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Low-Temperature Hydrothermal Alternation of Dolerites from the Djavakheti Plateau (Georgia)

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Abstract

The zones of hydrothermal alternations have been manifested in the dolerites of the calc-alkalic series of Late Pliocene – Early Pleistocene (1.8 Ma) in the extreme East of the Javakheti volcanic plateau. The hydrothermally altered zone is related to the areas of the unloading of existing hydrothermal fluids within broken and brecciated zones of mother rocks. The association of low temperature minerals has been developed in hydrothermal alternation zones. The identification of secondary minerals was done through using: chemical, optical, X-ray diffraction (XRD) and geochemical research methods. In the mineral complexes of hydrothermal alternation zones, collections of zeolites are not widely presented. They integrate chabazites and thomsonites – varieties of Ca and Na-Ca. Widely spread is calcites and montmorillonites. Pumpellyites and organic material are insignificantly represented. Chabazite create well developed, often facolite-type crystals. They are presented in the form of large crystal individuals and druses. Thomsonites are developed in the form of radial and radially fibrous fibrillar aggregates. Montmorillonites are widely spread minerals, which are represented by globular, reniform and scaly aggregates; In the association of secondary minerals, calcite is considered to be one of the main minerals. The mineralogical composition of mother rocks significantly determines the formation of Ca and Na-Ca zeolites and their local distribution in the hydrothermal alternation zones. Zeolites are mainly formed as a result of the compositional transformation of base plagioclase, and montmorillonite as a result of the olivine and pyroxene transformation. The process of the secondary transformation of dolerites takes place under pulsation influence of solutions enriched with alkali Na-Ca and CO_2 in low depths (surface or subvolcanic conditions) within the condition of low temperature (120^{o}C) and pressure.

Keywords: Calcite, Chabazite, Djavakheti, Georgia, Zeolite

Introduction

The presence of hydrothermally altered dolerite zones in the territory of the Gomareti plateau has been known for more than 35 years (Tutberidze, 1979). The aim of the study of the altered dolerites from the study area is to determine mineralogical changes, which are caused by interaction of rock-forming minerals by cold meteoric water at low temperature with enriched Na, Ca and CO_2 and with low SiO_2 deficient condition. The study of the collected materials from the hydrothermally altered zones was conducted `by using binocular microscope, analysis of thin sections petrography, X-ray diffraction analysis of clay, chabazite, thomsonite and calcite minerals.

This paper is based on the study results of the existing materials.

Geological Setting

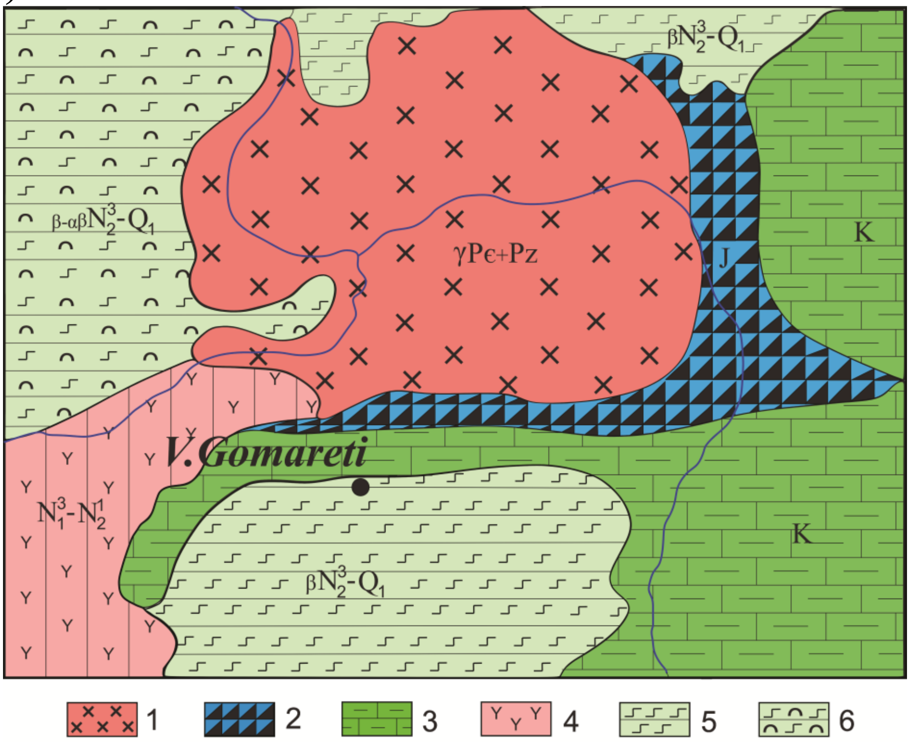
The Gomareti plateau is located in the extreme East of the Javakheti volcanic highland. Javakheti highland is a classic example of the continental collision volcanism.

