Petrogeochemical features of the Neogene collision volcanism of the Lesser Caucasus (Azerbaijan)

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Abstract. The article is devoted to the petrogeochemical features of Neogene collision volcanism in the central part of the Lesser Caucasus within Azerbaijan. The main goal of the study is to determine the thermodynamic conditions for the formation of Neogene volcanism in the central part of the Lesser Caucasus using the available petrogeochemical material. Using factor analysis, as well as the “IGPET”, “MINPET”, “Petrolog-3” programs, material balance calculations were performed that simulate the phenocryst fractionation process, the crystallization temperature, pressure, and figurative nature of the rock-forming minerals of the formation rocks were calculated. It was determined that at the early and middle stages of crystallization of the rocks of the andesite-dacite-rhyolite formation, the fractionation of amphibole played an important role in the formation of subsequent differentiates. Based on computer simulation, it was revealed that rocks of the andesite-dacite-rhyolite formation were formed by fractional crystallization of the initial high-alumina basaltic magma of high alkalinity in the intermediate magma foci. The calculations of the balance of the substance, simulating the process of fractionation of phenocrysts, as well as magnetite, confirmed the possibility of obtaining rock compositions from andesites to rhyolites as a result of this process. In this case, the process of crystallization differentiation was accompanied by processes of contamination, hybridism and mixing. Based on the geochemical features of rare and rare-earth elements, changes in their ratios, the nature of the mantle source and the type of fractionation process are determined. It was revealed that the enrichment of formation rocks by light rare earths, as well as by many incoherent elements, is associated with the evolution of enriched mantle material. Under high water pressure, as a result of the fractionation of olivine and pyroxene, high-alumina basalts are formed from primary high-magnesian magma, which can be considered parental magma. It was established that, in contrast to the elevated Transcaucasian zone in the more lowered East Caucasus, under conditions of increased fluid pressure and reduced temperature, the melt underwent fractional crystallization in the intermediate centers, being enriched with alkaline, large-ion lithophile elements, light REEs, etc. This is evidenced by the presence of large crystals of feldspars, the contamination of these minerals by numerous crystals of biotite, magnetite, several generations of these minerals, zonality, as well as the presence of related “water” inclusions, such as hornblendites, hornblende gabbro, etc. The physicochemical conditions for the formation of Neogene volcanic rocks of the Lesser Caucasus are determined.

Key words: Neogene collision volcanism, petrogeochemical features, crystallization differentiation, physical and chemical conditions of association, Lesser Caucasus

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Петрогеохімічні особливості неогенового колізійного вулканізму Малого Кавказу (Азербайджан)

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Анотація. Стаття присвячена петрогеохімічним особливостям неогенового вулканізму центральній частині Малого Кавказу в межах Азербайджану. Основна мета дослідження – на основному петрогеохімічному матеріалі з’ясувати термодинамічні умови неогенового вулканізму у центральній частині Малого Кавказу. За допомогою факторного аналізу, а також програм «IGPET» і «MINPET», «Петролог-3» проведено розрахунки балансу речовини, що моделюють процес фракціонування вкривлений, підрахована температура кристалізації, тис, фугітивність пороетвоючих мінералів порід формаций. Визначено, що на ранніх і середніх стадіях кристалізації порід андезит-дацит-ріолітової формаций фракціонування амфіболу зіграло важливу роль для утворення наступних діференціатів. На основі комп’ютерного моделювання було виявлено, що породи андезит-дацит-
Introduction. One of unsolved tasks in the magmatic petrology is the origin of andesites and rhyolites and therefore this aspect is described in a sufficient amount of scientific publications. And, in particular, a still more complicated problem is the origin of andesites which form an integral category with basalt, dacite and rhyolite. There are a number of hypotheses that explain the origin of andesites:

1) crystallization differentiation of basalt magma;
2) partial melting of the rocks of the lower horizon of the Earth’s crust; 3) partial melting of the Oceanic crust which underwent subduction; 4) partial melting of rocks of the Earth’s mantle; 5) assimilation of the material of the Earth’s crust with melted basalt; 6) integral process of crystallization and assimilation.

All these hypotheses have mutually exclusive inconsistencies. To solve this problem, as a unique object, the andesite-dacite-rhyolite association of the Upper Miocene – Lower Pliocene age could be taken, which belongs to late-collision stage of the development of the central part of the Lesser Caucasus. In order to solve these tasks, the survey of different types of rocks on the modern level is needed. Geochemical peculiarities of coherent and non-coherent elements and their relationship allow one to determine the character of the source of the mantle and the type of the process of fractioning. Crystallization differentiation, mingling of the magmas, evaluation of the role of the process of assimilation in the formation of the rock association are solved using computer modeling with well-known software IGPET and MINPET, FC modeller (Keskin, 1997). To explain the origin of the rocks of andesite-dacite-rhyolite association, in this article the model of fractional crystallization is used.

Unlike the main and acidic volcanic rocks, the nature of the middle rocks, particularly andesites, trachyandesites and Caucasus formations close to them in basicity, has long been a subject discussion in the literature.

They are usually considered as typically crust (Genshaft Y. S., 1977), mantle formations, (Kyshiro I., 1977; Kyshiro I., Yoder H.S. Jr., 1969) or the products of fractioning of femic minerals of the basalt magma or assimilating-fractional crystallization (AFC) of basalt magmas and finally, as hybrid rocks formed as a result of mingling of crust and mantle magmas (Gushchin A.V., 1977; Ivanova, T.A., Ganzeev, A.A., Gushchin A.V., 1989; Molyavko V.G., 1990; Popov V.S., Semina V.A., Nikolayenko Y.S., 1987, Tolstoy et al., 1980 and others).

