

Calcic amphibole growth and compositions in calc-alkaline magmas: Evidence from the Motru Dike Swarm (Southern Carpathians, Romania)

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ABSTRACT

A Late Pan-African calc-alkaline dike swarm (basalt-andesite-dacite-rhyolite) has been investigated in a region of over 2000 km² in the Alpine Danubian window, South Carpathians (Romania). Amphibole phenocrysts and microphenocrysts have been investigated by wavelength-dispersive microprobe analysis and BSE imaging. The Ca-amphibole population, represented in all the lithologies, displays a large compositional range, interpreted as the result of two processes: (1) magmatic evolution (kaersutite → Ti-pargasite → pargasite → Ti-magnesiohastingsite → magnesiohastingsite → edenite → tschermakite → magnesiohornblende) linked to magmatic differentiation from andesitic basalt to rhyolite; and (2) deuteric alteration of the primary amphibole related to late-emplacement hydrothermal activity (yielding numerous varieties comprising those cited above). In all rock types, amphibole phenocrysts equilibrated at a nearly constant pressure of about 0.6 ± 0.1 GPa, but their temperatures of crystallization ranged from 1000–900 °C for basaltic andesites to 700–600 °C for dacites. In rhyolites, edenite to magnesiohornblende crystals reflect a continuous range of *P-T* conditions from 700 °C/0.6 GPa to 600 °C/0.1 GPa, in agreement with their change of habit from euhedral to subhedral. Complex zonations in pargasite-magnesiohastingsite (including resorption) are interpreted in term of self-organization of oscillatory zoning without significant heating and/or magma mixing.

Keywords: Crystal structure, calcic amphibole, crystal growth, magmatic zonation, igneous petrology, calcalkaline magma, thermobarometry

INTRODUCTION

In calc-alkaline magmas, such as those of the Late Pan-African Motru Dike Swarm (MDS) in Romania, Ca-amphibole occurs in all petrological facies from andesitic basalts to rhyolites. It represents the main ferromagnesian phase in the lithologic sequence and evolved in composition during magmatic differentiation. Because olivine is lacking in the MDS, even in the less differentiated basalts, amphibole phenocrysts took the place of this more common phase in playing an essential role since the onset of fractional crystallization.

Amphibole composition has been used classically as a differentiation index. However, the high H₂O content of many calc-alkaline magmas results in pervasive late-emplacement deuteric alteration to propylitization and partial modification and/or replacement of primary by secondary amphiboles. Distinction between amphibole parageneses may then become difficult, which so far has limited the potential interest of this phase for petrological models.

This study was aimed at providing a better understanding of the complex chemical compositions and thermobarometric conditions of primary and secondary amphiboles produced during magmatic growth. Using the Motru Dike Swarm as an

illustration, we have characterized the evolution of Ca-amphibole compositions in relation to magmatic and hydrothermal activity throughout melt emplacement. Back-scattered electron images and detailed microprobe investigations of a large population of amphiboles has allowed us to reconstruct the various stages of complex magmatic growth and resorption history of the phenocrysts and of their alteration products (up to rare talc pseudomorphs). This evolution is further constrained quantitatively through *P-T* estimates of the conditions of crystallization based on the Al-content empirical barometer (Schmidt 1992) and Ti-content empirical thermometer (modified expression of Otten 1984) for amphiboles.

GEOLOGICAL SETTING

The dikes studied in this work belong to a major Late Pan-African calc-alkaline dike complex, the Motru Dike Swarm (MDS) that crops out within the Danubian window of the South Carpathian Mountains in Romania (Fig. 1). There, south Carpathian crystalline units were thrust upon the Moesian cratonic platform during the Cenozoic Alpine orogeny in two major nappes: the upper and lower Danubian units (Berza et al. 1983, 1994) recognized on the basis of their Mesozoic cover (Stanoiu 1973; Kräutner et al. 1981). Intruding the Precambrian basement of the lower unit, the MDS, defined by Berza and Seghedi (1975) and recently revisited by Féménias (2003), represents the last (pre-

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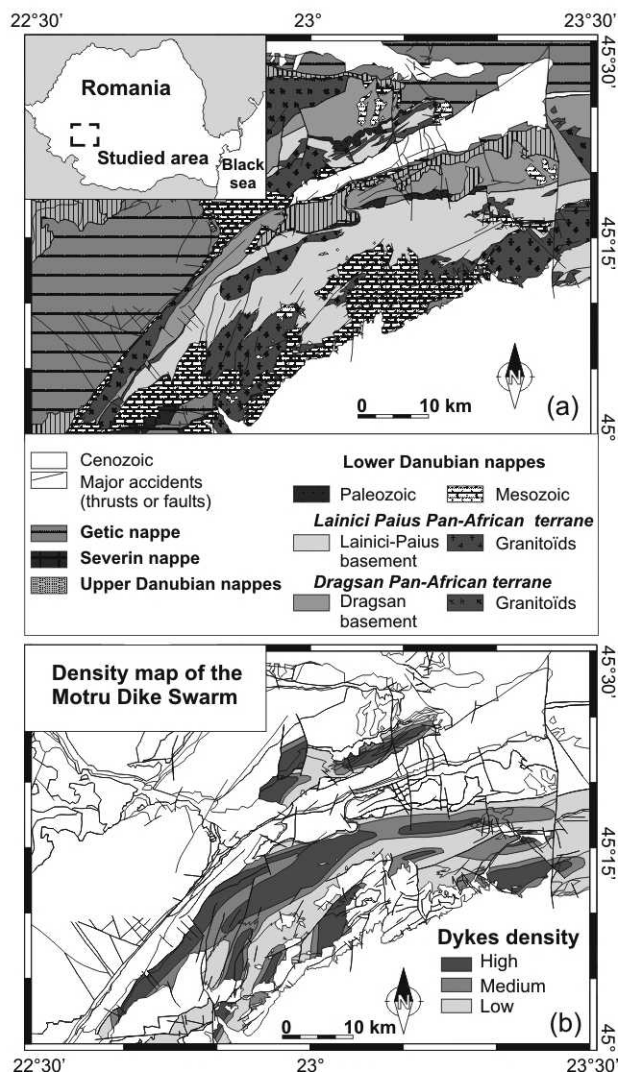


FIGURE 1. (a) Map of the pre-Alpine units of the South Carpathian Mountains, from the IGR 1/50 000 map modified, after Berza et al. (1994) and Féménias et al. (2004). (b) Relative distribution of the dikes of the Motru Dike Swarm into the Lainici-Paius unit and location of the studied dikes (after Féménias et al. 2004).

Silurian) magmatic event in these Pan-African terranes.