The heterogeneous rocks of Khrami crystalline massif which are the oldest ones, are divided into Precambrian and Late Variscan formations. The Precambrian igneous and metamorphic complex which consists of the gneiss-migmatitic rocks, is represented by biotite-cordierite plagiogneisses, biotite-hornblende quartz-diorite ortogneisses, plagiomigmatites, granitogleisess and granite-migmatites- dated as 931±6 Ma. years old (Tedliashvili, 2014). The Late Variscan igneous sediments is represented by granitoids - dated as 325-330±6 Ma years old (Tedliashvili, 2014). Volcano-sedimentary formation of Jurassic and Cretaceous age overlay uncomfortably on the rocks of Khrami crystalline massif.

Cenozoic was a time of active magmatism in the Javakheti volcanic highland, revealed by 3 major magmatic phases: The magmatism started in the Late Miocene-Early Pliocene, peaked in the Late Pliocene-Early Pleistocene and extended into the Late Pleistocene (Skhirtladze, 1958; Tutberidze, 2004). The Gomareti effusive complex is presented by the dolerite and Basaltic lava series in the Late Pliocene-Early Pleistocene age (1.7-1-8 Ma; Ages based on Paleontology and K/Ar geochronology). They cover in nonconformity the Jurassic and Cretaceous formations and the metamorphic complex of Khrami crystalline massif (Figure 1).

The existence of hydrothermal alternation zones in artificial exposures was first discovered in some dolerite Lava flows of the Gomareti Plateau in 1979 (Tutberidze, 1979). The hydrothermally altered zones are connected with the areas of collapse zones of host rocks (Figure 2). Brecciated zones create favorable conditions for movement and loading of the hydrothermal system.

Figure 1. *Schematic Geological Map of the Research Area (After Skhirtladze, 1958)*



Legend: 1-Paleozoic and Precambrian rocks 2-Lower Jurassic and Upper Paleozoic (undifferentiated), 3-Cretaeous (undifferentiated), 4- Late Miocene-Early pliocene effusive formation (andesite, dacite, liparite), 5-Late Pliocene- Early pleistocene effusive formation Gomareti s Plateau (dolerite, basalte). 6--Late Pliocene-Early pleistocene effusive formation (Dolerite, Basalt, andesite).

Figure 2. *Roadside Artificial Outcrop Hydrothermal Alternation Zone of the Study Area*

Methods of Study

Major element analyses of primary and secondary mineral bearing dolerites were conducted in the petrochemical analytical laboratory of the department of Geology of the Tbilisi State University; petrographic studies were carried out with Nikon Polarizing microscope (OPAX) at the Department of Geology (TSU). XRD patterns were recorded with a ДРОН-4 diffractometer operating with Co radiation (α = 1.7989 Å) in laboratory roentgeno-structural analyses of Tbilisi State University.

Petrography

Unaltered dolerites are gray, dark green to light green in color. Their texture is almost hollocrystalline- it varies from subophitic to ophitic and is almost idiomorphic-granular. Porphyritic texture is rare. The most common rock-forming phenocrysts are plagioclase (59.3-64%) and augite (21.9-15.5%) with a subordinate number of olivine (11.4-8.5%) and apatite. Opaque minerals are present by magnetite and ilmenite. Some dolerite rocks have suffered alteration due to extensive zeolitization, carbonization, chloritization and clay-like mineralization. The amygdule walls and vesicles are filled with, zeolite, calcite and clay minerals. Some of these amygdules also have organic materials.

All the host rocks in the study area are calc-alcaline dolerite (Skhirtladze 1958; Tutberidze, 2004); The concentrations of SiO_2 wt% ranges from 49,24 to 52,31, CaO wt% ranges from 7.62 to 8.90; Mg wt% ranges from4 .62 to 6.21, Al_2O_3 wt% ranges from 15.48 to 17.05 Na_2O wt% ranges from 3.70-4.10 ; Chemical compositions of dolerite give in Table 1 (an.1-3).

