann 1995; Oberti et al. 2000; Tiepolo et al. 2000), which are not very well constrained at present. Third, H isotope compositions are very sensitive to late-stage processes, like degassing and hydrothermal alteration. These uncertainties preclude simple and straightforward interpretations of geochemical data on amphiboles. Nevertheless, a combined approach using several independent methods can lead to reliable reconstruction of mantle geochemistry.

The Pliocene-Pleistocene alkaline basalts of the Pannonian Basin frequently contain amphibole megacrysts, which have been thoroughly studied for crystallochemical characteristics and trace element compositions (Zanetti et al. 1995). In recent studies, Downes et al. (1995) and Dobosi et al. (1998, 2003a) reported the trace element contents and O-Sr-Nd isotope data of the amphibole megacrysts. Their major conclusion is that the amphiboles reflect the primitive mantle source beneath the Pannonian Basin. The alkaline basalts and their mantle xenoliths have been widely investigated, making the region one of the best known areas of the world (see for example Kurat et al. 1991; Downes et al. 1992, 1995; Dobosi et al. 1995; Downes & Vaselli 1995; Embey-Isztin & Dobosi 1995; Harangi et al. 1995; Konečný et al. 1995a,b; Szabó et al. 1995a,b; Török & De Vivo 1995; Huraiová et al. 1996; Szabó et al. 1996; Kempton et al. 1997; Rosenbaum et al. 1997; Hurai et al. 1998; Seghedi et al. 2004). The trace element and radiogenic isotope studies showed that the mantle source was contaminated by subducted crustal material (as exemplified by the calc-alkaline volcanism that preceeded the alkaline basaltic one), especially in the central areas (Downes et al. 1992; Embey-Isztin & Dobosi 1995; Szabó et al. 1996; Seghedi et al. 2004). These results suggested that the amphibole megacrysts may provide useful information on the metasomatizing fluids and melts. H and O isotope studies coupled with H_2O wt. % and Fe^{3+} % determinations on mantle-derived rocks and their minerals from the Carpathian-Pannonian region are very rare (Hurai et al. 1998; Demény et al. 2001, 2004). In this study we report major and trace element data, stable isotope compositions and redox characteristics from amphibole megacrysts and a hornblendite vein (from Szigliget, Balaton Highland, Hungary, see also Embey-Isztin 1976) and compare the compositions to those obtained on xenolith-hosted amphiboles from Southern Slovakia (Hurai et al. 1998). With the combined use of these methods we discuss the processes coincidental with amphibole crystallization.

Geological background and samples

The Neogene volcanism developed after and probably in response to a series of tectonic events, which formed the Carpathian Basin. The main factors controlling the Neogene evolution of the Carpathian Basin and related post-extensional volcanism are continental collision in the Central and Eastern Alps, which induced extensional collapse of the orogenic terranes, subduction of the European plate along the Carpathians and related calc-alkaline volcanism, updoming of the asthenosphere and heating, as well as thinning of the lithosphere (e.g. Embey-Isztin et al. 1990; Szabó et al. 1992; Horváth 1993). Adiabatic decompression in the rising mantle caused partial melting and the melts erupted as basaltic lava flows and tuffs (Dobosi et al. 1995; Harangi et al. 1995; Konečný et al. 1995a,b). The alkaline basaltic volcanism span the period of 17 to 0.5 m.yr. (see Pécskay et al. 1995 and Konečný et al. 1995a for review). Alkali basalts are remarkably fresh (Embey-Isztin & Scharbert 1981; Embey-Isztin et al. 1993a,b), moderately porphyritic and holocrystalline. The basalts comprise phenocryst olivine (forsterite (Fo) content of 78–86), in some cases accompanied by clinopyroxene. The matrix is composed of plagioclase, Ti-rich clinopyroxene, olivine, titanomagnetite occasionally coexisting with ilmenite, and apatite (Embey-Isztin et al. 1993a). Sr, Nd, and Pb isotope ratios have values between inferred DM (depleted mantle), EM II (enriched mantle II), and HIMU (high μ, high $^{238}U/^{204}Pb$) (Salters et al. 1988; Embey-Isztin et al. 1993a; Embey-Isztin & Dobosi 1995; Harangi et al. 1995). The isotope compositions of the lavas of the central part of the Carpathian-Pannonian region plot closer to the EM II composition than those of the marginal areas with a higher amount of an asthenospheric component. Low Nb/La, Ce/Pb, $^{143}Nd/^{144}Nd$, $^{206}Pb/^{204}Pb$, and high $^{87}Sr/^{86}Sr$ and $^{207}Pb/^{204}Pb$ ratios have been interpreted as evidence for a relationship of the EM component with a metasomatic enrichment process of the mantle lithosphere during Tertiary plate subduction (Rosenbaum et al. 1997).

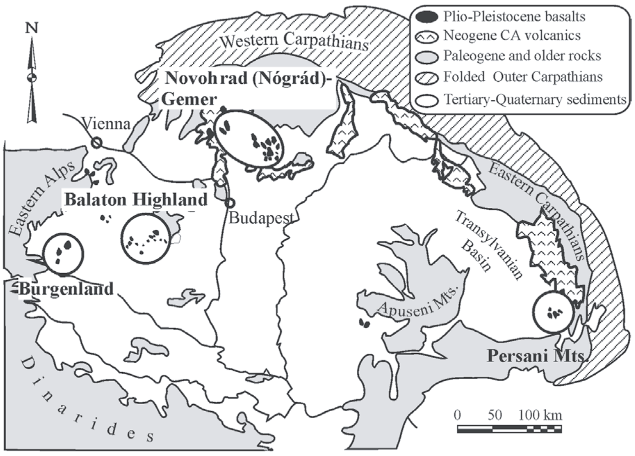

Fig. 1. Geological sketch-map of the Carpathian-Pannonian region and sample locality areas. After Dobosi et al. (1998).