This swarm contains numerous subvolcanic dikes defining a complete differentiated series from basaltic andesite to rhyolite (50–72 wt% SiO₂). On the basis of their size, mean orientation, and magnetic fabric, two populations have been identified (Féménias et al. 2004): (1) narrow dikes (<1 m) with a N80° mean wall direction and a symmetrical AMS (anisotropy of magnetic susceptibility) fabric; and (2) thicker dikes (>1 m to several meters) with a N-S mean wall direction and an asymmetrical AMS fabric. The two populations describe a common regional stress field during a brittle emplacement continuum (Féménias et al. 2004).

SAMPLING AND ANALYTICAL PROCEDURES

Through a MDS regional survey in a mountainous area of 2000 km², some 150 dikes have been sampled. A representative selection of thin sections of 55

samples has been the subject of petrological and mineralogical investigation. Representative analyses of the amphiboles are listed in Table 1. Major-element compositions of amphiboles have been determined by WDS electron microprobe (Cameca SX50) at the Centre d'Analyses par Microsonde en Sciences de la Terre (CAMST, University of Louvain) using a combination of natural and synthetic mineral standards. Operating conditions were as follows: accelerating voltage of 15 kV; beam current of 20 nA; counting time of 10 s for Fe, Mn, Ti, and Cr, 16 s for Si, Al, and K, and Mg, and 24 s for Na.

PETROLOGY OF THE MOTRU DIKE SWARM (MDS)

The MDS is essentially composed of andesitic, trachyandesitic to dacitic dikes, with basaltic andesites, basaltic trachyandesites, and rhyolites being less common (classification according to Le Maitre 2002). Textures are typically aphyric to micro-porphyritic. Porphyritic basaltic andesites and andesites contain euhedral brown amphibole and/or plagioclase microphenocrysts, whereas porphyritic dacites and rhyolites have euhedral plagioclase, green hornblende, and partly resorbed quartz (Fig. 2). The dikes have chilled margins implying a high-level (subvolcanic) emplacement. These margins consist of few microphenocrysts (amphibole and clinopyroxene in basaltic andesites, plagioclase and biotite in andesites) in a secondary (=deuteric) groundmass. In highly hydrated basaltic to andesitic lithologies, plagioclase is locally deeply retrogressed into epidote ± calcite ± white mica and commonly appears as ghosts. The groundmass consists of tiny quartz, plagioclase, ferromagnesian phases (amphibole and rare clinopyroxene), oxides, and devitrified glass. Mn-rich ilmenite is the main oxide of the MDS; it occurs either as euhedral to subhedral crystals forming glomeromorphic assemblages (mean grain size: 100–400 μm) or as single tiny (a few tens to a hundred micrometers) anhedral to skeletal grains. Deuteric alteration and propylitization occurred during and/or just after dike emplacement and induced a low temperature - low pressure secondary paragenesis. Locally, pseudomorphs of leucoxene replace Ti-bearing silicate phases; chlorite, calcite, talc, epidote, and pyrrhotite-pyrite (tertiarily altered into goethite and hematite) developed locally as millimeter-sized euhedral grains. A pseudomorphic replacement of calcic amphibole by talc has been observed and interpreted as a strongly evolved propylitic process (Féménias 2003).

AMPHIBOLE COMPOSITION

Structural formulae of amphiboles from the MDS were calculated on an anhydrous basis assuming 23 O atoms per half unit cell, with the general form A₀₋₁B₂C₅T₈O₂₂(OH)₂ representing one formula unit. According to the IMA classification and Fe³⁺ calculation proposed by Leake et al. (1997), all the amphiboles from the MDS are calcic (⁸⁷Ca > 1 apfu) and belong to two sub-groups of this classification. Group 1 is defined by ^Λ(Na + K) < 0.5 apfu (Fig. 3a), and mostly contain high Si contents (¹Si > 6.5 apfu) characteristic of magnesiohornblende and actinolite, with minor tschermakite (¹Si < 6.5 apfu). Magnesiohornblendes correspond to core compositions of amphibole phenocrysts in rhyolites and dacites, and rim compositions of amphibole phenocrysts from andesites. Actinolite is present in numerous lithologies associated with the deuteric paragenesis. Core compositions for amphiboles from basaltic andesites, andesites, and trachyandesites belong to Group 2, defined by ^Λ(Na + K) > 0.5 apfu (Fig. 3a). This group mostly contains low Si contents (¹Si < 6.5 apfu)

TABLE 1A. Selected representative microprobe analyses (major elements in wt%, structural formula) for calcic amphiboles of the calc-alkaline Motru Dike Swarm

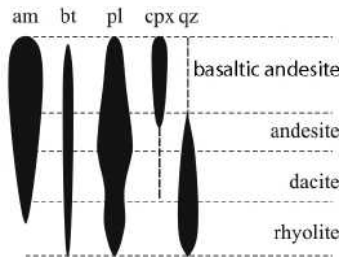
Rock Name	AB 1	AB 2	AB 3	AB 4	AB 5	AB 6	AB 7	AB 8	A 1	A 9	A 3	A 4	A 10	A 5	A 7
SiO ₂	55.65	40.90	44.08	49.91	43.70	41.71	42.19	41.71	53.17	45.02	43.60	45.40	43.50	44.86	43.30
TiO ₂	0.00	4.44	1.96	0.20	2.37	2.75	3.63	3.68	0.03	1.98	2.19	1.68	2.06	2.81	2.33
Al ₂ O ₃	0.93	11.10	10.63	6.47	9.41	10.07	11.19	10.88	2.44	11.12	11.18	9.82	11.49	9.60	10.97
FeO	10.16	14.24	12.15	12.94	15.71	19.43	10.45	13.60	15.26	10.77	11.28	11.23	11.47	12.94	12.53
MnO	0.34	0.27	0.19	0.21	0.31	0.30	0.18	0.19	0.34	0.14	0.16	0.19	0.10	0.18	0.13
MgO	17.30	11.69	14.18	14.76	11.45	9.11	14.54	12.04	13.82	14.39	15.03	15.44	13.95	13.39	13.67
CaO	12.84	11.28	11.16	11.86	10.75	10.86	11.34	11.53	12.10	11.59	11.43	11.36	11.69	10.79	11.72
Na ₂ O	0.15	2.50	2.18	0.97	2.27	2.39	2.43	2.29	0.28	1.71	2.06	1.62	1.97	2.14	1.96
K ₂ O	0.04	0.94	0.41	0.12	0.95	1.10	0.48	1.00	0.05	0.80	0.54	0.45	0.61	0.42	0.55
Cr ₂ O ₃	0.00	0.03	0.08	0.00	0.00	0.00	0.54	0.13	0.00	0.00	0.03	0.11	0.09	0.00	0.00
Cl	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.03	0.08	0.06	0.04	nd	0.07
F	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.23	0.26	0.27	0.25	nd	0.35
Sum	97.41	97.39	97.02	97.43	96.92	97.72	96.97	97.03	97.48	97.78	97.82	97.62	97.23	97.13	97.58

Notes: AB = Basaltic andesite; A = Andesite. 1 = actinolite; 2 = kaersutite; 3 = magnesiohastingsite; 4 = magnesiohornblende; 5 = titanian-edenite; 6 = ferro-pargasite; 7 = titanian-magnesiohastingsite; 8 = titanian-pargasite; 9 = edenite; 10 = pargasite; 11 = titanian-magnesiohornblende; 12 = tschermakite; 13 = ferro-hornblende.

