Geochemical Peculiarities in K- and Si –Metasomatic Processes of Qooshchi Complex, Northwest Iran

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Abstract

Qooshchi granite has been intruded as an anorogenic, A type, within plate granite in an area north west of Orumieh Lake in western Azerbaijan, northwest Iran. The Precambrian crystalline basement has been intruded by gabbros and diorites. The gabbros are tholeiitic and metaluminous and are suggested to have been converted into alkalic through calc-alkalic compositions during K- and Si-metasomatism. The resulting granitic rocks (leucometasomatites) appear as apophyselike bodies within the gabbros and in the marginal parts of Qooshchi granite. Any further rise in the temperature could have caused melting of the metasomatized rocks and their subsequent recrystallization as pink Qooshchi granite.

Keywords: Iran, Azerbaijan, A-type granite, K-metasomatism, Si-metasomatism.

Introduction

On the basis of field observation, and microscopic and geochemical studies it is concluded that an intensive metasomatism has overprinted the country rocks, especially the gabbros (Fig. 1) in the Qooshchi area. A prior event of intensive deformation and cataclasis preceded the metasomatism, allowing the introduction of hydrothermal fluids. The gabbros are tholeiitic and metaluminous (Behnia, 1995) and are suggested to have been converted into alkalic through calc-alkalic composition during Si- and K-metasomatism. These rocks despite their dark color and mineralogy are more silicic than a normal gabbro and plot in most chemical diagrams as tonalites (Behnia, 1995).



Figure 1. Geologic map of Qooshchi area (simplified and modified after Khodabandeh and Amini Fazl, 1991, with the addition of the biotite granite and leucometasomatites).

Introduction of K- and Si-bearing fluids into the deformed portions of gabbros has caused the replacement of plagioclase crystals by microcline, myrmekite, and more sodic plagioclase as well as the replacement of ferromagnesian silicates by quartz (Behnia, 1995; Behnia and Collins, 1998; Behnia et al., 2003). In this process the composition of metasomatized rocks, hereafter called leucometasomatites, has been changed to potassic (with high-K contents, 7.5 wt %) and metaluminous to peralkaline and mildly peraluminous compositions (Behnia, 1995).

Microscopic studies of five samples in a transition zone from gabbro (samples 013 and 012) to monzonite (sample 011) to quartz monzonite (sample 010) and finally to granite (leucometasomatite, sample 009) show distinct metasomatic textures with all stages of conversion of plagioclase, pyroxene, and biotite crystals (Behnia, 1995; Behnia and Collins, 1998; Behnia et al., 2003) confirming the metasomatic origin of these rocks. In the transition zone, microcline first appears as tiny inclusions within plagioclase crystals and then develops into small, scattered islands within these crystals. In the advanced stages these islands coalesce and turn into a large microcline crystal having remnants of plagioclase islands inside. The plagioclase islands are optically continuous and have corroded appearance. Pyroxene first is replaced by biotite along fractures. In the later stages the pyroxene alteration results in complete or nearly complete replacement by biotite. Biotite (both primary and secondary), in particular shows progressive replacement by quartz along cleavage directions. The process continues to the stage that only remnant stringers of biotite remain before totally disappearing in the quartz. (Behnia, 1995; Behnia and Collins, 1998; Behnia et al., 2003).

Unlike the leucometasomatites, the Qooshchi granite which is an alkali feldspar granite lacks the metasomatic textures. Instead, granophyric and graphic textures and existence of perthitic K-feldspar (orthoclase) with uniformly distributed albite lamellae provide evidence that this granite formed from a magma. In the following sections geochemical evidence supporting the metasomatic origin of leucometasomatites and possibly pink Qooshchi granite is provided.

Regional Setting

Figure 1 shows the simplified geologic map of the Qooshchi area. The Precambrian crystalline basement has been intruded by gabbroic and dioritic rocks, north and east of the area. Qooshchi granite extends nearly east-west and appears to intrude the gabbros. Mafic enclaves and mafic dyke-like bodies exist in this granite. Haghipour and Aghanabati (1988) have estimated a Cretaceous-Eocene age for the Qooshchi granite on the basis of field observations. In addition to the main granite body, hereafter called pink Qooshchi granite, four other distinct varieties of granitic rocks can be recognized according to their mineralogy, texture, and exposed features. (1) Myrmekite-bearing granitoids (leucometasomatites) occur either as apophyse-like bodies within gabbros or in the marginal parts of the main body. These rocks are monzogranite and syenogranite according to their modal compositions; (2) Biotite granite; (3) two-mica granite, occur as small bodies within the metamorphic complex; and (4), lensoidal granitic rocks are exposed in a phlogopite mine that contains abundant sphene, garnet, and calcite.

Geochemical Changes

Chemical changes for major and trace elements are shown in Table 1 for gabbros, and transition zone from the gabbro into the apophyselike leucometasomatite bodies, and also for Qooshchi granites. Table 2 shows trace element analyses for some other samples in the area. Concentrations of major elements and Y, Ba, Sc, Ga, and Cr have been determined by spectrometry in the Geological Survey of Iran, and concentrations of other elements have been determined by XRF method by the Atomic Energy Organization of Iran.