The amphibole megacrysts of the alkaline basalts have been interpreted as fragments of igneous cumulates precipited from an early magma intrusion and brought to the surface by later basaltic magmatism (Szabó & Taylor 1994; Downes et al. 1995; Huraiová et al. 1996; Dobosi et al. 2003a). The localities studied in this paper are in Burgenland (Tobaj and Güssing, Austria; samples Tob, Gü), the Balaton Highland (Balatonboglár, Mindszentkálla, Szigliget, Bondoróhegy, Hungary; samples: Bb, Bog, M, Szg, Bo), the Nógrád (Hungary)-Gemer (Slovakia) region (Mašková, west of Lučenec, Slovakia, and Szilváskő, east of Salgótarján, Hungary; samples: Mas, Szil) and the Persani Mountains (Trestia Valley, Romania; samples: Trs) (see also Fig. 1). Hornblendite veins from composite mantle xenoliths from Szigliget (samples Szg and Sz-3024) (see also Embey-Isztin 1976) are also studied. The amphibole megacrysts reach 1–3 cm in diameter. The collection criteria were the unaltered state and the freshness of the host rocks. Out of the collection, only those megacrysts were analysed whose fragments were clear and inclusion-free under binocular microscope. The purity of the amphibole separates was checked by the standard XRD technique.

Analytical methods

Mineral major element compositions were determined with a JEOL Superprobe 733 electron microprobe at the Laboratory for Geochemical Research of the Hungarian Academy of Sciences. The conditions used were: wavelength dispersive spectrometers, 15 kV accelerating voltage, 40 nA beam current, 20 μm beam diameter, 6×4 s counting time. For F and Cl analyses beam current was modified to 100 nA. Standardization was conducted by using mineral and artificial glass standards (BaF_2 and scapolite for F and Cl, respectively). The raw data was corrected using the ZAF correction program provided by JEOL. The relative errors of major element analyses are lower than 2 % for oxides with >10 wt. %, about 5–7 % for oxides with 1–5 wt. %, and about 30 % for halogens. The H_2O content of amphiboles was determined using the vacuum fusion method adapted after Vennemann & O'Neil (1993).

Hand-picked amphibole grains were powdered using an agate mortar and pestle under ethanol, which dries quickly at room temperature, thus, oxidation during prolonged grinding was avoided. The ^{57}Fe Mössbauer spectra of amphiboles were recorded at room temperature in constant acceleration mode with a Wissel spectrometer using ^{57}Co(Rh) source at the Department of Nuclear Chemistry, Budapest. The Fe^{3+} contents were calculated from the relative spectral contributions of the doublets of the corresponding Fe^{2+} and Fe^{3+} species, using a Lorentzian least square fitting by Mösswinn®. In order to avoid even the residual minor texture, the samples were recorded at the magic angle (54.7 deg), resulting in symmetrical doublets in the spectra. This method is trivially applicable for single crystals, but it is also good for polycrystals if the microcrystals have random distribution in the plane perpendicular to the direction of the gamma rays, a condition which is very easy to meet. Analysis of the spectra under such conditions, as far as the Fe^{2+} to Fe^{3+} ratio is concerned, is very reliable (±1 %). Further deconvolution of the spectra into several Fe^{3+} and Fe^{2+} doublets is rather ambiguous, but it does not interfere with the Fe^{2+}/Fe^{3+} ratio if the fit in the statistical sense is correct. This is due to the fact that the higher velocity lines of the Fe^{2+} doublets do not overlap with the Fe^{3+} doublet lines.

Laser ablation ICP-MS trace element analyses were carried out on a VG Elemental PQ2+ ICP-MS coupled to a 4D Engineering (Hannover, Germany) excimer laser system at the Southampton Oceanography Centre. Measurements were made using a 30 µm laser beam focused on the polished sample surface. Following a pre-ablation time of 10 seconds, data were collected for 30 seconds. The analytical protocol followed the blank–standard–sample–standard pattern. For the purpose of calibration and monitoring instrument performance during the analysis session, a polished piece of the NIST 610 glass standard containing the trace elements of interest was used. After collection, the trace element data were corrected for any instrumental drift, gas blank subtracted and then calibrated against the NIST 610 standard (using the 'preferred average' values of Pearce et al. 1997). To correct for matrix effects between the NIST 610 standard and the various minerals analysed, internal corrections were applied using appropriate element abundances (e.g. Ca, Ti, etc.) determined by electron microprobe analyses. On the NIST 610 standard, 10 repeat measurements are reproducible to within 5 %. Accuracy of the LAM-ICP-MS analyses was checked by comparison with INAA data on amphibole samples. The REE concentrations are accurate within 15 %. Classical ICP-MS techniques may produce better accuracy, however, laser-ablation analysis has the advantage of choosing the freshest (i.e. least altered) mineral surface, which may be difficult with bulk analysis. The accuracy is reflected by Fig. 3, which shows good agreement between trace element data obtained on similar samples but in different laboratories (see also Dobosi et al. 2003a).

H and O isotope compositions, and water contents were measured on hand-picked amphibole separates by conventional extraction and mass spectrometric techniques (Clayton & Mayeda 1963; Vennemann & O'Neil 1993; Demény 1995; Demény et al. 1997) using Finnigan MAT delta S and 252 type mass spectrometers at the Laboratory for Geochemical Research, Budapest and the University of Tübingen, respectively. Some of the amphibole megacrysts have been analysed using the laser-based method at the University of Tübingen. The method used was adapted after Sharp (1990) using F_2 as reagent, a Pt-disc sample holder, and measuring the $^{18}O/^{16}O$ on O_2 gas (Rumble & Hoering 1994; Kasemann et al. 2001). The results are expressed in the δ-notation ($\delta = (R_1/R_2-1)\times1000$ where R_1 and R_2 are the D/H or $^{18}O/^{16}O$ ratios in the sample and the standard, respectively) in per mil (‰) relative to V-SMOW. Reproducibilities are ±2 ‰ for δD and better than ±0.15 ‰ for ^{18}O values of the minerals analysed in duplicate. NBS-28 quartz and UWG-2 garnet standards yielded $\delta^{18}O$ values of 9.64 ‰ and 5.83±0.11 ‰ (1 σ, n = 5, theoretical value: 5.8 ‰, Valley et al. 1995), respectively, during the course of the laser-based analyses.