TABLE 1B. Selected representative microprobe analyses (major elements in wt%, structural formula) for calcic amphiboles of the calc-alkaline Motru Dike Swarm

Rock Name	A 11	A 8	A 12	T 1	T 13	T 14	T 4	T 5	T 7	T 8	D 9	D 4	D 12	R 1	R 4
SiO ₂	45.47	43.34	44.14	53.37	52.46	47.35	47.73	44.47	42.70	42.91	46.94	47.04	43.76	52.80	49.19
TiO ₂	2.81	2.91	2.00	0.12	0.20	0.88	2.01	3.06	3.60	3.47	0.55	0.89	1.28	0.33	1.33
Al ₂ O ₃	9.12	11.66	10.96	1.45	1.10	4.84	6.90	9.55	10.20	10.21	12.46	10.21	12.08	3.90	8.86
FeO	13.47	12.41	12.17	17.67	20.41	22.53	15.43	13.35	13.50	13.56	4.86	7.69	16.40	11.07	6.72
MnO	0.18	0.20	0.16	0.41	1.03	0.93	0.40	0.20	0.23	0.21	0.12	0.16	0.28	0.62	0.04
MgO	12.75	12.36	14.22	11.79	9.61	8.87	11.31	12.82	13.06	12.74	17.66	17.63	12.26	16.70	17.77
CaO	10.83	11.56	11.16	12.41	12.48	10.16	11.24	11.49	11.06	11.19	11.83	11.14	8.82	10.91	11.63
Na ₂ O	1.46	1.68	1.74	0.29	0.13	1.37	1.40	2.17	2.34	2.34	2.10	2.10	1.94	0.62	1.50
K ₂ O	0.47	1.05	0.68	0.06	0.06	0.48	0.48	0.55	0.59	0.59	0.20	0.21	0.25	0.20	0.24
Cr ₂ O ₃	0.16	0.06	0.03	0.03	0.00	0.07	0.01	0.01	0.00	0.00	0.64	0.00	0.07	0.20	0.12
Cl	nd	0.06	0.06	0.00	nd	0.10	nd	nd	0.05	0.05	nd	nd	nd	nd	nd
F	nd	0.22	0.31	0.17	nd	0.28	nd	nd	0.34	0.34	nd	nd	nd	nd	nd
Sum	96.72	97.52	97.62	97.76	97.48	97.87	96.91	97.68	97.67	97.61	97.37	97.06	97.15	97.33	97.40

Notes: A = Andesite; T = Trachyandesite; D = Dacite; R = Rhyolite. 1 = actinolite; 2 = kaersutite; 3 = magnesiohastingsite; 4 = magnesiohornblende; 5 = titanian-edenite; 6 = ferro-pargasite; 7 = titanian-magnesiohastingsite; 8 = titanian-pargasite; 9 = edenite; 10 = pargasite; 11 = titanian-magnesiohornblende; 12 = tschermakite; 13 = ferro-hornblende.

**FIGURE 2.** Sketch illustrating modal evolution of the main phases during magma differentiation of the Motru Dike Swarm.

characteristic of magnesiohastingsite, pargasite, and kaersutite, with minor edenite (¹Si > 6.5 apfu). Such magnesiohastingsite, pargasite, and kaersutite correspond to core compositions of amphibole phenocrysts from andesitic basalts, trachyandesites and andesites, whereas edenites result from a moderate alteration of the Si-poor amphiboles and, accessorially, to core compositions of amphiboles from dacites. Core compositions of amphiboles from andesites are less titaniferous than those from basaltic andesites and trachyandesites (Fig. 3b), with the exception of some titanian-edenite. Basaltic andesites and trachyandesites also contain titanian-pargasites and kaersutites that represent the first step in the alteration of titanian-edenite compositions. All the amphiboles in rhyolites and dacites have low Ti contents

(Ti < 0.25 apfu). Regardless of the amount of Na + K in the A site, the $X_{Mg} [=Mg/(Mg + Fe^{2+})]$ of the MDS amphiboles ranges from 0.5 to 1 (Figs. 4a and 4c), making them all magnesian. Rare ferro-hornblende, ferro-edenite, titanian-ferro-pargasite, and ferro-actinolite have been observed as accessory alteration products near rims or cracks. Primary magnesiohornblendes in the rhyolites are more magnesian than those resulting from secondary recrystallization of andesite (Fig. 4c). Actinolites derived from basaltic andesite phenocrysts are somewhat more magnesian than those from andesites (Fig. 4c). Within the magnesiohastingsite-pargasite population, the $Fe^{3+}/IVAl$ ratio (Fig. 4b) discriminates andesite magnesiohastingsites ($Fe^{3+}/IVAl > 1$) from basaltic andesite and trachyandesite pargasites ($Fe^{3+}/IVAl < 1$). Most amphiboles from these two lithologies are thus characterized by a low Fe^{3+} content, although a local increase in Fe^{3+} has been observed, linked to zonation in andesite phenocrysts and alteration products.

AMPHIBOLE GEOTHERMOBAROMETRY

Numerous studies have dealt with parageneses of calcic amphibole in mafic (meta-) igneous rocks (Allen et al. 1975; Allen and Boettcher 1978; Helz 1973; Spear 1981; Ernst and Liu 1998). These studies make it clear that, with increasing P - T conditions, calcic amphiboles exhibit increases in $Mg/(Mg + Fe)$ and in K, Al, Na, and Ti contents, and commensurate decreases



FIGURE 3. Compositional variations of calcic-amphibole from the Motru Dike Swarm. Cation proportions are per formula unit. Amphibole classification after Leake et al. (1997).

in Si and total Fe + Mg + Mn + Ca.

