DIFFUSION CORONAS AROUND QUARTZ XENOCRYSTS IN BASALTIC ANDESITE FROM CĂPUŞ (CIONCA HILL, GILĂU MOUNTAINS - ROMANIA)

NICOLAE HAR¹, ANA - MARIA RUSU²

ABSTRACT. Diffusion coronas consisting of Al – poor pyroxene (augite), glass and silica polymorphs are developed around the quartz xenocrysts in the olivine basaltic andesite from Cionca Hill (Gilău Mountains). The quartz of xenolithic origin was magmatically corroded and sometimes reacted with the basaltic melt. According to the time of coexistence between quartz and the basaltic melt, two different spatial disposition of the pyroxene of reaction can be noticed. For a shorter reaction time the Al – poor pyroxene are commonly tangentially to the quartz rim while for the crystals which presumably had longer reaction time the pyroxene are radially from points on the outer corona margins. The glass of the coronas has a high content of SiO₂ (73.994 – 78.515 wt %) and alkalis (Na₂O + K₂O = 5.617 – 7.046 wt%). Pyroxene of reaction from different parts of the corona were analysed. Analyses performed on the crystals of pyroxene point out a very high chemical homogeneity. According the chemical composition and using the diagram of Morimoto et al. (1988), all the analysed crystals are represented by augite.

Key words: basaltic andesite, quartz xenocrysts, diffusion coronas, pyroxene of reaction, Apuseni Mountains

Introduction

Calc-alkaline olivine basaltic andesite of Eocene age outcrops in Cionca Hill (Căpuş area) at the limit between the crystalline basement of the Gilău Mountains and sedimentary formations belonging to Transylvania depression. The basaltic andesite from Căpuş represents the last volcanics of the Late Cretaceous – Early Paleogene stage of the alpine magmatic cycle in the northern Apuseni Mountains, previously magmatic rocks consisting of rhyolites, dacites, andesites connected with intrusive bodies of granitic, granodioritic and dioritic composition. During its ascension to surface the basaltic melt assimilated magmatic xenoliths of intermediate composition.

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¹ "Babeş – Bolyai" University, Department of Mineralogy

² "Babeş – Bolyai" University, Department of Chemistry

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The assimilation processes are responsible for the hybrid features of the resulted basaltic andesite.

Table 1. Chemical composition of the basaltic andesite from Căpuș (Har, 1999)

#	Sample	Mg#	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O	Total
	109	59,7	54,04	1,02	15,66	7,70	0,10	5,76	7,98	2,39	1,97	0,29	2,14	99,05
	436	62,5	54,12	0,95	16,55	7,13	0,12	6,00	8,25	2,55	1,83	0,15	2,00	99,65
	average	61.1	54.08	0.98	16.10	7.41	0.11	5.88	8.11	2.47	1.90	0.22	2.07	99.35

Thus, minerals with different genesis are present in the basaltic andesite from Căpuș (Har, 1999):

- crystallized from the basaltic melt (olivine, plagioclase feldspar, pyroxene, magnetite, apatite etc.);
- of xenolithic origin (xenocrysts) as plagioclase feldspar, quartz, pyroxene and biotite;
- secondary minerals as carbonates, serpentine, talc, epidote and iron oxide – hydroxides;
- pyroxene of reaction developed in the diffusion coronas around the quartz xenocrysts.

In this paper new data are presented regarding the chemistry and the environment of the pyroxene of reaction. Har (1999) reported the presence of pyroxene of reaction from the Cionca basaltic andesite. Three chemical analyses performed on three different crystals of pyroxenes pointed out the presence of augite. New and more chemical analyses on reaction pyroxene as well as on the volcanic glass present around the pyroxene crystals are now available.

Analytical techniques

Thin sections were studied under the polarized microscope in order to identify the best diffusion coronas around the quartz xenocrysts. The SEM has been used for imaging the pyroxene of reaction and their spatial relationship with the quartz xenocrysts and volcanic glass.