Results

The major element compositions of amphiboles determined by electron microprobe analyses are listed in Table 1. Classification of amphiboles was conducted according to Leake et al. (1997) based on chemical compositions determined by means of electron microprobe analyses. The proportion of Fe^{3+} was also calculated according to Schumacher (1997), though Fe^{3+}/Fe_{tot} ratios were determined by Mössbauer spectroscopy (see Table 2). Taking crystal chemical considerations into account, Schumacher (1997) established 3 maximum and 3 minimum criteria. These criteria allow the determination of an interval rather than an exact value for the Fe^{3+}/Fe^{2+} ratio. The calculations yielded 0 as the minimum value for all of the studied amphiboles, thus, Table 1 shows only the upper limit Fe^{3+}/Fe^{2+} ratios along with ion numbers calculated for 23 oxygens. All of the studied amphiboles plot in the calcic amphibole field of Leake et al. (1997). The lines in Fig. 2 show the variations of the ion number calculations between the lower and upper limits of Fe^{3+}/Fe^{2+} ratios calculated for the individual amphibole samples according to Schumacher (1997). The ion numbers were also calculated using the Fe^{3+}/Fe^{2+} ratios determined by Mössbauer spectroscopy. These latter data plot on the lines obtained by using the method of Schumacher (1997), except for two samples (M-2001 and M-2002, see Tables 1 and 2), where the calculated upper limit is lower than the ratio obtained by Mössbauer spectroscopy, thus as a consequence the calculated substitution at the "C" crystal position is lower than 5. The large range between lower and upper Fe^{3+}/Fe^{2+} ratio limits (reaching 0.97) make the classification based on calculated Fe^{3+}/Fe^{2+} ratio ambiguous (see also Fig. 2). Thus, a firm classification can be made using the Mössbauer spectroscopy data. Fig. 2 shows that the studied amphiboles are kaersutites and magnesio-hastingsites at Mašková, pargasites at Tobaj and Güssing (Burgenland) and magnesio-hastingsites at the other localities. As shown by Table 1, the most significant

Table 1: Chemical compositions (major elements in weight %, trace elements in ppm) of amphibole megacrysts from alkaline basalts of the Carpathian-Pannonian region. Electron microprobe data are averages of two analyses selected from 4–5 analyses on the basis of reliablity (e.g. oxide total). Fe^{3+}/Fe_{total} are **maximum** ratios calculated following Schumacher (1997). Trace element compositions are averages of 8–10 laser spot analyses.

	Tob-1	Tob-2	Gü-1	M-2001	M-2002	MAS-1	MAS-2	MAS-3	Szil-1	Trs-2007
SiO_2	40.47	41.43	40.54	39.29	39.66	39.74	39.76	40.71	38.94	39.37
TiO_2	3.27	3.35	3.75	3.67	3.70	5.43	4.29	5.10	3.99	4.28
Al_2O_3	14.54	14.45	14.10	14.48	14.67	15.57	14.81	15.68	15.35	15.42
FeO	7.84	8.80	7.92	13.93	14.22	9.38	9.72	10.51	12.17	13.24
MnO	0.05	0.08	0.10	0.15	0.15	0.09	0.10	0.12	0.15	0.17
MgO	15.70	15.0	14.76	11.17	10.93	14.32	14.06	13.33	12.35	11.45
CaO	10.31	10.15	10.85	9.88	10.28	10.05	10.14	10.28	10.51	10.05
Na_2O	2.37	2.47	2.32	2.69	2.54	2.94	2.68	2.97	2.58	2.70
K_2O	2.00	1.94	1.96	1.92	2.05	0.82	1.21	0.89	1.50	1.64
Cl	0.02	0.03	0.02	0.04	0.04	0.02	0.02	0.02	0.04	0.06
F	0.01	0.01	0.03	0.03	0.03	0.02	0.01	0.02	0.01	0.02
SUM	96.58	97.73	96.35	97.24	98.25	98.36	96.80	99.60	97.59	98.37
Fe^{3+}/Fe_{total}	0.966	0.787	0.431	0.402	0.312	0.816	0.735	0.000	0.503	0.432
Si	5.841	5.930	5.942	5.834	5.856	5.650	5.768	5.851	5.704	5.747
Al(iv)	2.159	2.070	2.058	2.166	2.144	2.350	2.232	2.149	2.296	2.253
Al(vi)	0.315	0.367	0.378	0.369	0.409	0.259	0.300	0.507	0.354	0.401
Ti	0.355	0.361	0.413	0.410	0.411	0.581	0.468	0.551	0.440	0.470
Fe^{3+}	0.914	0.829	0.419	0.695	0.548	0.910	0.866	0.000	0.751	0.698
Mg(c)	3.378	3.209	3.225	2.473	2.406	3.035	3.040	2.856	2.697	2.492
Fe^{2+}(c)	0.032	0.225	0.552	1.035	1.208	0.205	0.313	1.086	0.740	0.918
Mn(c)	0.006	0.010	0.012	0.019	0.019	0.011	0.012	0.000	0.019	0.021
Mg(b)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe^{2+}(b)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.177	0.000	0.000
Mn(b)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.015	0.000	0.000
Ca(b)	1.594	1.557	1.704	1.572	1.626	1.531	1.576	1.583	1.650	1.572
Na(b)	0.406	0.443	0.296	0.428	0.374	0.469	0.424	0.225	0.350	0.428
Na(a)	0.258	0.242	0.363	0.347	0.354	0.341	0.330	0.602	0.382	0.336
K	0.368	0.354	0.367	0.364	0.386	0.149	0.224	0.163	0.280	0.305
ΣKation	15.626	15.596	15.730	15.710	15.740	15.490	15.554	15.765	15.663	15.642
(Na+K)a	0.63	0.60	0.73	0.71	0.74	0.49	0.55	0.77	0.66	0.64
Mg#	0.99	0.93	0.85	0.71	0.67	0.94	0.91	0.69	0.79	0.73
Rb	14	16	13			3	5			
Sr	296	417	415			478	402			
Y	8	9	10			15	14			
Zr	30	52	54			31	34			
Nb	13	16	16			12	16			
Cs	0.05	0.04	0.09			0.04	0.10			
Ba	235	302	309			160	273			
La	3.0	4.6	4.7			2.2	3.2			
Ce	10	15	14			8	11			
Pr	1.7	2.5	2.4			1.5	2.1			
Nd	10	14	15			10	13			
Sm	2.9	4.1	4.0			3.6	4.2			
Eu	1.0	1.3	1.5			1.5	1.7			
Gd	2.7	3.6	4.0			3.1	3.2			
Tb	0.35	0.46	0.48			0.60	0.71			
Dy	1.7	2.2	2.7			3.6	3.4			
Ho	0.30	0.35	0.33			0.55	0.57			
Er	0.67	0.84	1.02			1.57	1.36			
Tm	0.07	0.09	0.09			0.18	0.16			
Yb	0.51	0.75	0.71			1.22	1.11			
Lu	0.06	0.07	0.06			0.14	0.11			
Hf	1.4	2.2	2.0			1.2	1.6			
Ta	0.68	0.80	0.92			0.54	0.74			
Pb	0.13	0.30	0.33			0.23	0.21			
Th	0.07	0.07	0.04			0.00	0.00			
U	0.03	0.06	0.02			0.05	0.12			