Pressure conditions of crystallization, deduced from contact aureoles or experimentally controlled, have been observed to be correlated linearly with the Al-content in amphibole, and, many calibrations of the Al-in-amphibole barometer have been published (Hammarstrom and Zen 1986; Hollister et al. 1987; Johnson and Rutherford 1988; Rutter 1989; Blundy and Holland 1990; Schmidt 1992; Anderson and Smith 1995; Ernst and Liu 1998). The Anderson and Smith (1995) calibration is T -dependent; the pressure estimate is corrected for the temperature effect. It appears that this correction dramatically increases when the temperature increases from 800 up to 1100 °C. Anderson and Smith (1995) recognized that “the new expression probably should not be applied to plutons with temperatures much >800 °C because such conditions are far outside the range of experimental calibration...” p. 554). Indeed, when this calibration is applied to the high- T Ti-pargasite of the MDS, it leads to much lower (even negative!) P estimates than for the (low- T and low-Ti) magnesiohornblende. According to experimental data summarized by Ernst and Liu (1998), the range of P - T estimates for the Motru amphiboles does not justify the use of a coupled geothermobarometer. Indeed, Ernst and Liu (1998) have clearly shown in their Figure 8 that the Al_2O_3 content of Ca-amphibole and T are very poorly correlated and that the TiO_2 content of Ca-amphibole and P are not correlated in the temperature range 700–1100 °C at $P = 0.5 \pm 0.5$ GPa. All the barometer expressions usable for the Motru amphiboles give, within error, similar P estimates [see Fig. 1 of Anderson and Smith (1995) for a similar observation]. Comparisons of these experimental calibrations,

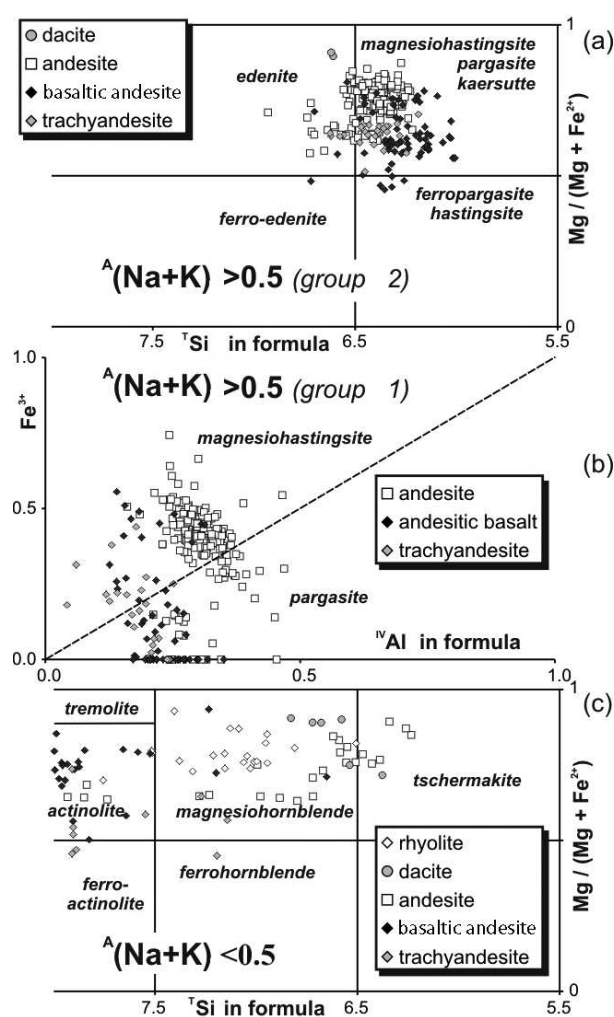


FIGURE 4. Compositional variations of calcic-amphibole from the Motru Dike Swarm. Symbols as in Figure 3.

however, show the important influence of fluid composition on equilibration of amphibole and that of the buffer phase assemblage. Considering the normal MDS assemblage $amp + pl + Kfs + qz + il$ and the usual lack of fresh plagioclase, the experimental calibration of Schmidt (1992) has been used, for it reduces the uncertainty on pressure estimates (± 0.06 GPa).

In the reduced P - T domain ($P = 0.5 \pm 0.5$ GPa; $T = 900 \pm 400$ °C), the only usable experimental data for T estimates are those from Helz (1973, 1976, 1979). According to these data and to the more recent works (Otten 1984; Ernst and Liu 1998), Ti solubility appears to be a suitable geothermometer for the MDS amphiboles. Indeed, as in the mineral assemblages reported here, the synthesized calcic amphiboles [Helz (1973) and references in Ernst and Liu (1998)] are associated with Ti-rich minerals (ilmenite, rutile, titanite) and may be considered as Ti-saturated. However, the graphical semi-quantitative calibration of Ernst and Liu (1998) yields large uncertainties whereas the independent quantitative calibration of Otten (1984) introduced a change of slope (in fact a mathematical artifact) at 970 °C in the linear

relation between Ti and T that makes this calibration inapplicable to the high-Ti amphiboles of the Motru Dike Swarm. However, in the original data set of Helz (1973), the experimental bulk compositions, the P - T domain of the experiments, and the related mineral association (Helz 1982), on the one hand, and the fact that the FMQ buffer is applicable to the MDS samples on the other hand, it is possible to derive a unique T calibration from the Ti content of these amphiboles. We propose a quantitative thermometer applicable to high- T (>700 °C) amphibole crystallizing in Ti-saturated calc-alkaline magma. Our T estimates are globally in agreement with those deduced from the Blundy and Holland (1990) thermometer. Nevertheless, we did not use their calibration because fresh plagioclase is rare; most plagioclases of the Motru rocks have suffered strong deuteric alteration.

Solubility of Ti in calcic amphibole buffered by a Ti-rich phase displays an ideal solid-solution behavior:

$$K_D \approx [\text{Ti}]_{\text{amphibole}} \quad (1)$$

Because it is independent of low-pressure variations (Otten 1984; Ernst and Liu 1998), K_D may be expressed as a simple function of temperature:

$$\ln K_D = \frac{b}{T} + c \quad (2)$$

Hence,

$$\ln [\text{Ti}]_{\text{amphibole}} = \frac{b}{T} + c \quad (3)$$

where b and c are two constants. According to the FMQ data of Helz (1973),

$$\ln [\text{Ti}]_{\text{amphibole}} = \frac{2603}{T} - 1.70 \quad (4)$$

where $[\text{Ti}]_{\text{amphibole}}$ is expressed in atoms per formula unit (apfu). The quality of the fit to the data ($r^2 = 0.951$) yields an uncertainty (2σ) that ranges from ± 15 to ± 55 °C for temperatures ranging from 600 to 1000 °C, respectively.