It has to be noted that such hypotheses are broadly applied for Late Cenozoic volcanic rocks of the Caucasus, regardless of the region of distribution and age. This is especially the case with regard to the latter hypothesis. We think that solving the question of origin of middle rocks of Caucasus requires accurately conducted formation analysis, series full information of depth structure of the region. Therefore, it is recommended to separately analyze origin of Miocene-Pliocene andesites and other related rocks of calc-alkaline series, acidic Upper Pliocene-Lower Quaternary rhyolite-trachyrhyolites and Upper Pliocene-Quaternary trachybasalt-trachyandesibasalt-trachyandesite series of the Eastern Caucasus. Their origins could not be united under the same process, especially with the volcanic zone of the Transcaucasian transverse elevation and the Greater Caucasus. Each formation is a separate formation. In our opinion, as the main reason, the origin of the middle rocks as a result of mingling of the main and acidic melting took place mainly within the Transcaucasian transverse elevation and the Greater Caucasus, where Pre-Paleozoic basement is highly elevated and thickness of granite layer is great.
Furthermore, as reported (Popov V.S., Semina V.A., Nikolayenko Y.S., 1987), in Late Cenozoic volcanites of these zones there are “forbidden” parageneses which have crystallized from crust and main melts; minerals of the rocks of metamorphic basement – garnet, cordierite and others, numerous xenoliths, xenocrystals of crust origin.

Therefore, in our opinion, the rocks of Upper Miocene-Lower Pliocene andesite-dacite-rhyolite associations are the result of fractional crystallization of the original basalt magma, which is substantiated below.

Materials and methods. The basis for the presented article is petrogeochemical and mineralogical analyses of rocks of andesite-dacite-rhyolite association of the Lesser Caucasus collected by the authors during field surveys (1982-1988) (Imamverdiyev, 2000, Gasanguliyeva, 2014). A total of 60 silicate components (X-ray spectral) (the article demonstrates the results of only 16 analyses), 75 microelements, results of microprobe and microelemental analysis of 20 samples of rock-forming minerals were used. The content of the rock-forming oxides in the rocks was determined using X-ray fluorescent method on a multi-channel X-Ray spectrometer CPM-25 (Institute of Geology and Geophysics of the Azerbaijan National Academy of Sciences, Baku). The concentration of impurity microelements was determined using X-ray spectral, flame-photometric, atomic absorption methods in the laboratories of the Institute of Geology and Geophysics of the Azerbaijan National Academy of Sciences, Bronnitskii Geological-Geochemical Expedition of the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, and also Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences and the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences (Moscow) and California State University, Northridge, rare-earth elements - neutron activation method in the laboratory of Bronnitskii Geological-Geochemical Expedition of the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements. Microprobe analyses determinations of the composition of minerals were performed using X-ray micro-analyzer JXA-8200 of JEOL Company (Japan) in the Institute of Geology of Ore Deposits Petrography Mineralogy and Geochemistry of the Russian Academy of Sciences and Russian Geological Research Institute (VSEGEI) (Saint Petersburg).

Tectonic-magmatic conditions of the formation of Neogene volcanism in the Central Part of the Lesser Caucasus (Azerbaijan). In the Azerbaijanian part of the Lesser Caucasus, the Neogene volcanism is widely developed in the Lachin anticlinorium, Kelbajar superimposed trough, Gochass and Sarybaba synclinoriums and the Nakhchivan zone. Neogene volcanism, being a continuation of the overall evolution of the Lesser Caucasus has manifested in these structures. These structures are complicated by numerous anticlines and synclinoriums, faults of north-north east direction. Along these faults, in the Neogene rocks, numerous vertical and steep dykes of rhyolite and dacite composition have formed. Having analyzed all studies mentioned above, N. A. Imamverdiev (2002) designated 3 associations in the Late Cenozoic rocks of the Central part of the Lesser Caucasus: 1. Late Miocene-Early Pliocene andesite-dacite-rhyolite association, in the composition of which 2 complexes are designated: a) dacite-rhyolite (Upper Sarmatian-Agdzhagyz suite); b) andesite-dacite (Meotian-Pontian-lower Pliocene - Basarkecher suite). 2. Late Pliocene-Early Quaternary trachyrhyolite. 3. Late Pliocene-Quaternary trachybasalt-trachyandesite association.

This article focuses on petrogeochemical peculiarities of the first association.

In the composition of andesite-dacite-rhyolite association, similarly to the Agdzhagyz suite, an dacite-rhyolite complex is designated. Products of this complex, of Upper Sarmatian age, are seen in north-west and east parts of the Kelbajar volcanic-tectonic depression and form a volcanic layer of over 350 meters thick, composing sub-volcanic bodies and extrusive domes.

The age of the second andesite-dacite complex was determined as Meotian-Pontian and Lower Pliocene and corresponds to the Basarkecher suite (Kashkai, Khain and Shyhalibeli, 1952). Rocks of the Basarkecher suite with angular and azimuthal unconformity are embedded on the volcanogenic layer of the Agdzhagyz suite, in some places on sedimentary layers of Eocene and Cretaceous Epochs and differ by pattern of folding and extent of metamorphism. In turn, the suite is with unconformity overlaid by volcanic rocks of Lower Pliocene and Quaternary periods. The rocks of this suite are broadly distributed in the Kelbajar Superimposed Trough, East-Goyche, Sarybulaq, Mikhtoken ranges in the upper parts of the rivers Terter, Vorotan, Hakari, and the in the Kelbajar and Karabakh volcanic uplands (Fig. 1).

Thus, the peculiarities of the Upper Miocene Lower Pliocene age of the volcanites are that they are composed mostly of average acidic and acidic pyroclastic and effusive associations. The
composition of vulcanites mostly corresponds to andesite, trachyandesite, dacite, trachydacite, rhyolite and trachyrhyolite and on very rare occasions consists of andesibasalt and basalt. According to geological data, the age of the asso- tiation is determined as Late Miocene-Lower Pliocene (Kashkai et al., 1952).

**Petrography.** The Upper Sarmatian dacite-rhyolite complex. Dacite, rhyodacite and rhyolite are the main rocks of the dacite-rhyolite complex. *Dacites* are mostly porphyry rocks. Phenocrysts are composed of plagioclase, hornblende, sometimes quartz and biotite. The size of phenocrysts reaches 3-10 mm. The structure of the main mass is hyalopilitic, pilotaxitic, hyaline. The quantitative-mineralogical composition of dacites is as follows: the main mass is 50-75%, plagioclase – 15-20%, hornblende – up to 5%, quartz – 2.5%, biotite – 2-3%, ore mineral – 1-2%. The main mass comprises microlites of altered acidic plagioclase, quartz, sometimes potassium feldspars, sintered glass.