chemical differences are in the MgO, FeO and TiO_2 contents. Areal variations among sampling localities have not been observed. The Cl and F contents are rather low ranging between 0.02 and 0.06 wt. % and 0.01 and 0.03 wt. %, respectively. Although the halogen contents are close to detection limits, a firm correlation with MgO content occurs. The F and Cl analyses were conducted using separate standardization procedure, thus any measurement-related artifact can be excluded. The mg# numbers tend to decrease with increasing F+Cl content (Table 1, the correlation calculation yields $R^2 = 0.84$). Interestingly, the halogen contents have no relationship with the H_2O content of the amphiboles (Table 1), thus, they are not subject to simple OH^-–F+Cl substitution.

Trace element compositions are listed in Table 1. The samples show only small, but firm variations (Fig. 3). Chondrite-normalized REE and primitive mantle-normalized trace element diagrams (Fig. 4) show that the megacrysts studied are very similar to those analysed by Dobosi et al. (2003a) from the Balaton Highland Volcanic Field (western part of the Pannonian Basin). Even within the small variations observed, sys-

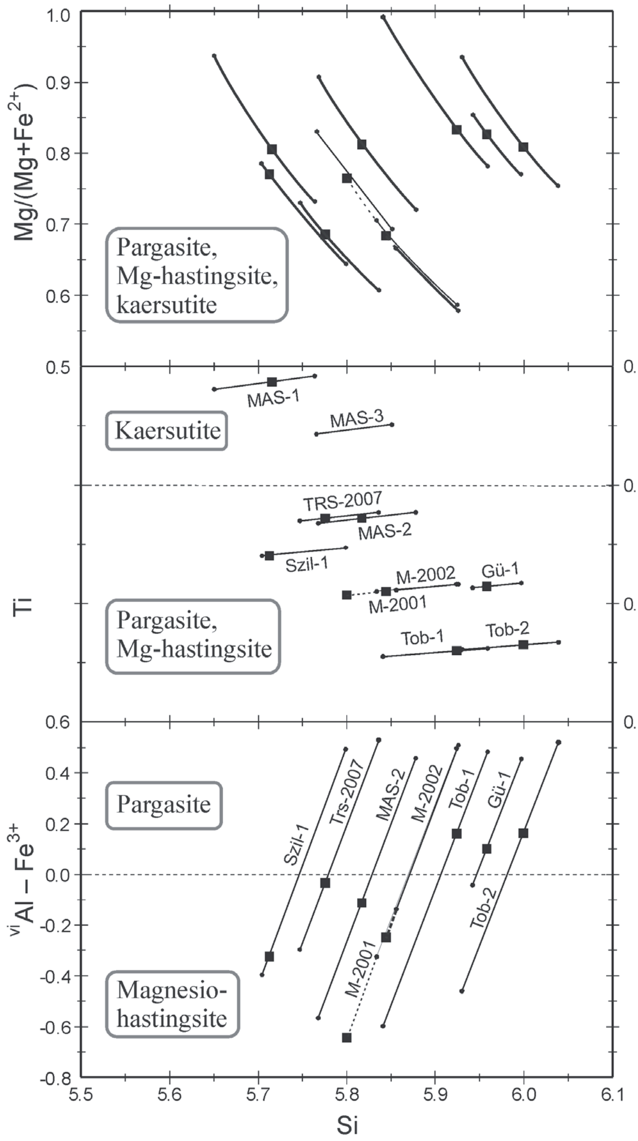

Fig. 2. Classification diagrams of Leake et al. (1997) for calcic amphiboles. The lines represent intervals obtained by Fe^{3+}/Fe_{tot} calculation using the method of Schumacher (1997); diamonds are the compositions calculated on the basis of Mössbauer spectroscopy data (listed in Table 2).

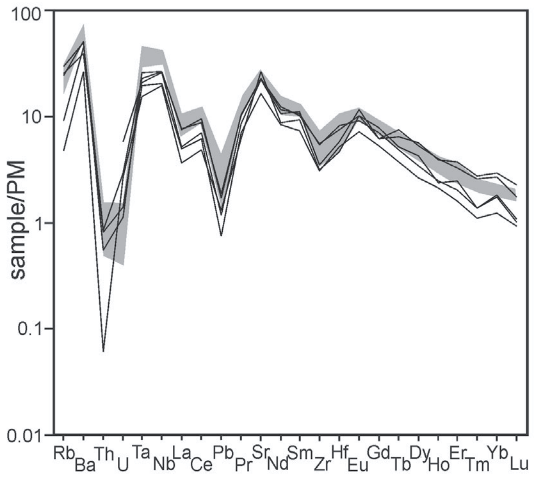

Fig. 3. Trace element contents normalized to the primitive mantle (Hofmann 1988) in amphibole megacrysts from the Carpathian-Pannonian region. Shaded field: amphibole megacrysts of Dobosi et al. (2003a).

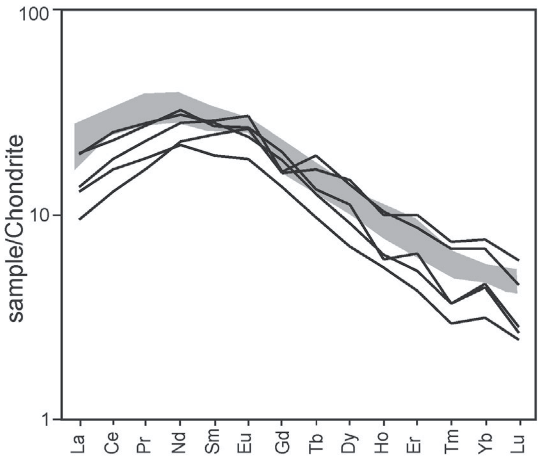

Fig. 4. Chondrite-normalized (Anders & Grevesse 1989) REE-contents in amphibole megacrysts from the Carpathian-Pannonian region. Shaded field: amphibole megacrysts of Dobosi et al. (2003a).

tematic relationships with major element and stable isotopic compositions are detected (Figs. 5, 7). Fig. 5 shows that there is a negative correlation between mg# and La/Sm ratios in the amphibole megacrysts of the Pliocene-Pleistocene basalts. The Tob-1 megacrysts have peculiar chemical and oxygen isotope characteristics (see Figs. 5, 6, 9), but being only an outlier, this difference will not be discussed.