Most of the calcic amphiboles in the basaltic andesites from the MDS crystallized at relatively high pressures (Figs. 5a and 5b: ~70% of analyses yield pressures between 0.6 to 0.7 GPa) regardless of the crystal size, the location of the analysis (core or rim), or the nature of the amphibole (kaersutite, titanian-pargasite, magnesiohastingsite, or titanian- magnesiohastingsite). Titanian-magnesiohastingsites, and pargasites from andesites, as well as core compositions of edenites, ferro-edenites, and tschermakites from dacites and rhyolites, display similar pressure conditions of crystallization (Figs. 5a and 5b). In contrast, magnesiohornblendes from rhyolites and dacites show a broader range of values (0.7 to <0.2 GPa) in relation to the subhedral habit of these amphiboles, which may reasonably represent the progressive cooling of the dikes. Titanian-pargasites and titanian-magnesiohastingsites from trachyandesites display a slightly but significantly lower mean pressure (~75% of analyses yield pressures between 0.5 to 0.6 GPa), which distinguishes them from basaltic andesite amphiboles.

In contrast to crystallization pressure, temperatures (Figs. 5a and 5b) are more sensitive to the nature and habit of crystals.

Temperatures vary according to amphibole mean compositions (as well as X_{Mg}), and show a large range of values from 1100 to 600 °C (temperatures for actinolite were not investigated) irrespective of the nature of the host lava. Nevertheless, amphibole-core temperatures decrease continuously from basaltic andesites (1000–1100 °C for kaersutite and titanian-pargasite) to dacites and rhyolites (60–750 °C for magnesiohornblendes and edenites); rim compositions and alteration products are at the origin of the dispersion of the values for any a given chemical environment. In andesitic basalts, trachyandesites and andesites, the correlation between Ti-content of amphibole (temperature) and amphibole type is thus characteristic of the late-emplacment (at sub-surface conditions) alteration features of the deep amphiboles (Al does not vary significantly). This correlation results from easier diffusion of Ti than Al in the crystal structure during the deutericization and/or propylitization events.

Populations of amphibole compositions (Figs. 5a and 5b) hence characterize a progressive decrease in temperature during a first stage of crystallization, with magma differentiation (from basaltic andesites to dacites) at a constant pressure of 0.6–0.7 GPa and, in a second stage, a progressive decrease in pressure, showing that crystallization proceeded during the ascent of the dacites and rhyolites. Amphiboles from trachyandesites also integrate this scheme of evolution, but at a lower pressure.

AMPHIBOLE GROWTH STRUCTURES

Almost all phenocrysts of calcic amphibole in basaltic andesites to andesites display zoning observable microscopically in polarized light and on BSE images. Zoning is complex and characterized by two types of internal boundaries. The first type, which is dominant, is “geometric,” concentric, and regular (Fig. 6, stages 1, 3, 5, 7, and 9); it shows up as transitions from one band to another without sharp discontinuities and looks like a crystalline growth structure (i.e., Vance 1965). The second type is not concentric, but is commonly irregular (Fig. 6, stages 2, 4, 6, and 8); it cuts across internal boundaries of type 1 and/or 2 without distinction, and shows up as a sharp discontinuity within the grain. Many boundaries of type 2 are curvilinear and commonly associated with resorption gulfs and/or slight blunting of the internal crystal edges. Some of them are associated with cracks and penetrate throughout the core of the crystal, modifying its morphology during growth (Fig. 6, stage 6). All the observed zoned amphiboles from the MDS, whatever their size, display several boundaries of each type.

A detailed electron microprobe investigation of these zonations was performed on several phenocrysts and microcrysts of amphibole. Fifteen to 90 points were analyzed on each crystal, depending on size (from 100 up to 2000 μm). All the results are roughly similar and only one representative magnesiohastingsite-pargasite zoned crystal is shown here as an example (Fig. 6). Microprobe analyses of this single amphibole yield an overall magnesiohastingsite composition, with some pargasite and rare tschermakite point analyses. In a general way, Si and Mg-contents increase slightly from core to rim (from ~6.3 to ~6.4 and ~3.0 to ~3.3 apfu, respectively) whereas the Ca-content decreases from 1.83 to 1.74 apfu. Sodium, K, Ti, and Al-contents are roughly constant all along the profile, whereas the Mn-content shows a U-shaped profile (0.25–0.1–0.25 apfu). In detail, a majority of