*Rhyodacites* are distinct from dacites by higher content of quartz (5-8%) and biotite (3-5%), presence of potassium feldspar in the main mass. The main mass (45% of the volume of the rock) consists of acidic plagioclase, potassium spar and quartz sintered by glass. The structure of the main mass is spherulite, vitreous, microfelsitic. It has fluidal texture.

*Rhyolite and trachyrhyolite* complexes the upper part of the cross-section of the Agdzhagyz suite. Rhyolites are dominant in the composition of the complex. In the lower part of the cross-section they are replaced by rhyodacites, in the upper part – trachyrhyodacites and form their own flows. Phenocrysts of these rocks comprise acidic plagioclase, quartz, biotite and potassium feldspar. Quantitative-mineralogical composition of rhyolites is as follows: main mass – 60-70%, plagioclase – 10-20%, biotite – 3-5%, potassium feldspar – sanidine – up to 5%, quartz – 5-10%, ore mineral – 1-2%. In trachyrhyolites, the amount of sanidine increases (8-10%), while quartz decreases (4-5%). The main mass is composed of feldspars, quartz and glass, differs by vitreous, felsitic, microfelsitic structures.

Crystallization of mineral parageneses varies.
Usually the first to crystallize is magnetite, then sometimes biotite and hornblende crystallize together, and then plagioclase, quartz and orthoclase. Sometimes, one can see the following situation: magnetite, biotite, and then pyroxene. Afterwards, plagioclase+quartz+hornblende appear, and finally, in small amount K-Na feldspar is distinguished.

During the effusive stage, a process of cooling occurs in the residual melt, and crystallization of plagioclase, grains of quartz, and sometimes potassium-sodium feldspar in the rocks continues. Crystallization of phenocrysts of acidic rocks takes place in two stages: 1) intratelluric stage – due to saturation with water from the melt, release of dark-coloured minerals, such as hornblende, biotite, and then plagioclase; 2) phenocrysts form closely to the surface (especially quartz, acidic plagioclase, K-Na feldspars and others).

Rocks of lava facies of andesite-dacite complex are represented by dacite-trachydacite, andesite-trachyandesite and quartzitic latites. Dacite and trachydacites are composed of fractioned, pelitized phenocrysts of feldspar of 3-5 mm in length, and, on rare occasions, microcrystals of quartz. In many cases quartz is absent. Of coloured minerals, biotite in rare cases is recorded as micro phenocrysts.

Mineralogical composition of dacites is as follows: the main mass was 65-70%, plagioclase (An$_{30-40}$) – 20-25%, biotite – 5-10%, quartz – 5%. The main mass has felsitic, vitrophyric, microlitic, spherulite structure, fluidal texture. These rocks are characteristic of cavities filled with aggregates of fine-grained quartz. In dacites, secondary minerals are represented by chlorite and sericite.

The Meotian-Pontian-Lower Pliocene andesite-dacite complex is composed mainly of andesite and its moderately alkaline types. Andesites, trachyandesites, quartz latites are the most distributed large-porphry rocks, macroscopically composed of plagioclase, potassium-sodium feldspar, hornblende, sometimes notably seen are phenocrysts of biotite. Quartz latites are different from andesites and trachyandesites by content of potassium-sodium feldspars. The structure of rocks is porphyric, the main mass has an andesite, vitrophyric, pilotaxitic structure.

Depending on the mineral parageneses, these rocks are divided into pyroxene and pyroxene-hornblende types. Mineralogical composition of rock, depending on the type, changes as follows: feldspars (25-35%), hornblende (10-15%), clinopyroxene (5-10%), biotite (3-5%), main mass 50-60%. The main mass comprises feldspars, hornblende, clinopyroxene, volcanic glass and ore mineral.

The content of plagioclases in rocks includes An$_{0.40}$ and forms paragenesis with amphibole, biotite, clinopyroxene, potassium-sodium feldspar. Plagioclases of the second generation crystallized during their effusive stage have relatively acidic content (An$_{20-30}$). Potassium-sodium feldspar in rocks is present in quartz latites, trachyandesites. The content ranges Or$_{50-55}$ Ab$_{20-25}$ An$_{0.3-0.5}$ Fs$_{17-23}$ (for andesites). They belong to intermediate structural-optic type and are monoclinic, and not homogenous, represented by albite and orthoclase phases. The content of clinopyroxene changes from middle rocks to acidic and the share of Fs component increases: Wo$_{36.3-41.4}$ En$_{43.9-40.0}$ Fs$_{19.0-21.6}$ (for andesites), Wo$_{40.0-44.4}$ En$_{45.4-44.8}$ Fs$_{15.2-11.2}$ (for quartz latites) and Wo$_{41.7-42.7}$ En$_{36.3-34.6}$ Fs$_{22.0-22.7}$ (for dacites). Compositions of amphiboles, according to B. E. Leake (Leake, 1968), correspond to tschermakite, pargasite and magnesium hornblende (Imamverdiyev, 1999, Imamverdiyev et. al., 2017).

Therefore, early crystallization of magnetite, hornblende, biotite, appearance of clinopyroxene liquidus, the structural position of feldspars indicate that crystallization of magma melt and evolution occurred in the conditions of high pressure of water vapor in intermediary hotbeds. During the development, relatively acidic types of rocks of the association (dacites and rhyodacites) interacted with the surrounding rocks.

Very little research has been done on the crystalline inclusions in volcanic rocks of Neogene age of the Lesser Caucasus. Short reports about their composition and distribution could be found in the studies by N. A. Imamverdiyev (1988, 2002), A.Dj. Ismail –Zadeh (1986, 1989, 2001), Y.S. Genshaft (1983, 1986), V.G. Molyavko (1990) and other authors.

N. A. Imamverdiyev (2002) divides crystalline inclusions of andesite-dacite-rhyolite association into two types: 1) cumulate rocks of parent material, i.e. homogenous inclusion, and 2) crust xenolytes, i.e. inclusions occupied by melt from rocks of the Earth’s crust. Mantle-derived phenocrysts were not found in the Neogene Vulcanites.