The stable isotope compositions also show some variations. The $\delta^{18}O$ values (Table 2) of amphibole megacrysts scatter around the primary mantle compositions (5.5 ‰, Mattey et al. 1994; Chazot et al. 1997) with an average of 5.45±0.23 ‰ (1 σ, n = 15). These $\delta^{18}O$ values are very similar to those reported by Dobosi et al. (1998, 2003a) for amphibole megacrysts from the alkaline basalts (5.27±0.15 ‰, 1 σ, n = 8). Although the variations in the $\delta^{18}O$ values are close to the analytical precision, the oxygen isotope compositions are negatively correlated with MgO and positively with La/Sm(N) ratios (Fig. 6).

The hydrogen isotope compositions show a wide variation from −107 ‰ to −15 ‰ (Table 2). The δD values are plotted as a function of H_2O contents of amphiboles (Fig. 7). The δD and $\delta^{18}O$ data on xenolith-hosted amphiboles from the Pliocene to Pleistocene maar volcanoes and tuff cones of Southern Slovakia (Hurai et al. 1998) plot in the normal mantle ranges. Although Fe^{3+} contents are given only on the basis of electron microprobe analyses for two amphibole samples analysed for δD and $\delta^{18}O$, they can be used as a rough estimate of the oxidation state. Thus, the data of Hurai et al. (1998) will be used for comparison for the discussion of δD-$\delta^{18}O$-H_2O wt. %-Fe^{3+} correlations (see also Figs. 7, 8, 10 and 11). A slight positive correlation appears with low δD values

Table 2: Oxygen and hydrogen isotope compositions, water content (in weight %) and Fe^{3+} contents (in % as $100\times Fe^{3+}/Fe_{total}$) of amphibole megacrysts from alkaline basalts of the Carpathian-Pannonian region.

Sample	$\delta^{18}O$	δD	H_2O	Fe^{3+}
Tob-1	5.8	–29	1.33	28.28
Tob-2	5.2	–19	1.20	
Tob-3	5.5	–25	1.28	28.33
Gü-1	5.4	–24	1.25	30.68
Gü-2	5.2	–31	1.24	31.11
Bog-2001	5.5	–29	1.11	
M-2001	5.9	–107	0.60	56.11
M-2002	5.6	–61	1.04	36.63
MAS-1	5.1	–31	0.82	34.47
MAS-2	5.1	–75	0.87	40.69
MAS-3	5.4	–56	0.97	31.79
Szil-1	5.5	–15	0.99	46.45
Trs-2007	5.5	–49	1.15	28.14
Trs-2008	5.5	–59	1.05	29.20
Trs-2018	5.4	–50	1.16	31.00
Szg-3024		–61	1.00	29.34
Szg		–61	1.11	27.79
Bb-2		–52	1.29	32.96
Bo-20		–81	1.22	

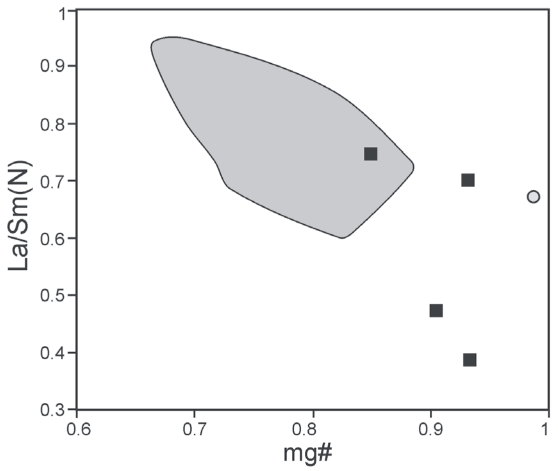

Fig. 5. La/Sm ratios normalized to the primitive mantle (Hofmann 1988) in amphibole megacrysts vs. their mg numbers. Filled square: this study, grey circle: Tob-1. Shaded field: amphibole megacrysts of Zanetti et al. (1995) and Dobosi et al. (2003a).

associated with low H_2O contents, suggesting that degassing may be responsible for the large δD variation observed. Systematic δD differences between sampling localities do not exist.

One of the most important parts of the information needed for the interpretation of hydrogen isotope compositions is the Fe^{3+} content of the amphiboles (Dyar et al. 1992; Feldstein et al. 1996). Fe^{3+} contents expressed as percentages ($100\ Fe^{3+}/Fe_{tot}$) also show a large scatter from 28 to 56 % (Table 2). When the Fe^{3+} contents are plotted as a function of H_2O %, a slight negative correlation appears (Fig. 8), that again points to H_2-degassing, which causes iron oxidation in the amphibole structure (Feldstein et al. 1996; King et al. 1999). Similarly to the hydrogen isotope compositions, the oxidation state of amphibole is sensitive to late stage processes, whose effects can be superimposed on the primary features, thus a combined evaluation is needed to explain the observed variations. The hornblendite veins have chemical and isotopic characteristics very similar to those of the megacrysts (see Tables 1 and 2), thus they will not be discussed separately.