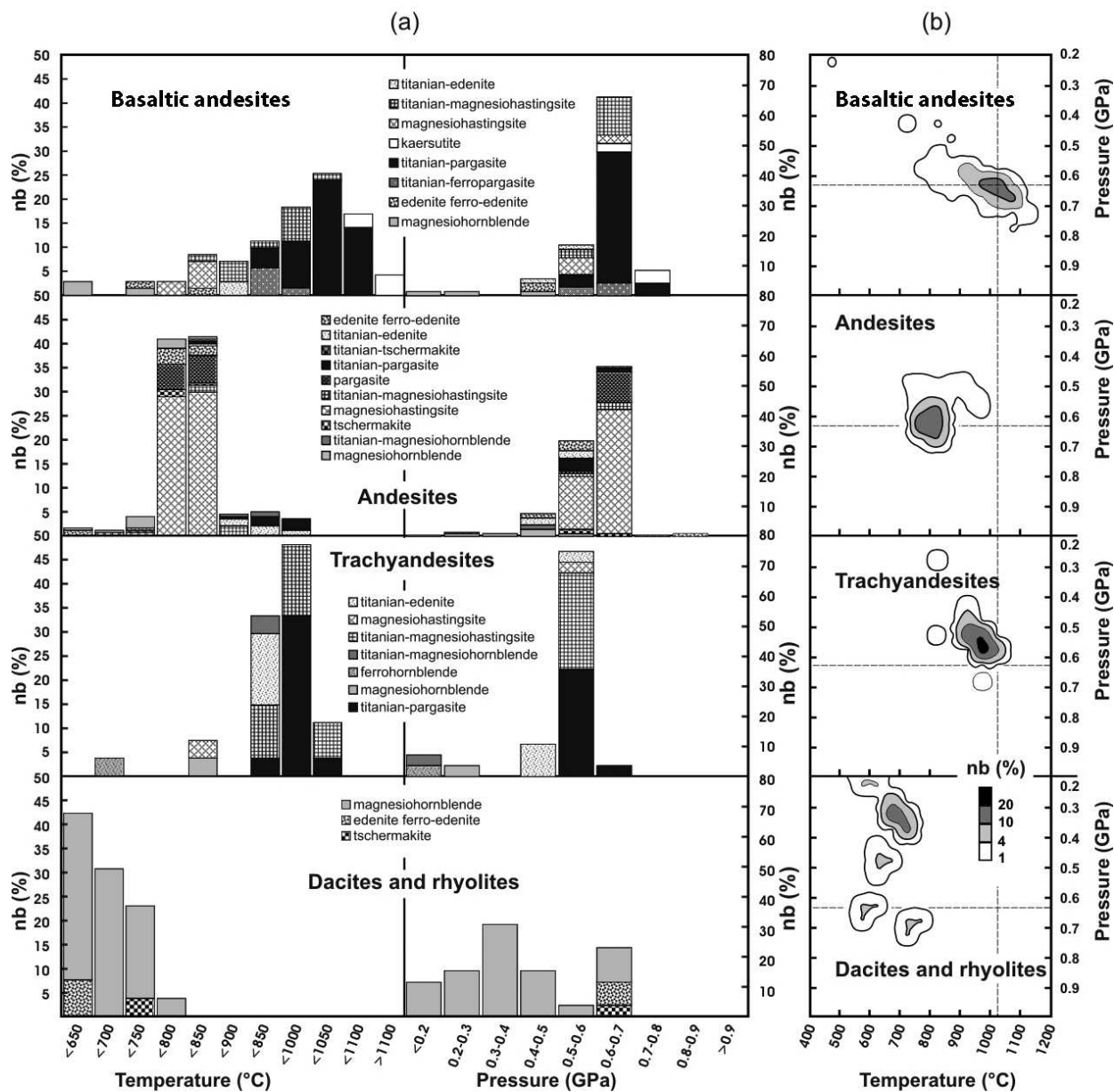


FIGURE 5. Statistical pressure and temperature distribution of amphibole crystallization for the principal lithologies of the Motru Dike Swarm. Symbols as in Figure 3.

the elements—with the exception of Na, Ti, and Al—display complex variations, which may be described at different scales. Indeed, at a small scale (ca. 20 μm), the crystal displays oscillatory characteristics (i.e., $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ and X_{Mg} between 170 and 400 μm on Fig. 6), more or less linked to the visible internal boundaries of both types. This oscillatory zoning is roughly “normal” with an outward decrease of X_{Mg} and an increase of the $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ratio. At a larger scale (up to 200 μm), chemical evolution within the crystal translates into continuous changes without clear polarities; both types of internal boundaries are then generally linked with chemical steps and/or jumps. How-

ever, no evident systematic distinction can be made between these two types of boundaries, especially when the type 2 is not clearly associated with resorption gulfs (Fig. 6). Beyond this detailed description, zoning may be summed up according to the thermodynamic behavior of each element in calcic-amphiboles: Ti, Na, and Al, which are strongly P/T -dependent do not vary significantly, whereas elements that are dependent on the system chemistry show small-scale variations, showing up as slight oscillations. The very weak apparent temperature ($T = 792 \pm 17$ °C) and pressure ($P = 0.63 \pm 0.02$ GPa) variations are not interpreted as having any geological significance.

DISCUSSION

Calcic amphibole composition variations

The calc-alkaline Motru Dike Swarm is characterized by prominent calcic-amphibole phenocrysts and/or matrix microcrysts. These calcic amphiboles represent the main ferromagnesian phase in the absence of olivine, but unlike olivine, they remain on the liquidus throughout the magmatic sequence ranging from basaltic andesites to rhyolites. These amphiboles display a wide range in composition from Si-poor, Ti-rich kaersutite to Si-rich actinolite. The absence of significant differences in composition between small (<50 μm) and large (up to 3000 μm) amphiboles precludes the possibility of many generations of crystals. Although this range of compositions does not seem to be correlated directly with the nature of host lava (many types of amphibole being present in each lithology), detailed studies of each population show that this variety results from superimposition of two contrasted processes illustrated by: (1) cores, which represent unperturbed and unaltered amphiboles, illustrating a magmatic evolution (kaersutite \rightarrow Ti-pargasite \rightarrow pargasite \rightarrow Ti-magnesiohastingsite \rightarrow magnesiohastingsite \rightarrow edenite \rightarrow tschermakite \rightarrow magnesiohornblende) correlated to the degree of magmatic differentiation of the host lava (respectively from basaltic andesite to rhyolite); and (2) rims, which represent perturbed- and/or altered-amphibole compositions, that are compatible with the secondary deuteric (Laverne et

al. 1995) paragenesis common to all rocks; these compositions are interpreted as resulting from partial deuteric alteration of primary amphiboles related to late-emplacement hydrothermal activity (inducing the many varieties comprising those cited above) and not as a new generation of crystals, as inferred from their high mean Al-contents, which are not compatible with a low- P , high-level of crystallization.

 P - T records and magma-chamber processes

In all rock types, primary amphiboles were equilibrated at about the same pressure ($0.6\text{--}0.7 \pm 0.1$ GPa), although their temperatures of crystallization range from $1000\text{--}900$ $^{\circ}\text{C}$ for basaltic andesites to $700\text{--}600$ $^{\circ}\text{C}$ for dacites and rhyolites. Magma differentiation of the MDS is thus characterized by progressive cooling. This cooling occurred during fractional crystallization in deep magma chambers emplaced at the same level within the lower crust (~ 20 km). In rhyolites, edenite to magnesiohornblende grains reflect a continuous range of P - T conditions from 700 $^{\circ}\text{C}/0.6$ GPa to 600 $^{\circ}\text{C}/0.1$ GPa in agreement with their change of habit from euhedral to subhedral. These amphiboles record the different stages of crystallization in continuum: they began to grow in a deep environment and developed during magma ascent from chambers to the surface. Trachyandesitic lithologies, which are less common in the MDS, may correspond to hot magma trapped in shallower chambers. Their specific whole-rock compositions do not affect the nature of the amphibole, which