Table 1. *Chemical Compositions of Dolerites, Chabazite, Thomsonite and Montmorillonite of Study Area*

	Host rock			Chabazite	Thomsonite	Montmorillonite
	1	2	3			
SiO_2	49.39	52.31	49.24	43.95	42.15	43.28
TiO_2	1.45	1.32	1.36	0.02	0.04	0.23
Al_2O_3	17.05	16.70	15.48	18.47	23.66	11.73
Fe_2O_3	8.02	6.67	4.46	0.52	0.52	6.54
FeO	1.72	2.34	6.14	0.02	0.22	0.29
MnO	0.14	0.14	0.18	0.07	0.07	0.21
MgO	4.62	5.14	6.21	1.46	2.62	10.86
CaO	8.37	7.62	8.90	11.24	8.37	2.69
Na_2O	3.70	4.10	4.09	0.25	1.80	0.20
K_2O	0.90	1.40	1.27	0.10	0.40	0.25
P_2O_5	0.32	0.38	0.40	-	-	-

Plagioclase. Plagioclase is a major rock-building mineral of the zeolite-bearing dolerites of the Gomareti Plateau. Among the unaltered dolerites of the study area, plagioclase is almost fresh and occurs both as phenocrysts as well as smaller crystals in the groundmass. Phenocrysts are characterized by anhedral-subhedral grains. The anorthite molecule varies from 60 to 64%. The Ca-rich plagioclase is most susceptible to hydrothermal alteration to more sodic varieties due to the late stage action of hydrothermal solutions (Deer et. al., 1992); Many plagioclase phenocrysts have been zeolitization and calcitization.

Olivine. Olivine phenocrysts were relatively rarer than plagioclase and pyroxene; Crystals of olivine occur as colorless in the form of subhedral to anhedral grains; the size of grains is variable in size from a 0.8 up to1.5- 2 mm; 2V very large-varying from 86 to 88^0, Ng-Np=0.026-0.031; Olivines are corroded, exhibit weathering and change to bowlingite; Olivines are altered by clay, serpentine, chlorite and opaque minerals

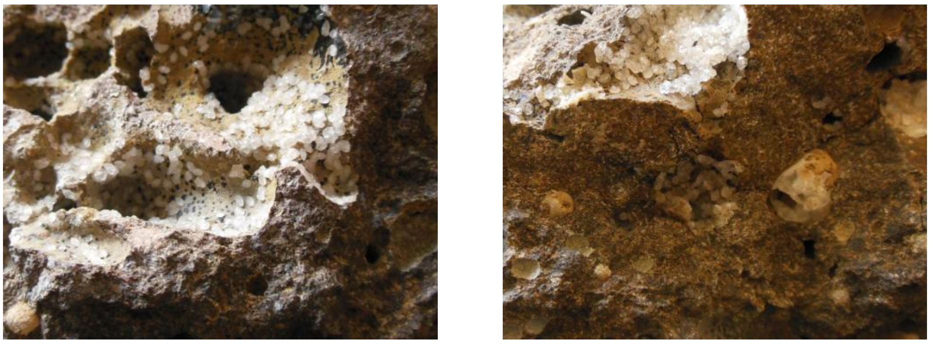
Pyroxene. Clinopyroxene occurs as anhedral to subhedral grains, between plagioclases crystals- from 0.7–1.5 mm in size. Some of the pyroxene have a grain size more than 1,5 mm. Based on its optical properties (2V = 58, Ng-Np= 0.021) pyroxene belongs to augite. Pyroxene is altered by chlorite and clay minerals.

Secondary Mineral Association

The secondary mineral complexes of hydrothermal alternation zones of the Gomareti plateau are presented by zeolites, calcites, clay minerals and organic materials. Collections of zeolites are not widely presented. They integrate zeolites - chabazites and thomsonites of Ca and Na-Ca composition. Widely spread are the calcites and smectites. Pumpellyite and organic materials are insignificantly represented. Most zeolites and calcite occur as coarse-grained aggregates, which are easily identifiable. The zeolites and associated secondary minerals are locally abundant in amygdules, fissure veins and vesicle in hydrothermal alternation dolerite on the study area.