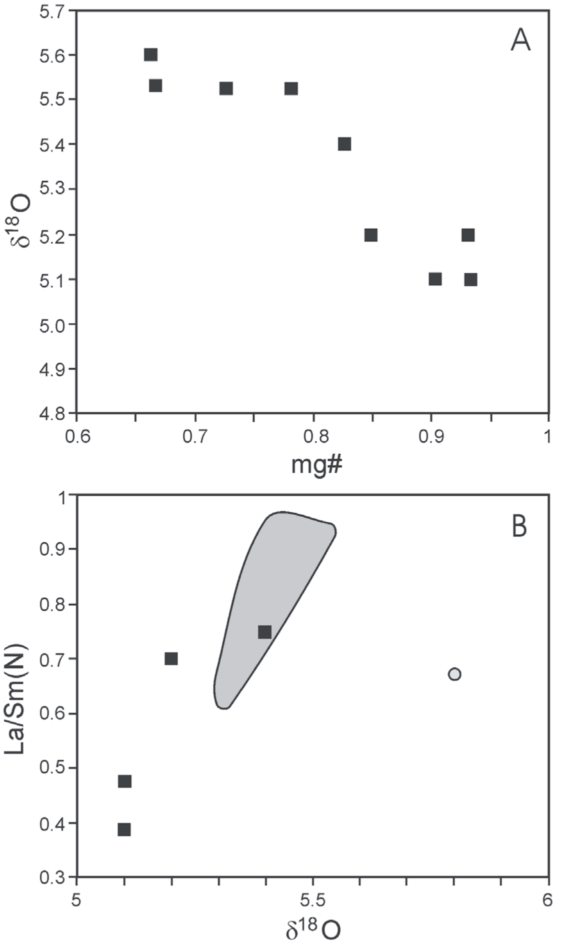

Fig. 6. A — $\delta^{18}O$ values (in ‰ relative to V-SMOW) vs. **mg** numbers. **B** — $\delta^{18}O$ values vs. La/Sm ratios normalized to the primitive mantle (Hofmann 1988). Legend as in Fig. 5.

Discussion

Origin of $\delta^{18}O$ variation

The first question about the origin of amphibole megacrysts is their primary mantle nature, which is best reflected by the oxygen isotope composition. Although the $\delta^{18}O$ range of the megacrysts is very close to the normal mantle composition with a small scatter, a systematic variation appears. The negative correlation between $\delta^{18}O$ values and MgO contents (Fig. 6) may be related to several processes: (i) crystal chemical effects, (ii) crustal contamination either by assimilation during magma transport through the crust or by source contamination by subducted material, (iii) fractional crystallization, or (iv) partial melting. Since the oxygen isotope fractionation due to Mg-Fe variation does not exceed 0.2 ‰ (Zheng 1993), the effect of crystal chemistry on the observed oxygen isotope variation (0.5 ‰, excluding Tob-1 amphibole on the basis of its chemical compositions, see Results) can be excluded. Crustal contamination processes may explain the $\delta^{18}O$

and MgO variation. Trace element compositions, especially certain trace element ratios that are sensitive to crustal material addition (Ce/Pb, Nd/Pb, Ba/Th, etc.) can attest the contamination hypothesis. However, no correlation between these ratios and the $\delta^{18}O$ values could be observed (Fig. 9), thus contamination is unlikely as a cause of the $\delta^{18}O$-MgO variation. Fractional crystallization of the basaltic magma can also produce the observed changes provided that high-MgO and low-$\delta^{18}O$ minerals (e.g. olivine) are crystallized. Apart from the amphibole megacrysts, the basalts contain numerous pyroxene, spinel and olivine mega- and xenocrysts. Crystallization of forsteritic olivine and Mg-Al spinel from the basaltic magma has been modelled using MgO % = 15 wt. % and $\delta^{18}O$ = 5.1 ‰ as starting compositions, theoretical mineral compositions and published mineral-melt oxygen isotope fractionations (Mattey et al. 1994; Chazot et al. 1997). The calculations indicate that about 30 % of the magma should have crystallized as olivine and spinel in order to explain the observed $\delta^{18}O$-mg# variation. Zanetti et al. (1995) observed varying correlations between mg# and elements with different compatibility, which they interpreted as resulting from fractional crystallization from evolved melt. However, olivine and spinel crystallization cannot explain the relationships between oxygen isotope composition and some trace element ratios (e.g. La/Sm, see Fig. 6) considering the very low mineral-melt partition coefficients for olivine and spinel (Beattie 1994; Horn et al. 1994). Due to the low partition coefficients, crystallization of olivine and spinel would not affect the trace element content of the residual melt significantly. Other minerals (e.g. pyroxene and amphiboles) with higher mineral-melt coefficients have lower MgO contents or higher $\delta^{18}O$ values, resulting in lower mineral-melt oxygen isotope fractionation (Mattey et al. 1994; Chazot et al. 1997). The degree of crystallization that would be needed to explain the observed $\delta^{18}O$ variations (>99 % for pyroxene and >85 % for amphibole considering Rayleigh fractionation) is unreasonably high.

Generation of basaltic magma due to a low degree partial melting of a peridotitic source may result in elevated $\delta^{18}O$ values in the basalt (Eiler 2001) and would also produce low MgO content and elevated La/Sm ratio in accordance with the relationships observed in this work. The melting process may also produce volatile-rich magma. However, as we have seen degassing may affect the amphiboles, thus the amphiboles' water contents may not reflect magma compositions. The slight increase in halogen contents may also be related to the melting process. However, the halogen contents of amphiboles strongly depend on crystal chemistry (Morrison 1991). The negative F+Cl–MgO correlation can also be related to the Mg-Cl avoidance, as suggested by Morrison (1991).

In summary, the oxygen isotope compositions of amphibole megacrysts are in accordance with their mantle origin. According to relationships among major, minor and trace element contents, the small $\delta^{18}O$ variations observed may be explained in terms of varying degrees of partial melting.

Origin of mantle fluids

Hydrogen isotope compositions may provide additional information on the origin of the fluids responsible for amphibole

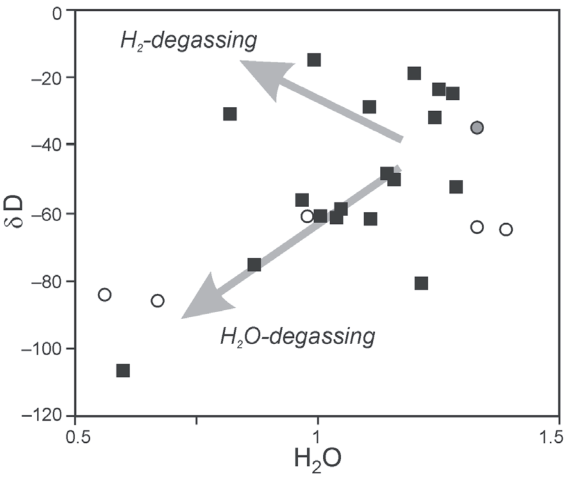

Fig. 7. δD values (in ‰ relative to V-SMOW) vs. H_2O contents (in wt. %) in amphibole megacrysts and hornblendite veins. See text for degassing effects. Open circles: from Hurai et al. (1998) and J. Hoefs (pers. comm.).