Homogenous inclusions are represented by pyroxenites, mildly-alkaline gabroids, hornblendites, amphibolized gabros and diorites. These rocks are partly melted, oval irregular in shape, macroscopically completely crystalline, fine and average-grained. For these rocks with surrounding rocks, recreational interrelation is absent. This type of inclusion is mainly composed of the main plagioclase, diopside-augite and hornblende. Many phenocrysts undergo intense cataclysis and following partial amphibolization.
Mineral composition of xenolytes to a certain extent correlates with phenocrysts of the rocks which contain them. Therefore, broadly distributed amphibole-containing inclusions are even more broadly distributed in hornblende type of the middle rocks.

The second type of phenocrysts includes rocks which become occupied by the melt while traveling to the surface from the surrounding Meso-Cenozoic sediments. Usually they are broadly distributed among average- and acidic explosive rocks. Among these xenolytes, quartz-feldspar rocks, quartz diorites, amphibolites, shieists can be seen.

Petrochemistry. According to silica acidity, the rocks of association form antitonic sequence from dacite-rhyolites to andesites (SiO$_2$ $\geq$ 60%) (Table 1), and according to the ratio (Na$_2$O+K$_2$O)-SiO$_2$ (Le Bas et al., 1986) are the rocks of normal alkalinity and more rarely moderately alkaline (Fig. 2). On the diagram K$_2$O-SiO$_2$, the volcanites correspond to highly-potassium calc-alkaline series and differ from the series of normal alkalinity.

The rocks of this association are characterized by different contents of petrogenic oxides of the elements. In the volcanic rocks of the association, with increase in the content of SiO$_2$, the contents of TiO$_2$, Al$_2$O$_3$, FeO*, MgO, CaO, Na$_2$O, K$_2$O, P$_2$O$_5$, andesite-trachyandesite-quartz lattites, dacite-trachydacites and rhyodacite-rhyolites form individual groups. The calculations showed that the share of the total dispersion for the first factor equaled 58.5%, and affects the two element association: I – SiO$_2$ (-0.86); II – TiO$_2$ (0.77), Al$_2$O$_3$ (0.66), Na$_2$O (0.76), P$_2$O$_5$ (0.83), FeO* (0.71). The share of the second factor in the total dispersion equals 14.69% and affects the association of the following elements: MgO (0.63), CaO (0.78) and K$_2$O (-0.86). This is explained by the fact that SiO$_2$ and K$_2$O with other petrogenic elements give negative correlation, indicating fractioning in the process.

![Fig. 2. Positions of the contents of the rocks of the Late Cenozoic volcanic associations of the Lesser Caucasus on the diagram TAS (Le Bas et al., 1986). (Note: all the analyses of the authors are indicated)](image)

The rocks of this association are characterized by different contents of petrogenic oxides of the elements. In the volcanic rocks of the association, with increase in the content of SiO$_2$, the contents of TiO$_2$, Al$_2$O$_3$, FeO*, MgO, CaO, P$_2$O$_5$, decrease due to titanomagnetite, clinopyroxene, plagioclase and possibly apatite. At the same time, there was seen some increase in Na$_2$O and K$_2$O in the rocks with the increase in the silica acidity. The process of increase in potassium alkalinity is accompanied by crystallization of potassium feldspar in more acidic types of rocks.

The main petrochemical types of the rocks of andesite-dacite-rhyolite associations were divided using factor analysis on the basis of over 60 analyses. On factor F$_1$-F$_2$ diagram (Fig. 4), developed on the basis of nine petrogenic elements (SiO$_2$, TiO$_2$, Al$_2$O$_3$, FeO*, MgO, CaO, Na$_2$O, K$_2$O, P$_2$O$_5$), andesite-trachyandesite-quartz lattites, dacite-trachydacites and rhyodacite-rhyolites form individual groups. The calculations showed that the share of the total dispersion for the first factor equaled 58.5%, and affects the two element association: I – SiO$_2$ (-0.86); II – TiO$_2$ (0.77), Al$_2$O$_3$ (0.66), Na$_2$O (0.76), P$_2$O$_5$ (0.83), FeO* (0.71). The share of the second factor in the total dispersion equals 14.69% and affects the association of the following elements: MgO (0.63), CaO (0.78) and K$_2$O (-0.86). This is explained by the fact that SiO$_2$ and K$_2$O with other petrogenic elements give negative correlation, indicating fractioning in the process of differentiation of feldspar, titanomagnetite and apatite. As we will mention later, during increase the amount of SiO$_2$ in the association, the amount of titan oxides, aluminum, iron, magnesium, calcium, phosphorus in the rocks decreases, while alkali concentration (Na and K) increases. The reason of such pattern is fractioning of the mentioned minerals.
During increase in the amount of SiO₂ in the volcanic rocks due to fractioning of titanomagnetite, clinopyroxene, plagioclase,apatite, the amount of TiO₂, Al₂O₃, FeO*, MgO, CaO, P₂O₅ decreases. This pattern clearly manifests during the change in the amount of SiO₂ between 60-68%. In other words, for the association of dacites from andesites, fractioning of the abovementioned minerals plays the leading role. This pattern can be explained by crystallization of potassium feldspar in more acidic rocks (Gasanguliyeva, 2014).

Therefore, in the development of the rocks of the association, a quite sufficient role was played by the fractioning of titanomagnetite, plagioclase, clinopyroxene, amphibole and apatite.

Thus, association of the late-collision Neogene highly potassium calc-alkaline series with peculiar petrochemical content is characteristic of the central

![Fig. 3](image-url) Positions of the content of the Late Cenozoic vulcanite associations of the Lesser Caucasus on the diagram K₂O-SiO₂ (Peccerillo A., Taylor S.R., 1976).

![Fig. 4](image-url) Diagram of distribution of F₁ and F₂ factors in the rocks

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part of the Lesser Caucasus and is distinct from the typical calc-alkaline of the series of normal alkalinity, formed in other geodynamic conditions.

The peculiarities of the inclusions in the rocks of andesite-dacite-rhyolite assoiation depend on the type, mineral composition, and also their genetic type. Relative (homogenous) inclusions (xenoliths) are presented by pyroxenites, hornblendites, gabroids, diores. In these rocks, the content of silica changes 45.0-57.9%, the content of MgO is relatively higher than in the containing andesites, and the rocks are characterized by relatively higher contents of TiO₂, CaO, Kuno differentiation index (S.I) (Table 1) (In the article, only 16 analyses are shown). These xenoliths are characterized by average ferruginosity (F=42-65), but lower than in the containing andesites.