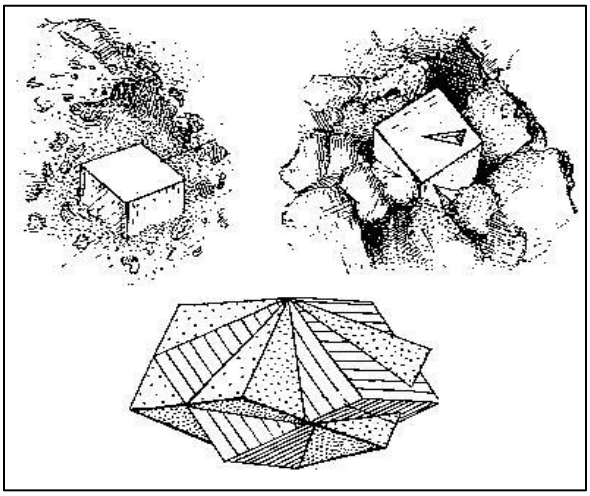
Chabazite. The most widespread zeolite in the alternation zone of the study area is chabazite. Chabazite is presented in the form of well-developed forms, individual aggregates and monomineral druse on the amygdule, vesicle and voids walls (Figure 3, a,b).

Figure 3. *Amygdaloids and Vesicle Filled by Chabazites (a)(Left) Habazite and Spheroidal Calcites (b)(Right) in Alternation Dolerite Gomareti Plateau*



Habit chabazite is mostly presented by euhedral, often cube-like rhombohedra crystals with complicated twinning gives the varietal name of "Phacolite" (Azicuki et al., 1987; Bottrill et al., 1997) (Figure 4).

Figure 4. *Chabazite with Rhombohedral Form (a, b), "Phacolite"-Twinned*



Chabazites (c) from the Alternation Zone Gomareti Plateu

The size of crystals ranges from 1.7 to 2 mm in size. It is white, rarely colorless. In some vesicles the chabazite forms a thin layer. It is associated with other secondary minerals such as: thomsonite, calsite, montmorillonite. Its optical properties are: Ng 492, Np 1.490, Ng-Np=0.002.

Chemical composition chabazite is shown in Table 1. High MgO (1.31%) content is revealed in the studied chabazites thus showing great similarity to chabazites of the Bazhenovsky field (Russia) (MgO=1.31%, Cokolova, 1967). X-ray data of study chabazites is givin in Table 2 (an.1).

Table 2. *X-Ray Powder Pattern of Chabazite, Thomsonite, Montmorillonite and Calcite of the Study Area*

Chabazite		Thomsonite		Calcite		Momtmorillonite	
1		2		3		4	
2θ°	dÅ	2θ°	dÅ	2θ°	dÅ	2θ°	dÅ
10.87	9.44	17.89	5.8	16.49	6.23	14.87	6.90
14.9	6.90	19.81	5.2	17.99	5.72	16.28	6.32
16.51	6.23	24.05	4.33	19.70	5.22	21.71	4.75
30.00	3.43	29.97	3.48	27.15	3.82	23.82	4.33
35.75	2.91	32.28	3.3	29.97	3.46	26.84	3.85
36.15	2.88	36.7	2.85	31.17	3.33	32.27	3.219
41.99	2.49	42.04	2.43	34.59	3.01	35.58	2.93
59.53	1.80	54.41	1.95	42.24	2.48	36.19	2.88
70.31	1.55	62.76	1.71	46.27	2.27	41.82	2.50
72.53	1.51	-	-	50.83	2.09	48.66	2.17
74.14	1.48	-	-	55.82	1.91	59.43	1.80
83.61	1.34	-	-	57.13	1.87	72.18	1.51
				78.36	1.42	96.62	1.20

Thomsonite. Thomsonite is a satellite mineral of chabazite in the studied hydrothermally altered dolerites. It is colourless to white. Chabazite is often abundantly developed in the form of anhedral forms and compact-grained aggregates which makes the identification of the mineral difficult. However, it sometimes exhibits a radiated and radiate-fibrous nature. In vesicles thomsonite, it often occurs as a thin film on the wall (Figure 5). Its optical properties are: Ng 525, Np 1.513, Ng-Np=0.012 (Tutberidze, 1979).

A chemical analysis of thomsonite is given in Table 1 (an.5); X-ray data given in Table 2 (an.2).