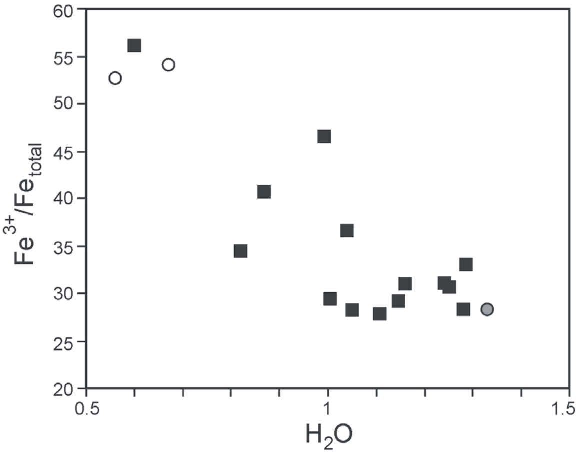

Fig. 8. Fe^{3+} contents (in % relative to Fe_{total}) vs. H_2O contents (in wt. %) in amphibole megacrysts. Open circles: from Hurai et al. (1998) and J. Hoefs (pers. comm.).

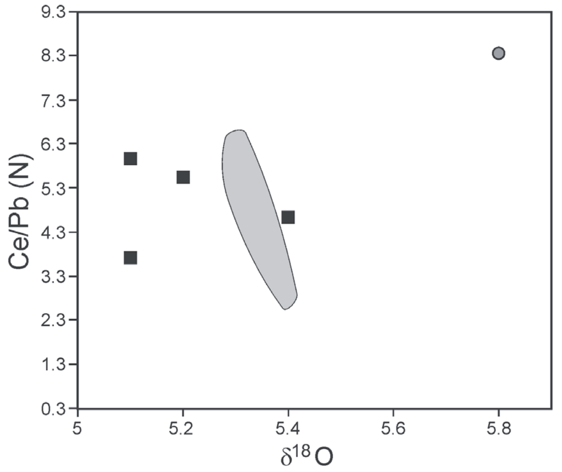

Fig. 9. Primitive mantle normalized (Hofmann 1988) Ce/Pb ratios vs. $\delta^{18}O$ values (in ‰ relative to V-SMOW) in amphibole megacrysts. Legend as in Fig. 5.

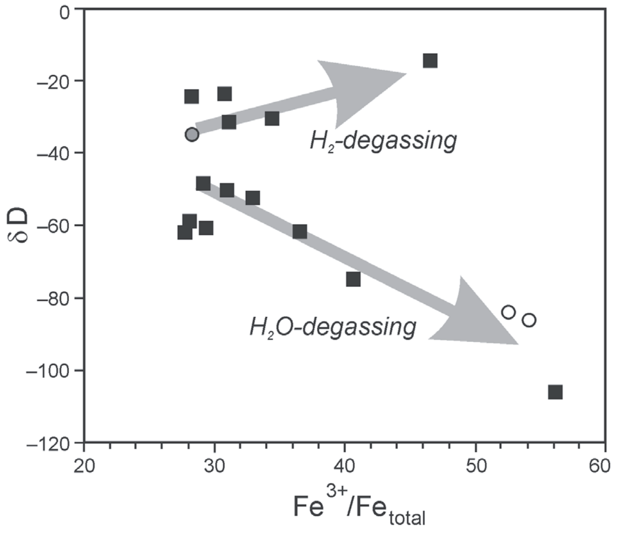

Fig. 10. δD values (in ‰ relative to V-SMOW) as a function of Fe^{3+} contents (in % relative to Fe_{total}) in amphibole megacrysts. Open circles: from Hurai et al. (1998). See text for degassing effects.

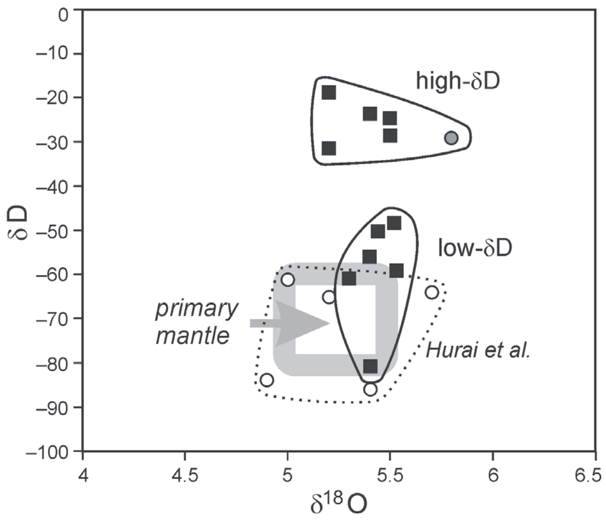

Fig. 11. δD vs. $\delta^{18}O$ values (in ‰ relative to V-SMOW) in undegassed amphibole megacrysts. Open circles: from Hurai et al. (1998). Mantle ranges: see text.

formation. To evaluate the obtained δD values, their primary nature should be proved and the effects of secondary processes, such as weathering, alteration and degassing have to be eliminated. Low temperature alteration can be ruled out owing to the absence of secondary minerals (Fe-oxide-hydroxides, chlorite, clay minerals) and elevated H_2O content. Further, preservation of primary mantle oxygen isotope signature and correlations with trace element ratios argue against significant alteration.

Degassing results in depletion in water in the amphibole and increasing oxidation in the case of hydrogen release. The positive correlation between δD and water content indicates that degassing may have indeed affected the studied amphiboles (Fig. 7).