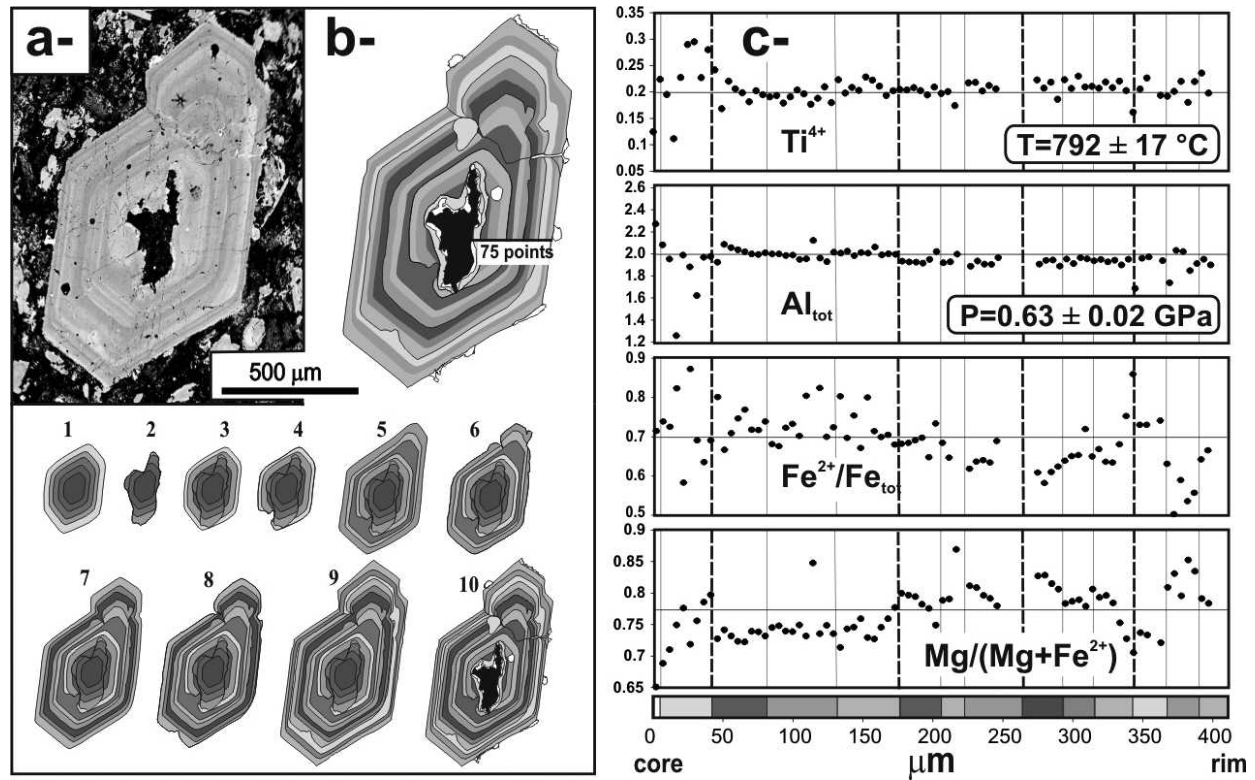


FIGURE 6. Zoning of a representative calcic-amphibole in andesite. (a) BSE image. (b) Sketch representation of the same amphibole crystal illustrating the mean observed internal boundaries and schematic growth history in 10 principal steps alternating growth-dominated stages (1, 3, 5, 7, 9) and resorption-dominated stages (2, 4, 6, 8). (c) Ti^{4+} , Al_{tot} , $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$, and X_{Mg} variations along the profile. Symbols as in Figure 3.

integrates the mineralogical sequence of the MDS described before. According to the higher level of their magma chambers, the chemical particularity of these rocks (higher $\text{Na}_2\text{O} + \text{K}_2\text{O}$ content) may be due to moderate crustal assimilation.

Pargasite and magnesiohastingsite display complex zoning and resorption features that have been correlated tentatively by combining BSE images with electron microprobe analyses. In any given sample, each amphibole crystal, regardless of its size, displays a similar chemical composition and internal type-features. These internal features have been detailed and visually divided into two types (types 1 and 2, depending on whether or not they are associated with resorption features, respectively). Although internal zoning boundaries of type 2 display significant changes in the amphibole composition, they are not really different from boundaries of type 1. All internal limits may be considered as growth disruptions, more or less marked by crystal resorption, and they do separate numerous domains within each amphibole. These domains do not show complete evidence for a single oscillatory process, although chemical zonations may be locally considered as "normal" (i.e., decreasing X_{Mg}). All these zoned grains display a duality between roughly constant P , T -dependent element-contents (i.e., Ti and Al) and variable system-dependent element-contents (i.e., Mg, Fe^{2+} , Fe^{3+}). Oscillatory zoning and repetitive resorptions cannot be the result of new pulses of magma in the chamber because: (1) the number of pulses (up to 10 in some grains) is unrealistic given the enormous difference between the time necessary to homogenize the magma and the time required to grow millimeter-sized phenocrysts (i.e., Kuo and Kirkpatrick 1982; Cashman 1992; 1993; Wörner 1996); (2) the resorption features are not linked to a significant change in thermo-dependent element-content and, thus, to some significant heating of the amphibole [e.g., as in the model developed for similar calc-alkaline dikes by Pudlo and Franz (1995)]; and (3) resorptions are not related to spongy textures, as is currently observed in magma mixing models (Tsuchiyama 1985). According to experimental results on oscillation processes in mineral phases, this oscillatory zoning and the more-or-less pronounced associated resorption may be interpreted in terms of self-organized oscillatory zoning (Wang and Merino 1993; Wang and Wu 1995) in a convective magma chamber without external contribution of heat and/or magma mixing processes (L'Heureux and Fowler 1996; L'Heureux and Jamtveit 2002).