Pyroxenes, silica specimens and glasses were analyzed by a Cameca Camebax electronprobe, with accelerating voltage of 15.0 keV, in the Department of Earth Sciences of Bristol University (Great Britain). The take off angle was 40° and the beam current was 15.0 nA for pyroxene, 25 nA for silica and 10 nA for glass. The results of the chemical analyses are presented as weight percentage of the main oxides: SiO₂, Al₂O₃, Cr₂O₃,

FeO, MgO, MnO, CaO, K₂O and Na₂O. The standard minerals used for the calibration of the electronprobe were: albite (Na), olivine (Mg, Si), corundum syn. (Al), sanidine (K), andradite (Ca), SrTiO₆ (Ti), Cr₂O₃ (Cr), MnO (Mn) and electrolytic iron (Fe).

Description of the coronas

The basaltic andesite contains xenoliths of intermediate magmatic rock partly assimilated by the host rock. They are broken and their minerals are spreaded into the basaltic mass (fig.1). Thus, crystals of xenolithic origin (xenocrysts) with specific size and composition (plagioclase feldspars, quartz, pyroxene and opacitized biotite) can be found. The quartz xenocrysts reacted with the basaltic melt generating pyroxenes of reaction, which are usually developed perpendicular to the limit between quartz and the basaltic rock (fig. 2).

*Fig. 1. Photomicrograph of magmatic xenolith in basaltic rock
(Plag – plagioclase, gl – glass; N+, 30x).*

Quartz xenocrysts are irregular and up to 1mm in diameter, most of them being surrounded by coronas which are about 100 μm or less in width, consisting of glass and pyroxene of reaction (fig. 3). The anhedral form of quartz xenocrysts is the result of dissolution processes that took place

Fig. 2. Photomicrograph of xenocryst of quartz with pyroxene of reaction (Q – quartz, Px- pyroxene; 1N, 40x)

under the influence of the basaltic melt. Quartz xenocrysts were probably derived from intermediate magmatic xenoliths, because different stages of disintegration into discrete crystals have been observed. Pyroxenes of reaction are not present in all diffusion coronas. Sometimes the quartz is entirely dissolved, its former presence being marked by a nest of pyroxene of reaction floating in a glassy mass (fig. 4). Coronas can be divided into two zones, from the inner to the outer parts (fig. 5):

- zone I consisting of glass, often associated with crystallites of silica polymorphs (tridimite). It is variable in thickness and sometimes is missing. In this case the pyroxenes of the next zone are developed right at the contact between quartz and the basaltic rock.
- zone II mainly composed by prismatic pyroxene of reaction and glass. The boundary between zone II and the basaltic rock is generally sharp.

Chemistry of the diffusion coronas

Quartz xenocrysts, glasses from diffusion coronas as well as from basaltic groundmass and the pyroxene of reaction were analyzed by electronprobe. The analyzed points are presented in fig. 3.

Two chemical analyses were performed on the quartz xenocryst. The results point out a pure quartz crystal with SiO_2 between 98.075 % and 99.300% and some very few amounts of alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O} = 0.003 - 0.007$ %) and Al_2O_3 (table 2).

Table 2 Chemical composition of the quartz xenocrysts

# Analyse no.	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Cr ₂ O ₃	MnO	FeO	total
399sil1	0.000	0.000	0.055	98.075	0.003	0.000	0.005	0.000	0.079	0.000	98.218
399sil2	0.007	0.000	0.047	99.300	0.000	0.000	0.012	0.078	0.000	0.000	99.445

Five crystals of pyroxene of reaction from different parts of the corona were analysed (fig. 3). All the chemical analyses were performed in the core of the crystals. The results show a very high chemical homogeneity of the analysed crystals (table 3).