Degassing of amphibole is often associated with oxidation, that is enrichment in Fe^{3+} (Dyar et al. 1992; King et al. 1999). This effect can be observed in the Fe^{3+}-H_2O plot (Fig. 8), which shows a weak negative correlation between these variables. Dyar et al. (1993) have suggested another mechanism for the water-deficient and oxidized nature of mantle kaersutites. Considering the diffusion rate of hydrogen and mantle-to-surface transport time of megacrysts, they found near-complete degassing of large crystals difficult. Instead, they proposed migration of oxidized metasomatic fluids in the mantle. However, amphibole has a good cleavage, which decreases the effective grain size in term of diffusion. This is indicated by host melt infiltration into cleavage planes observed during hand-picking under binocular microscope. Thus, we consider degassing a more likely process. Degassing may occur as dehydrogenation (H_2-loss) and dehydration (partial breakdown of amphibole). Dehydrogenation means preferential loss of the light H isotope, leaving the residual amphibole enriched in deuterium (Dyar et al. 1992; Vennemann & O'Neil 1996). This process may explain the compositions of the strongly D-enriched samples shown in Fig. 7, as the high-δD group (> –40 ‰) shows negative correlation in agreement with dehydrogenation. On the other hand, H_2O loss would cause a negative δD shift in the amphibole (Suzuoki & Epstein 1976; Graham et al. 1984; Vennemann & O'Neil 1996). This process appears in the low-δD (< –50 ‰) group in Fig. 7. On the basis of the data plotted in Figs. 7, 8 and 10, the samples likely to have suffered degassing (low H_2O %, Fe^{3+}/Fe_{tot} > 35 %) must be excluded from the evaluation of primary δD characteristics of parental magma.

Fig. 11 shows the hydrogen and oxygen isotope compositions of undegassed amphiboles. It is apparent that only some samples fall close to the average upper mantle compositions ($\delta^{18}O = 5.5 \pm 0.2$ ‰, δD = –70 ± 10 ‰, Boettcher & O'Neil 1980; Kyser & O'Neil 1984; Mattey et al. 1994; Chazot et al. 1997; Javoy 1998). Hence, these samples may represent the primary uncontaminated asthenospheric mantle. The low-δD group partially overlaps the field of xenolith-hosted amphiboles from Southern Slovakia (Hurai et al. 1998). However, the amphiboles with the lowest δD values have low H_2O contents (< 0.7 wt. %, see also Fig. 7) indicating degassing, thus the primary compositions for the xenolith-hosted amphiboles studied by Hurai et al. (1998) can be estimated at about –60 ‰.

Although the megacrysts studied in this paper are characterized by mantle-like $\delta^{18}O$, they form two groups according to their δD values (Figs. 10, 11). As shown in Fig. 10, the high-D group cannot be produced from the low-δD one by dehydrogenation as they have identical Fe^{3+} contents. Indeed, the Fe^{3+} content of 27 % seems to reflect an initial oxidation degree characteristic of the mantle source. Thus, the δD values also represent mantle compositions ranging from about –60 to –20 ‰. The low δD limit is close to the normal mantle range, but the high δD values are rather rare in terrestrial rocks and are usually found in rocks, which have undergone seawater-rock exchange (e.g. Stakes & O'Neil 1982; Yui & Jeng 1990). The constant $\delta^{18}O$ values exclude contamination by seawater-bearing sediments regarding the strong ^{18}O-enrichment in sedimentary rocks ($\delta^{18}O$ ~ 15–30 ‰, Hoefs 1987). The most likely explanation of the D-enrichment in the mantle is subduction of high-δD rocks (e.g. serpentinites in the lower oceanic crust) and subsequent release of D-enriched fluids, which may have metasomatized the upper mantle. Unfortunately no H-O isotope study is available from oceanic crust relics from the Eastern Alps and Carpathians. Serpentinites and ophicarbonates of the Western Alps display large H isotopic variations (from −150 ‰ to −30 ‰, Burkhard & O'Neil 1988; Früh-Green et al. 1990). The high δD values record a high-temperature interaction of the oceanic crust with seawater. According to the serpentine-water H isotope fractionation (Wenner & Taylor 1973), the fluid released from the subducted serpentinite mass would be even more enriched in deuterium (approaching −20 ‰) than the source rock. This fluid would enter the mantle causing the metasomatism and D-enrichment.

Serpentinite devolatilization may occur at mantle depths (Scambelluri et al. 1995, 1997), carrying large amounts of high-δD fluid into the mantle. An independent indication of subducted oceanic crust material under the Carpathian-Pannonian region is the presence of mafic granulite xenoliths with low $\delta^{18}O$ values and MORB-like Sr-Nd isotope compositions in the alkaline basalts (Dobosi et al. 2003b). Subduction of oceanic crust has been presumed to have taken place during the Alpine orogenesis in the Carpathian-Pannonian region, producing high-D metamorphic rocks (Demény et al. 1997) with δD values very similar to those detected in this study.

It is important in the evaluation of the above model that an areal variability has been observed in radiogenic isotope compositions of the Pliocene-Pleistocene alkaline basalts of the CPR (Embey-Isztin & Dobosi 1995), which was related to an increased amount of the subducted component in the central part of the region. The constant oxygen isotope compositions throughout the region indicate that the contamination was not induced by direct melt addition from subducted crust, since such process would have shifted the oxygen isotope compositions to higher values. Our results indicate that the radiogenic isotope variations may have been caused by metasomatism triggered by release of fluid from the subducted slab.

Conclusions

Amphibole megacrysts and hornblendite veins from composite mantle xenoliths of Pliocene-Pleistocene alkaline basalts of the Carpathian-Pannonian region were studied in this paper to investigate the origin of mantle fluids, which induced hydrous mineral formation. Former studies have proven that the megacrysts represent cumulate phases formed during an early upwelling of basaltic magma, and were brought to the surface by subsequent magma pulse. The $\delta^{18}O$ values of the amphiboles support their primary mantle origin. Correlations with the MgO contents and La/Sm ratios are interpreted in terms of varying degrees of partial melting and amphibole crystallization from the evolved basaltic melt. The halogen contents (F, Cl) of the amphiboles are very low, and their variations can either be related to the partial melting process, or to the Mg-Cl avoidance rule.

Water and Fe^{3+} contents and H isotope compositions indicate degassing effects. Dehydrogenation is subordinate, whereas dehydration prevails in the studied amphibole megacrysts. Undegassed amphiboles show a wide δD range from normal mantle compositions (about −60 ‰) to unusually high values (−20 ‰) attributed to metasomatism incidental to fluid release from subducted oceanic crust. The trace element and O isotope co-variations indicate negligible direct melt addition to the mantle. Radiogenic isotope variations observed in previous studies may be related to fluid-mediated element transport from the subducted slab.

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