**Geochemistry.** In vulcanites of differentiated andesite-dacite-rhyolite assoiation, from andesites to rhyolites, at increase in SiO₂ and decrease in MgO, the coherent elements, as in the petrogenic oxides and macroelements, give dependency expressed linearly or sometimes with broken trend (Imamverdiyev et al., 2017). At the beginning of these trends, there are figurative points of hypogene inclusions. Therefore, in homogenous inclusions of the main content composed of the main plagioclase, olivine, clinopyroxene, hornblende, magnetite, there are observed increased amounts of elements of groups of iron and strontium. Distribution of these elements in the rocks of the assoiation is controlled by fractioning of the rock-forming minerals. It should be mentioned that in the inclusions, the decrease in these elements is more notable, and in the transition to containing andesites, the geochemical trends disrupt. Such distribution of macro- and microelements in the inclusions indicates the comagmaticity with the volcanic rocks.

The amount of incompatible elements (Rb, U, Th, Nb, Zr, Nb, Hf, LREE and others) in the hypogene inclusions is minimum, increasing in the sequence andesite-dacite-rhyolite. From middle to acidic rocks, the content of non-coherent elements increases approximately by 2.5-3 times (Table 1).

Typically incompatible elements Zr, Nb, Ta, U, Th accumulate in the melt and their ratio in the process of evolution of the magmatic melt does not change. On the diagram of the dependence of SiO₂, MgO, taken as index of differentiation of the indicated elements, their ratio minimally decreases, indicating the role of contamination along with the crystallization differentiation during the formation of the rocks. By contrast, La/Yb, K/Rb ratios in the rocks of the formation depending on the content of SiO₂ begin to increase or decrease. Increase in K/Rb ratio, increase in La/Yb ratio could be explained by high coefficient of distribution for K and Yb between the mineral and the melt. Hornblende could be such a mineral (Gasanguliyeva, 2014; Imamverdiyev et al., 2017). Fractioning of this mineral is the reason for decrease in K/Rb and increase in La/Yb ratios in the process of differentiation. When MgO in the rocks of the formation reduces, K/Rb ratio decreases and becomes controlled by crystallization of leucocratic minerals.

In the rocks of the assoiation, REE changes in small intervals and light lanthanides (åCe) dominate over heavy ones (åY) (Table 1). This is explained by high value of La/Yb ratio (25-40), and for the same reason, on the normalized diagram, curvature is seen in the distribution of REE. In the evolution of vulcanites, the sum of REE is observed in quartz lattites. Rocks of the assoiations differ also by Eu anomaly which bears important genetic information. In the middle rocks (quartz lattites, andesites), this ratio approaches one (Eu/Eu*≈0.94-1.05), in more acidic rocks, low minimum is observed (Eu/Eu*≈0.58-0.63) and indicates fractioning of plagioclase in the development of more acidic rocks (Balashov, 1976, Imamverdiyev, 2003).

Distribution of REE in the hypogene inclusions shows almost the same situation. In melanocratic inclusions, the content of light lanthanides is high and the form of the graph is more rounded, and in some rocks, slight Europium minimum was seen.

To evaluate the role of the mantle fluids and the extent of melting in the development of the rocks of the assoiation, we used the ratios of the elements with close geochemical properties.

The studies revealed that in the rocks of andesite-dacite-rhyolite assoiation, the content of Ba and Ba/Y, Rb/Y, Th/Yb ratios rapidly increases. To a certain extent, increase in Nb/Y and Nb/Yb ratios was seen. Enrichment of the rocks of formation with lithophylous and rare earth elements is due to relatively high degree of melting of fluid-enrichment melt. On the other hand, on the graphs of dependence of Ba/La, U/Nb, Zr/Nb, La/Nb ratios on Th/Nb, the increase in the latter clearly indicates the important role of the enrichment of the mantle formed due to fluids separate from the materials of subduction.

Thus, geochemical data, in particular high values of Th/Nb, Ba/Nb, K/Ti ratios in the studied rocks and also low values of Nb/Y and Ti/Y ratios in combination with regional geological data indicate that mantle sources under the Lesser Caucasus are metasomatized by more ancient subduction processes, they contain highly potassium and impoverished HFSE water-
Table 1: Content of petrogenic oxides (%) and microelements (ppm) in the presented samples of rocks of andesite-dacite-rhyolite association of the Lesser Caucasus (according to Imamverdiyev, 2000 and Gasanguliyeva, 2014)

| № | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Elements | | | | | | | | | | | | | | | | |
| № | | | | | | | | | | | | | | | | |
| SiO₂ | 61.09 | 63.26 | 63.8 | 62.94 | 62.32 | 62.99 | 64.81 | 65.99 | 68.19 | 73.74 | 74.21 | 44.92 | 45.92 | 45.94 | 49.8 | 57.92 |
| TiO₂ | 0.59 | 0.63 | 0.49 | 0.75 | 0.58 | 0.60 | 0.60 | 0.52 | 0.27 | 0.32 | 0.32 | 1.88 | 1.61 | 1.58 | 1.15 | 0.98 |
| Al₂O₃ | 15.70 | 17.15 | 15.41 | 17.15 | 16.9 | 16.60 | 17.03 | 16.41 | 15.77 | 14.76 | 15.67 | 14.85 | 16.15 | 13.09 | 8.46 | 16.99 |
| Fe₂O₃ | 3.47 | 3.93 | 2.5 | 4.94 | 3.91 | 3.28 | 3.38 | 3.59 | 1.69 | 1.41 | 1 | 9.98 | 6.29 | 9.66 | 5.62 | 5.13 |
| FeO | 1.29 | 0.62 | 0.94 | 0.43 | 1.01 | 1.29 | 0.73 | 0.28 | 0.43 | 0.28 | 0.43 | 1.15 | 1.45 | 1.74 | 3.33 | 1.6 |
| MnO | 0.06 | 0.06 | 0.06 | 0.09 | 0.04 | 0.09 | 0.03 | 0.09 | 0.04 | 0.05 | 0.03 | 0.16 | 0.11 | 0.19 | 0.18 | 0.1 |
| MgO | 1.85 | 2.29 | 1.77 | 1.86 | 1.95 | 1.90 | 1.43 | 1.31 | 0.05 | 0.37 | 1.05 | 7.81 | 7.47 | 8.13 | 12.43 | 2.62 |
| CaO | 4.85 | 4.23 | 5.34 | 5.25 | 4.24 | 4.32 | 3.97 | 3.19 | 1.32 | 1.58 | 0.54 | 10.96 | 14.7 | 13.47 | 13.74 | 6.74 |
| Na₂O | 4.19 | 4.43 | 3.93 | 3.3 | 4.07 | 4.08 | 4.27 | 4.05 | 4.57 | 3.48 | 2.06 | 4.05 | 2.23 | 2.99 | 2 | 4.32 |
| K₂O | 3.54 | 3.65 | 2.73 | 1.87 | 2.95 | 3.08 | 3.47 | 2.55 | 4.14 | 2.23 | 3.14 | 0.77 | 0.72 | 0.89 | 0.92 | 2.01 |
| P₂O₅ | 0.41 | 0.43 | 0.38 | 0.35 | 0.28 | 0.30 | 0.33 | 0.23 | 0.06 | 0.01 | 0.07 | 1.75 | 0.09 | 1.7 | 0.13 | 0.68 |
| LOI | 0.81 | 0.2 | 1.96 | 0.38 | 0.54 | 0.46 | 0.47 | 0.96 | 0.27 | 2.49 | 1.56 | 0.63 | 0.38 | 0.49 | 0.39 | 0.43 |
| Sum | 98.63 | 100.88 | 99.31 | 99.21 | 99.08 | 98.1 | 100.72 | 98.15 | 99.23 | 100.72 | 100.08 | 98.91 | 97.12 | 99.87 | 98.15 | 99.52 |

1-11 – rocks: 1-2-quartz latite, area near Ayıçınqıllı volcano; 3-4-andesite, lava flow between the volcanos Sarimsagli and Sarçalı; 5-6- andesite, area near Dikpillarakan volcano; 7- dacite, area near Galinkaya volcano; 8-dacite, south-west slope of the Sarimsagli volcano; 9- rhyodacite, slope of the Dikpillarakan volcano; 10-11-rhyolite, area near Moz village 12-16 – xenolithes: 12-14- amphibole gabbro; 15- pyroxenite; 16-quartz diorite «-« -undetermined.
rich fluids. According to L. I. Demina and N. V. Koronovsky (2008), the source of fluids in the conditions of collision could be dehydration. To solve this problem more accurately, a MORB-normalized spider-diagram of compatible and incompatible elements was used.

Compared with basalts of the mid-ocean ridges (MOR) of N-MORB type (Sun S.S., McDonough W.F., 1998), the rocks of andesite-dacite-rhyolite association are enriched with Sr, Rb, Ba, La, Ce, and poor in highly charged elements (Ta, Nb, Zr, Hf, Ti, Y, Yb) (Fig. 5).

As demonstrated in Fig. 5, N-MORB normalized distribution of microelements for andesites, quartz latites, dacites and trachyhydodacites repeats in general terms, indicating their genetic commonality. Deep minimum of Ta in the rocks of the association should be noted, as seen in the similar rocks formed in different geo-dynamic conditions (Frolova T.I., Burikova I.A., 1997). The reason for appearance of Ta and Nb minimum is explained by these authors. In our opinion, due to oxidized fluids, the first to crystallize is magnetite, which, while being removed from melt, also carries out the rare elements, including Ta and Nb, which easily enter the structure of titanomagnetites.

The rocks of this series are the analogues of calc-alkaline and, partly, mildly alkaline Neogene series of the Lesser Caucasus.

Petrological peculiarities. Analysis of the abovementioned petrogeochemical materials suggests the formation of andesite-dacite-rhyolite association in the Upper Miocene-Lower Pliocene periods in the Azerbaijanian part of the Lesser Caucasus, which belongs to highly potassium calc-alkaline or calc-alkaline and mildly alkaline petrochemical series. In the similar formations of Nakhchivan and Armenia, pyroxene-olivine, olivine basalts, dolerites and andesibasalts are present in subordinate amount.

Antidromic evolution of the rocks of the association, presence of homogenous mafic inclusions with cumulative textures indicate that initial magmas for the differentiated calc-alkaline series are volatile-rich highly alumina basalt magmas with relatively high content of alkali (Frolova T.I., Burikova I.A., 1997).

It is hard to judge the nature of original basalt magmas. However, based on the experimental data (Green D. H., Ringwood A.E., 1968; Yoder G. S., Tilly K. E., 1965; Yoder Kh. I., 1979; Ryabchikov I. D., 1987), the current most substantiated hypothesis is that the original basalt magma could have melted from the peridotite substrate of the upper mantle. At the same time, the compound of these magmas at the level of originating corresponds to cotectics with participation of olivine and clinopyroxene.

According to the experimental data, the cotectic olivine + clinopyroxene + plagioclase is the richest normative plagioclase at the depth of around 25 km, corresponding to the pressure of »7 kilobars (Popov V. S., 1981).

Summarizing the experimental studies, V. S. Popov (1981) came to a conclusion that the rocks of calc-alkalineseries originate or differentiate within the continental crust at the depth of no more than 20-30 km.
Table 2. Balance calculations between the rocks of andesite-dacite-rhyolite association

### High-potassium andesite – high-potassium dacite

| Oxides     | Co  | Cp  | Cpx | Pl  | Mt  | Amf | CD  |
|------------|-----|-----|-----|-----|-----|-----|-----|
| SiO₂       | 63.66 | 63.73 | 53.34 | 62.30 | 0.00 | 44.70 | 66.76 |
| TiO₂       | 0.67  | 0.57  | 0.54  | 0.00  | 6.14 | 3.06  | 0.52 |
| Al₂O₃      | 16.58 | 16.51 | 3.91  | 23.68 | 5.01 | 12.02 | 16.53 |
| FeO’       | 4.75  | 4.76  | 8.43  | 0.20  | 86.54 | 12.56 | 3.75 |
| MnO        | 0.08  | 0.07  | 0.23  | 0.00  | 0.00 | 0.14  | 0.07 |
| MgO        | 1.96  | 2.10  | 14.59 | 0.00  | 2.31 | 13.64 | 1.69 |
| CaO        | 4.39  | 4.08  | 18.44 | 4.54  | 0.00 | 10.34 | 3.42 |
| Na₂O       | 4.38  | 4.27  | 0.52  | 8.46  | 0.00 | 2.58  | 3.99 |
| K₂O        | 3.53  | 2.76  | 0.00  | 0.82  | 0.00 | 0.96  | 3.27 |