Fig. 3. Glass and pyroxene of reaction in the difussion corona of the quartz xenocrysts and the location of analyzed points

Table 3. Chemical composition of the pyroxene of reaction

# Analyse no.	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Cr ₂ O ₃	MnO	FeO	total
399pr1	0.219	17.518	0.644	53.505	0.000	20.738	0.216	0.004	0.229	6.711	99.784
399pr2	0.196	18.763	1.237	53.209	0.000	19.286	0.218	0.031	0.206	6.398	99.543
399pr3	0.212	18.979	0.989	53.740	0.006	19.021	0.233	0.076	0.224	6.903	100.383
399pr4	0.281	17.896	0.758	53.753	0.000	21.055	0.217	0.095	0.242	6.467	100.763
399pr5	0.202	17.352	0.807	53.993	0.018	20.641	0.180	0.058	0.245	6.592	100.090

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Fig. 4. Nestle of pyroxene of reaction in glassy mass

Fig.5. The zonation of the corona surrounding the quartz xenocryst

Ca – rich pyroxenes from the corona are low in the Al content, which may be due to the high silica activity environment. Spatial position of the pyroxene coronas right at the contact with the hosting rock suggests that the basaltic melt represents the source of the Ca, Mg and Fe.

Glasses from diffusion corona (399gl1, 399gl2, 399gl4 and 399gl5) as well as from the groundmass (399gl3) of the basaltic andesite were also analyzed (table 4).

Table 4. Chemical composition of the glasses

Analyse no.	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Cr ₂ O ₃	MnO	FeO	total
399gl1	3.426	0.135	10.174	75.938	2.535	0.352	0.475	0.013	0.000	0.779	93.826
399gl2	3.978	0.131	11.393	73.994	3.068	0.310	0.306	0.000	0.000	1.513	94.692
399gl3	3.946	0.577	11.220	72.610	2.463	0.789	0.531	0.026	0.195	1.501	93.859
399gl4	3.509	0.096	11.191	74.124	2.944	0.293	0.469	0.000	0.000	1.470	94.097
399gl5	3.158	0.266	9.150	78.515	2.459	0.423	0.393	0.000	0.000	1.493	95.856

Remarkably high alkalis content of the glass can be noticed ($\text{Na}_2\text{O} + \text{K}_2\text{O} = 5.644 - 7.064$ wt %). Such content of alkalis is typical for silica glass in diffusion coronas (Sato, 1975). Element mobility is proportional to the self-diffusion coefficient in the silicate melt and glasses, which for alkalis are larger than those of Si and Ca by factors of 2 or 3 at 1000 °C (Shewmon, 1963).

The studied diffusion coronas consist mainly of pyroxene of reaction and glass. It is very difficult to appreciate the participation of those two components but usually the predominance of the pyroxenes can be noticed. Several measurements evidence the participation of the two components in the following approximately amounts: pyroxene of reaction – 65 % and glass – 35 %. Taking into account the participation of the components the weighted average chemical composition of the diffusion coronas (pyroxene + glass) was calculated (table 5).

Table 5. Weighted average chemical composition of the diffusion coronas

Oxides	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Cr ₂ O ₃	MnO	FeO	total
%	1.37	11.81	4.24	61.34	0.99	13.21	0.28	0.03	0.03	4.65	97.95

When comparing the compositions of the basaltic rock versus the diffusion coronas, the following chemical behaviour can be noticed:

- the enrichment in MgO and CaO of the corona as the result of the diffusion of the Mg^{2+} and Ca^{2+} from the basaltic melt;
- the concentration of the alkalis in the glass of the corona;

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Such geochemical trend suggests the existence of a basic alkaline front migrated from the basaltic melt towards the coronas developed around the quartz xenocrysts.

Fig. 6. SiO₂ vs. MgO in the glasses from diffusion coronas and basaltic andesite groundmass.

Some chemical differences between the two types of glass can be also noticed, especially regarding the content of SiO₂, MgO and CaO. The enrichment of SiO₂ in the glass from the corona is the result of diffusion of Si⁴⁺ from the lattice of quartz xenocryst while the MgO and CaO contents are the highest in the glass of basaltic origin. The composition of the glass from the basaltic andesite groundmass has unusual high content of SiO₂. Its acidic composition suggests that the diffusion of Si⁴⁺ took place also in the external area of the actual corona.