Figure 5. *Walls of Vesikules are Covered with a Thin Film Thomsonites in Alternation Dolerite of the Gomareti Plateau*

Calcite. Calcite is a widespread secondary mineral in the altered dolerites of the study area. It occurs as combinations of scalenohedrons and rhombohedrons of widely variable size (Figure 6); Its size varies from less than 1 mm. to 20 mm; Calcite often fills voids of spheric forms (Figure 3b.) Calcite is white and colorless. Its optical properties are: Nm=.660; Np=1.495; Nm-Np=0.165 (Tutberidze, 1979).Composition of CaO=49.56%. X-ray data givin in Table 2 (an.3).

Figure 6. *Fully Developed with Single Calcite Crystals in Alternation Dolerite of the Gomareti Plateau*

Clay minerals**.** Clay minerals are abundant alteration products in the hydrothermal system of Gomareti Plateau. They are represented by compact earthy masses, reniform and rarely globular aggregates (Figure 7); It is white, gray brownish yellow to colourless.

Clay minerals can be identified only by using chemical analyses and by X-ray diffraction. Based on the analysis of this data clay minerals was defined as montmorollonite.The chemical analysis of montmorillonite is given in Table 1 (an. 6); X-ray diagram of the clay is given in Table 2 (an. 4).

Figure 7. *Vesicle Rimmed with Montmorillonite, Calcite and Thomsonite*

Origin of the Secondary Minerals

Mineral forming hydrothermal systems and the distribution of secondary minerals in the alternation zone have been controlled by such main factors as: pressure, temperature, fluids and the host rocks chemical composition (Walker, 1960; Brovne, 1978; Juan Manuel Triana et al., 2012).

Alternation dolerites of the study area are characterized by abundance of secondary minerals but not as a wide variety of diversity. They are presented by chabazite, thomsonite montmorillonite calcite and clay minerals. Zoning in the distribution of secondary minerals are not clearly observed. Chabazite and calcite were the first phases to form an alternation zone of the study area.

Clay minerals are good temperature indicators of the hydrothermal system. The temperature of forming of clay minerals varies from about 30° C to about 200° C. Chabazites, thomsonites, scolecites, and other minerals of zeolites group cover this temperature interval (Kristmannsdóttir, 1979; Kristmannsdóttir and Tomasson, 1978). Sources of the elements necessary for the formation of these secondary minerals are the alternation rock forming minerals: plagioclase, pyroxene and olivine; The olivines and pyroxenes are commonly replaced by clay minerals and chlorite, plagioclase is replaced by carbonates and zeolites. Zeolites are formed under a relatively high activity of alkalies and alkali earth elements and high pH values (Voudouris et al., 2010).

The association of secondary minerals in the hydrothermally altered dolerites of the studied area shows that their formation is possible through the interaction of rock-forming minerals by cold meteoric water at a low temperature with enriched Na, Ca and CO_2 and with low SiO_2 deficient conditions. The absence of quarz, crystoballite and tridymite among secondary minerals points to the reduced Si activity in waters.

From field observation we can assume first time crystallization of zeolites and calcite. The crystallization of calcites is conditioned by the richness and activity of calcium ion Ca^{2+} in fluid.

Calcium ion reduction in alkaline solution causes an increase and decrease, respectively; it causes a decrease of temperature, which conditions crystallization of chabazite and other Na- rich zeolites (Alt and Honnorez, 1984; Juan Manuel Triana et al., 2012). Chabazites are formed at lower temperatures; (when temperature reaches 100°). It has been proved experimentally that the stable phase of chabazite is 100 °C, (Hay et al., 2001).

Thomsonite crystallizes at low temperatures from about 30°C and appear in vesicles together with other low temperature minerals. (Moneer, 2010).

Conclusions

1. Secondary minerals present in the hydrothermally altered dolerites of the Gomareti plateau are not characterized by a wide spectre. The secondary mineral complexes are: zeolite (chabazite, thomsonite) calcite, clay minerals (montmorillonite) and organic material.
2. Chabazite is the most commonly spread Na-rich zeolite, which is formed after calcite. It forms well developed crystals and is easily identifiable. The amygdule walls of the alternation zone are covered with chabazite, thomsonite and clay minerals. In some vesicles the chabazite and thomsonite occurs as thin films.
3. The formation of zeolites and calcite seems to have happened as a result of compositional transformation of base plagioclase, and clay as a result of olivine transformation. The alterations could be caused by interaction of rock-forming minerals by cold meteoric water at low temperature enriched with Na-Ca and CO_2 and with low SiO_2 deficient conditions.

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