Weight share of phases: 0.751

### High-potassium dacite-rhyolite

| Oxides     | Co  | Cp  | Cpx | Pl  | Mt  | Amf | CD  |
|------------|-----|-----|-----|-----|-----|-----|-----|
| SiO₂       | 66.76 | 66.77 | 60.94 | 53.34 | 0.00 | 44.70 | 71.41 |
| TiO₂       | 0.52  | 0.53  | 0.00  | 0.00  | 5.83 | 3.06  | 0.27 |
| Al₂O₃      | 16.93 | 16.25 | 24.19 | 3.91  | 7.56 | 12.02 | 15.95 |
| FeO’       | 3.75  | 3.77  | 0.29  | 8.43  | 84.34 | 12.56 | 2.14 |
| MnO        | 0.07  | 0.05  | 0.00  | 0.23  | 0.00 | 0.14  | 0.04 |
| MgO        | 1.69  | 1.79  | 0.00  | 14.59 | 2.08 | 13.64 | 0.05 |
| CaO        | 3.42  | 3.33  | 5.48  | 18.44 | 0.00 | 10.34 | 1.33 |
| Na₂O       | 3.99  | 4.76  | 8.30  | 0.52  | 0.00 | 2.58  | 4.62 |
| K₂O        | 3.27  | 3.28  | 0.80  | 0.00  | 0.00 | 0.96  | 4.19 |

Weight share of phases: 0.690

### Rhyodacite-rhyolite

| Oxides     | Co  | Cp  | Pl  | Mt  | CD  |
|------------|-----|-----|-----|-----|-----|
| SiO₂       | 71.41 | 71.50 | 58.75 | 0.00 | 74.86 |
| TiO₂       | 0.27  | 0.08  | 0.00  | 1.13 | 0.08 |
| Al₂O₃      | 15.95 | 15.45 | 25.35 | 0.62 | 13.41 |
| FeO’       | 2.14  | 2.13  | 0.42  | 93.56 | 1.43 |
| MnO        | 0.04  | 0.05  | 0.00  | 0.58 | 0.06 |
| MgO        | 0.05  | 0.37  | 0.00  | 4.11 | 0.40 |
| CaO        | 1.33  | 2.07  | 7.19  | 0.00 | 0.97 |
| Na₂O       | 4.62  | 4.93  | 7.65  | 0.00 | 4.38 |
| K₂O        | 4.19  | 3.71  | 0.64  | 0.00 | 4.41 |

Weight share of phases: 1.270

FeO’=FeO+Fe₂O₃ (in counting for FeO)
Basalt fluids which appear at such depths lead to the development of alumina basalts, composition of which at atmospheric pressure significantly differs from the eutectic pressure. Such basalts are characteristic for Neogene calc-alkaline series of Nakhchivan and west Daralagez.

The appearance of such alumina melts could be related to the partial melting of ultrabase solid substrate, as well as differentiation at the same hypsometric level of deeper basalts with olivine deleted from them, and possibly orthopyroxene. The low content of elements of iron group (Ni, Co, Cr) in alumina basalts also indicates the association of these melts as the result of precipitation from the primary magma of olivine and chromospinelides. The high content of Cr in some rocks of the association could be due to primary chromospinelides which remained in the rocks.

In our opinion, from such primary magmas, as a result of fractional crystallization, Neogene middle and acidic rocks of the Lesser Caucasus could have been formed. The reality of such process is confirmed by spatial and temporal association of basalts and these rocks (within Nakhchivan, west Daralagez); presence of liquidus phases among femic minerals, as a result of fractioning of which acidic melts form; belonging of all rocks to the integral petrochemic series with preservation of heightened alkalinity; presence of several generations of hollow parageneses of minerals in all rocks of the series; finding of homogenous inclusions which have the main content, containing andesites; pattern of distribution of microelements; presence of Eu – minimums in middle and acidic rocks; distribution of more acidic, without notable features of crystallization, natural glass in andesites and dacites of the association.

All these data confirm fractioning of dark-coloured and partially leucocratic minerals in intermediate hotbeds, as a result of which middle and acidic differentiates have formed. The main evolutionary mechanism of the melt of the surveyed series is the crystallization differentiation. The calculations of the balance of the substance which model the process of fractioning of phenocrysts, and also magnetites, confirmed the possibility of development of the compounds of rocks from andesites to rhyolites as a result of this process.

This model correlates with the data of E. F. Osborn (1983). According to this author, in oxidative situation, during lower pressures, near the liquidus, magnetite and hornblende appear, which is the reason for the formation of middle and acidic rocks. According to the scheme of J. Gill (Gill J.B., 1981), andesites form as a result of fractioning from the basal magma of the association olivine + augite + magnetite.

Our assessments confirm the conclusions of these authors. Therefore, the fractioning of paragenesis of augite + hornblende + plagioclase + magnetite in the intermediate hotbeds caused association of dacite and rhyodacite from high-potassium andesite (Table 2). An attempt at calculation of the formation of the rocks of trachyrhyolite association out of rhyodacites failed because between the real and calculated compounds, the values of errors of connection equaled $\sum R^2 > 1$: this indicates absence of crystallization connection between rhyodacite and rhyolite.

**Physical-chemical conditions of the association.**

The temperature interval of crystallization of phenocrysts of quartz latites, andesites, dacite-rhyodacites lies within the range of $1,155^\circ\text{C} - 1,020^\circ\text{C}$. The assessments of the temperatures are based on the coefficient of distribution of Sr between Pl/glass (Drake M.J., Well D.F., 1975), coefficient of distribution of Ni between Cpx/glass and Ol/glass (Hakli T.A., Wright T.L., 1967), and also plagioclase geothermometer according to Kudo, Well (Kudo A.M., Well D.F., 1970). Temperature of the development of the rocks correlates well with the temperature of homogenization of quartz from these rocks (Panina et al., 1989, Imamverdiyev, 2000, 2003).