Pyroxene of reaction mineralogy

Based on the chemical composition, in order to identify the pyroxene species, the end members En, Wo and Fs were calculated (table 5). According the diagram of Morimoto et al. (1988) all the chemical analyses are typical for augite (fig. 7).

Table 5

	WO	EN	FS
399pr1	41.040	48.236	10.725
399pr2	38.153	51.646	10.201
399pr3	37.302	51.784	10.914
399pr4	41.128	48.639	10.234
399pr5	41.174	48.161	10.664

Fig. 7. The composition of the pyroxene of reaction plotted in diagram of Morimoto et al. (1988)

Small chemical differences in the composition of the analyzed crystals of pyroxene can be the result of the different exchange rate of the cations between the high silica environment and the basaltic melt in the different parts of the quartz xenolith. Different exchange rates can be noticed for Ca^{2+} and Mg^{2+} , while Fe^{2+} has a constant rate. This chemical behaviour is marked by the variable values of the WO and EN end – members, while FS is constant.

Discussion and conclusions

Olivine bearing basaltic andesite from Cionca Hill (Căpuș – Apuseni Mountains) contains xenocrysts of quartz originated from magmatic xenoliths incorporated during the ascension of the melt up to the surface. Reaction products are present at the contact between quartz xenocrysts and hosting rock, similar to those described by Sato (1975), Grove et al. (1988), Baker et al. (1991) and Luhr et al. (1995).

The coronas developed around quartz xenocrysts consist of Si rich glass and poor-Al clinopyroxene (0.644 – 1.237 wt% Al_2O_3) represented by **augite**. Luhr et al. (1995) concluded that reaction texture reflects both the length of time between incorporation of the quartz xenocrysts and eruption, and the rate of post – eruptive cooling. For a shorter reaction time the Al – poor pyroxene are commonly tangentially to the quartz rim (fig. 3) while for the crystals which presumably had longer reaction time the pyroxene are radially from points on the outer corona margins.

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Donaldson (1985) experimentally proved that the dissolution rate of the quartz in a basaltic melt is strongly controlled by the crystallisation state of the melt. A higher dissolution rate is present if the basaltic melt is superheated (above the liquidus temperature) than in case of a partly crystallized melt.

Phenocrysts of olivine in the basaltic andesite from Căpuș suggest that the melt was partly crystallized when quartz was incorporated. On the other hand, the presence of the volcanic glass in the groundmass of the rock points out a high rate of post – eruptive cooling. Thus, the reaction processes seem to be mainly controlled by the length of time between incorporation of the quartz xenocrysts and eruption. As far as both types of reaction textures are present, in order to explain variable time of coexistence between quartz and the basaltic melt, it is necessary to assume variable depth of quartz incorporation by the basaltic melt.

Quartz is sometimes totally assimilated and its former presence is marked by the presence of radially crystals of pyroxene into a glassy mass. In such cases the longest (up to 500 μm) and the best developed pyroxenes of reaction were identified.

SiO_2 rich glass surrounds the quartz xenocrysts. The dissolution of quartz is responsible for the SiO_2 enrichment of both types of glasses, from the diffusion coronas and from the basaltic andesite groundmass (outside of the coronas). The last one has unusual high content of SiO_2 for a basaltic glass (72.610 wt% SiO_2) proving that the diffusion processes is extended even outside of the present (visible) coronas.

The diffusion of Si^{4+} from the lattice of quartz into the basaltic groundmass had a high rate in the first stages of the assimilation process. The rate of diffusion outside the coronas became lower when the pyroxene of reaction started to grown up. The fringe of pyroxene extends the distance through which quartz components have to migrate in moving away from the quartz – melt interface, and hence reduces the dissolution rate (Donaldson, 1985).

The high silica environment around the quartz xenocrysts is responsible for the low Al content of the pyroxenes which growth in the external part of the diffusion coronas. Their crystallisation was controlled by the migration of the Ca^{2+} and Mg^{2+} cations, which together with Na^+ and K^+ cations generated an alkaline basic front from basaltic melt towards the reaction zone.

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