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REFERENCES CITED

- Allen, J.C. and Boettcher A.L. (1978) Amphiboles in andesite and basalt: II. Stability as a function of P - T - f_{O_2} - $P_{\text{H}_2\text{O}}$. *American Mineralogist*, 63, 1074–1087.
- Allen, J.C., Boettcher A.L., and Marland G. (1975) Amphiboles in andesite and basalt: I. Stability as a function of P - T - f_{O_2} . *American Mineralogist*, 60, 1069–1085.
- Anderson, J.L. and Smith, D.R. (1995) The effects of temperature and f_{O_2} on the Al-in-hornblende barometer. *American Mineralogist*, 80, 549–559.
- Berza, T. and Seghedi, A. (1975) Complexul filonian presilurian din bazinul Motrului (Carpatii Meridionali). *Dari de Seama ale sedintelor - Institutul de Geologie si Geofizica*, LXI/1, 131–149.
- Berza, T., Krätner, H.G., and Dimitrescu, R. (1983) Nappe structure of the Danubian window of the central South Carpathians. *Anuarul Institutului Geologie si Geofizica*, 60, 31–34.
- Berza, T., Balintoni, I., Iancu, V., Seghedi, A., and Hann, H.P. (1994) South Carpathians. Geological evolution of the Alpine-Carpathian-Pannonian system, ALCAPA II, field guidebook. *Romanian Journal of Tectonic and Regional Geology*, 75, 37–49.
- Blundy, J.D. and Holland, T.J.B. (1990) Calcic amphibole equilibria and a new amphibole-plagioclase geothermometer. *Contribution to Mineralogy and Petrology*, 104, 208–224.
- Cashman, K.V. (1992) Groudmass crystallization of Mount St. Helens dacite, 1980–1986: a tool for interpreting shallow magmatic processes. *Contribution to Mineralogy and Petrology*, 109, 431–449.
- (1993) Relationship between plagioclase crystallization and cooling rate in basaltic melts. *Contribution to Mineralogy and Petrology*, 113, 126–142.
- Ernst, W.G. and Liu, J. (1998) Experimental phase-equilibrium study of Al- and Ti-contents of calcic amphibole in MORB-A semi-quantitative thermobarometer. *American Mineralogist*, 83, 952–969.
- Féménias, O. (2003) Contribution à l'étude du magmatisme tardi- à post-orogénique. De sa source à sa mise en place en sub-surface: Exemples régionaux de l'essai de filons du Motru (Roumanie) et du complexe lité profond sous Beauvit (France), 450 p. PhD dissertation, Université Libre de Bruxelles.
- Féménias, O., Diot, H., Berza, T., Gauffriau, A., and Demaiffe, D. (2004) Asymmetrical to symmetrical magnetic fabric of dikes: Paleo-flow orientations and paleo-stresses recorded on feeder-bodies from the Motru Dike Swarm (Romania). *Journal of Structural Geology*, 26, 1401–1418.
- Hammarstrom, J.M. and Zen, E.-A. (1986) Aluminium in hornblende: an empirical igneous geobarometer. *American Mineralogist*, 71, 1297–1313.
- Helz, R.T. (1973) Phase relations of basalts in their melting range at $\text{PH}_2\text{O} = 5$ kb as a function of oxygen fugacity. Part I: Mafic phases. *Journal of Petrology*, 14, 249–302.
- (1976) Phase relations of basalts in their melting range at $\text{PH}_2\text{O} = 5$ kb as a function of oxygen fugacity. Part II: Melt compositions. *Journal of Petrology*, 17, 139–193.
- (1979) Alkali exchange between hornblende and melt: a temperature sensitive reaction. *American Mineralogist*, 64, 953–965.
- (1982) Phase relations and composition of amphiboles produced in studies of the melting behavior of rocks. In D.R. Veblen and P.H. Ribbe, Eds., *Petrology and experimental phase relations*, 9B, p. 279–354. *Reviews in Mineralogy*, Mineralogical Society of America, Chantilly, Virginia.
- Hollister, L.S., Grissom, G.C., Peters, E.K., Stowell, H.H., and Sisson, V.B. (1987) Confirmation of the empirical correlation of Al in hornblende with pressure of solidification of calc-alkaline plutons. *American Mineralogist*, 72, 231–239.
- Johnson, M.C. and Rutherford, M.J. (1988) Experimental calibration of an Aluminium-in-hornblende geobarometer applicable to calc-alkaline rocks. *EOS*, 69, 1511.
- Krätner, H.G., Nastaseanu, S., Berza T., Stanoiu, I., and Iancu, V. (1981) Metamorphosed Paleozoic in the South Carpathians and its relation with the pre-Paleozoic basement, 116 p., Guide to excursion A, Congress of Carpathian Balkan Association XII, Bucureati.
- Kuo, L.C. and Kirkpatrick R.J. (1982) Pre-eruption history of phyruc basalts from DSDP Legs 45 and 46: evidence from morphology and zoning patterns in plagioclase. *Contribution to Mineralogy and Petrology*, 79, 13–27.
- L'Heureux, I. and Fowler, A.D. (1996) Isothermal constitutive undercooling as a model for oscillatory zoning in plagioclase. *Canadian Mineralogist*, 34, 1137–1147.
- L'Heureux, I. and Jamtveit, B. (2002) A model of oscillatory zoning in solid solutions grown from aqueous solutions: Applications to the (Ba,Sr)SO₄ system. *Geochimica et Cosmochimica Acta*, 66, 3, 417–429.
- Laverne, C., Vanko, D.A., Tartarotti, P., and Alt, J.C. (1995) Chemistry and geothermometry of secondary minerals from the deep sheeted dike complex, hole 504B. *Proceedings of the Ocean Drilling Program, Scientific Results*, 137/140, 167–189.
- Le Maitre, R.W. (Ed.) (2002) *Igneous rocks. A classification and glossary of terms*. 2nd Ed., 236 p. IUGS-Cambridge University Press, U.K.
- Leake, B. E., Woolley, A. R., Arps, C. E. S., Birch, W. D., Gilbert, M. C., Grice, J.D., Hawthorne, F.C., Kato, A., Kisch, H.J., Krivovichev, V.G., Linthout, K., Laird, J., Mandarino, J., Maresch, W.V., Nickel, E.H., Rock, N.M.S., Schumacher, J.C., Smith, D.C., Stephenson, N.C.N., Ungaretti, L., Whittaker, E.J.W. and Youzhi, G. (1997) Nomenclature of amphiboles: Report of the Subcommittee on Amphiboles of the International Mineralogical Association Commission on new minerals and mineral names. *Mineralogical Magazine*, 61, 295–321.
- Otten, M.T. (1984) The origin of brown hornblende in the Artssjället gabbros and dolerites. *Contribution to Mineralogy and Petrology*, 86, 185–199.
- Pudlo, D. and Franz, G. (1995) Records of deep seated magma chamber processes from plagioclase and amphibole phenocrysts in pan-African dyke rocks of Bir Safsaf, SW-Egypt. In G. Baer and A. Heimann Eds. *Physics and Chemistry of dykes*. Balkema Rotterdam, 251–265.
- Rutter, M.J. (1989) Experimental data for a proposed empirical igneous geobarometer: Aluminium in hornblende at 10 kbar pressure. *Geology*, 17, 897–900.
- Schmidt, M.W. (1992) Amphibole composition in tonalite as a function of pressure: An experimental calibration of the Al-in-hornblende barometer. *Contribution to Mineralogy and Petrology*, 110, 304–310.

- Spear, F.S. (1981) An experimental study of hornblende stability and compositional variability in amphibolite. *American Journal of Science*, 281, 697–734.
- Stanoiu, I. (1973) Zona Mehedinti—Retezat: o unitate paleogeografica si tectonica distincta a Carpatilor Meridionali. *Dari de Seama ale sedintelor - Institutul de Geologie si Geofizica*, LIX/5, 127.
- Tsuchiyama, A. (1985) Dissolution kinetics of plagioclase in the melt of the system diopside-albite-anorthite, and origin of dusty plagioclase in andesites. *Contribution to Mineralogy and Petrology*, 89, 1–16.
- Vance, J.A. (1965) Zoning in igneous plagioclase: patchy zoning. *J. Geol.* 73, 636–651.
- Wang, J.H. and Wu, J.P. (1995) Oscillatory zonation of minerals and self-organization in silicate solid-solution systems: A new nonlinear dynamic model. *European Journal of Mineralogy*, 7, 1089–1100.
- Wang, Y. and Merino, E. (1993) Oscillatory magma crystallization by feedback between the concentrations of the reactant species and mineral growth rates. *Journal of Petrology*, 34, 369–382.
- Wörner, S.W.G. (1996) Crystal size distribution in Jurassic flows and sills (Victoria Land, Antarctica): evidence for processes of cooling, nucleation, and crystallisation. *Contribution to Mineralogy and Petrology*, 125, 1–15.

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