The value of $f_{02}$ in these temperatures for the indicated rocks is in the interval between $10^{-7.4}$ and $10^{1.5}$ atm, determined according to (Nikolyev G. S., Borisov A. A., Ariskin A. A., 1996; Sack R.O., Carmichael I.S.E., Rivers M., 1980), which is closer to the Mag – Hm buffer. The pressure calculated according to the method of (Frolova T. I., Perchuk L. L., Burikova I. A.,1989) for most of the magnesia basalts from the region (Bichank suite) varies 1.6-1.7 GPa, which corresponds to the border between the crust and the mantle (H=51-53 km) and correlates with the experimental studies. Therefore, according to I. Kushiro (1984), highly silica basalts original for most calc-alkaline series are in equilibrium with the mantle peridotite at the depth of 50 km (1.7 GPa) in the temperature of 1,320°C and water content of 1.5% in the melt.

**Discussion of the results.** Therefore, during the formation of rocks of andesite-dacite-rhyolite association, the leading mechanism was crystallization differentiation and there are evidences of relation between the middle rocks and the main and acidic rocks. Naturally, to explain this genesis of these rocks, the model of their crust-mantle origin is used, either as a result of assimilation of the crust material.
or mingling of crust and mantle magmas. It seems that these processes can occur, however it is doubtful that they dominate. First of all, because in the upper parts of relatively cold crust, partly crystallized basalt melts, manifested for example within Nakhchivan, Daralagez, could assimilate limited amount of the containing rocks. Secondly, because in the lower part of the crust, the acidic rocks are limitedly distributed, and for the formation of hybrid rocks of andesibasalt composition, up to 30-40% of the crust substrate of granite composition and even greater amount of middle rocks need to be assimilated (Popov V.S.,1982; Keskin M., Pearce J.A., 1994). Certain limitations affect also the processes of the mingling of the melts due to their different density and different temperature of crystallization, which could obstruct the formation of large amounts of relatively homogenous melts. Furthermore, the weakness of the hypothesis of the mingling is the inconstancy of the compounds and similar products – the model assessments of the processes of mingling (Popov V.S., 1982) indicate that for obtaining hybrid rocks of different basicity, in each particular case the original melts should change, which, taking into consideration the relative homogeneity of the main melts, is unlikely.

We assume only partial contamination with the crust materials in the processes of evolution of the main magma of the rocks of andesite-dacite-rhyolite association. Unlike the elevated Transcaucasian zone in more depressed Eastern Caucasus in the conditions of elevated fluid pressure and decreased temperature, the melt underwent fractional crystallization in the intermediate hotbeds, at the same time becoming enriched with alkaline, large-ion lithophyllous elements, light REE, etc. This is indicated by the presence of large crystals of feldspars, contamination of these materials with numerous crystals of biotite, magnetite, several generations of these minerals, zoning, and also presence of relative “aqueous” inclusions, such as hornblendites, hornblende gabbro and others. The observed high contents of aqueous minerals, high levels of lithophyllous elements, high concentrations of REE (5-15 times exceeding the chondritic content for heavy rocks and over 100 times for light ones) in the rocks of this association cannot be achieved due to the fractioning of the abovementioned minerals, because according to the data (Popov V.S., Semina V.A., Nikolayenko Y.S., 1987), their main concentrators are the accessory minerals.

It appears that increased contents of REE, and also Sr, Ba, U, Th, Rb in the considered rocks are due to low levels of selective melting of metasomatically changed substance of the mantle at great depths, as presumed by V.S. Popov et al. (Popov V.S., Semina V.A., Nikolayenko Y.S., 1987) and N. A. Imamverdiyev et al. (2000, 2003, 2017, 2018) regarding the formation of the Upper Pliocene-Quaternary mildly alkaline series of the Lesser Caucasus.

Conclusions:

1. Analysis of the presence of the abovementioned petrogeochemical materials suggests that the formation of the differentiated andesite-dacite-rhyolite association, belonging to high potassium calc-alkaline or calc-alkaline and mildly alkaline petrochemical series, in the Late Miocene-Early Pliocene periods in the Azerbaijani part of the Lesser Caucasus. Similar associations of Nakhchivan and Armenia, in the subordinate amount, contain pyroxene-olivine, olivine basalts, dolerites and andesibasalts.

Antidromic evolution of the rocks of the association and presence of homogenous mafic inclusions with cumulative textures indicate that the original magmas for the differentiated calc-alkaline series are volatile-rich high silica basalt magmas with relatively high content of alkali. It could be noted that most antidromic andesite-dacite-rhyolite magmatic systems were found in subductive island-arc conditions characteristic of long-existing hotbeds of acidic magma.

2. The studies revealed that in the rocks of andesite-dacite-rhyolite association, the content of Ba and Ba/Y, Rb/Y, Th/Yb ratios rapidly increase. To a certain extent, the increase in Nb/Y and Nb/Yb ratios is observed. The enrichment of the rocks of the association with lithophyllous and rare earth elements is due to the relatively high extent of the melting of the melt enriched with fluids. On the other hand, increase in Th/Nb ratios clearly indicates an important role of the enrichment of the mantle, formed due to fluids separated from the materials of subduction.

3. Rocks of andesite-dacite-rhyolite association were formed by fractional crystallization of the primary high silica basalt magmas of heightened alkalinity in the intermediate magmatic hotbeds. At the same time, the process of crystallization differentiation was accompanied by the processes of contamination, hybridism and mingling. Temperature interval of crystallization of phenocrysts of rocks of the association lies within 1,155°-1,020°C, value of fo2 for these rocks in these temperatures equals 10\(^{-14}\) to 10\(^{-15}\) atm, which approaches to the buffer Mag-Hm. Pressure for the most magnesia basalts of the region (Bichanak suite) varies 1.6 to 1.7 GPa, which corresponds to the border between the crust and mantle (H=51-53 km).
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