Transition zone of gabbros & Gabbro-Diorites leucometa somatites Leucometa somatifes **Oooshchi** granites Sample Aб 59G 36A 013 012 011 010 009 15A 16A 57A P19 P5 OR32 OR3 gabbro epidiorite gabbro gabbro monz. qtz. monz granite Wt% 47.60 53.30 48.60 62.00 65 50 64.90 68 70 75.50 75.20 74.53 76.04 77.20 77.00 71.90 72.30 SiO₂ TiO₂ 2.12 1.65 1.70 1.40 0.98 0.42 0.32 0.16 0.25 0.23 0.15 0.15 0.06 0.21 0.25 10.50 11.60 10.60 13.91 14.06 14.62 13.90 10.90 11.50 14.90 13.50 12.01 12.91 9.70 13.4 Al₂O₃ 13.43 8.88 9.60 8.80 4.20 1.702.02 1.75 4.29 1.701.50 11.801.401.711.77Fe₂O₃* 3.20 MgO 7.00 5.49 6.50 4.80 1.70<0.20 < 0.200.04 0.23 0.44 <0.02 <0.20 <0.20 <0.0 MnO 0.18 0.16 0.19 0.18 0.17 0.08 0.03 < 0.010.02 0.02 0.01 <0.01 <0.01 0.03 0.03 7.50 11.068.37 12.40 5.60 4.20 3.10 0.78 0.84 0.93 0.50 <0.70 <0.70 < 0.70 CaO < 0.7Na₂O 3.01 3.55 2.50 1.90 2.60 3.60 4.40 4.00 3.20 2.90 3.76 4.20 4.30 3.60 3.57 0.80 1.43 0.98 0.34 0.40 4.60 7.50 6.20 6.24 6.59 2.10 5.50 4.80 6.25 K_2O 6.42 < 0.01 0.31 0.34 0.02 <0.01 <0.01 0.31 0.26 0.26 0.15 0.05 0.03 0.01 0.04 0.04 P_2O_5 L.O.I. 0.17 0.32 0.22 0.04 0.38 0.12 0.30 0.18 0.48 ppm 4.00 20.00 Cu 39.00 22.00 19.00 6.00 4.00 2.00 9.00 11.00 11.00 15.00 15.00 10.00 8.00 2.00 Mo 4.00 3.00 7.00 40.00 71.00 39.00 45.00 45.00 Ph 138.00 56.00 79.00 93.00 5.00 20.00 Zn 31.00 28.00 Ni 49.00 31.00 28.00 19.00 9.00 3.00 11.00 9.00 65.00 52.00 43.00 47.00 23.00 46.00 46.00 53.00 Co Cr 70.00 69.00 43.00 34.00 9.00 13.00 < 5.00 10.00 v 220.00 250.00 140.00 30.00 60.00 60.00 80.00 90.00 31.00 29.00 25.00 49.00 49.00 55.00 72.00 73.00 As 115.00 132.00 205.00 >1000 269.00 79.00 83.00 Ba 11.00 2040.(203.00 156.00 Rb 17.009.00 74.00 123.00 119.00 184.0(195.0) \mathbf{Sr} 311.00 317.00 359.00 365.00 427.00 32.00 38.00 65.00 15.00 <1.00 6.00 6.00 24.0026.00 25.00 20.00 9.00 29.00 24.00 83.00 99.00 79.00 Nb Th 3.00 4.00 8.00 10.00 17.00 10.00 44.00 39.00 9.00 12.00 7.00 21.00 14.00 14.00 2.00 2.00 3.00 24.00 20.00 U 114.00 178.00 303.00 687.00 225.00 173.00 405.0(232.00 Zr Ga 10.0013.00 13.00 12.00 14.0017.0023.00 43.00 24.00 20.00 12.006.00 <5.00 <5.00 <5.00 <5.00 Sc 6.00 15.00 17.00 12.00 < 5.00 <5.00 68.00 62.00 Y

Table 1. Chemical analysis of major and trace elements in the gabbors,transition zone, leucometasomatites, and Qooshchi granites.

 Fe_2O_3 * = Total Fe

Table 2. Chemical analysis of trace elements in the gabbors,leucometasomatites and granites in Qooshchi area.

	Gabbro			Epidiorites					Leucometasomatites				Transition between leucometasomatite and granite				Qooshchi granites				
Sampl ppm	e MG	P2.6	007	001	35A	008	P 8	002	038	041	P6	P 7	P1.1	P4.4	P3.1	P3.2	036	P1.4	P2.2	P2.3	P4.3
Cu	1	4	30	2	49	31	19	1	1	5	5	1	7	1	1	6	1	1	2	2	0.0
Mo	11	11	10	9	6	9	4	13	9	9	9	13	12	10	11	11	12	10	9	9	9
Pb	53	40	8	4	20	19	2	180	47	24	6	60	52	51	49	54	28	36	42	65	153
Zn	97	92	57	57	76	84	65	37	4	71	16	39	57	16	12	24	11	27	58	32	199
Ni	18	18	35	17	46	53	60	6	3	1	4	7	7	6	3	8	4	4	6	10	10
Co	52	54	53	51	55	54	58	58	44	29	37	52	46	47	56	35	114	50	54	46	48
v	160	210	22	170	240	260	250	30	90	90	80	80	60	90	100	80	90	90	100	80	90
As	36	39	30	24	16	30	30	74	67	46	31	74	55	78	80	70	78	73	70	69	58
Rb	26	17	32	29	11	21	36	187	247	72	94	242	201	216	174	222	213	191	185	279	216
Sr	284	323	296	250	329	309	365	105	17	4	190	27	80	11	10	10	14	10	5	1	1
Nb	23	21	20	19	22	18	19	18	11	21	32	35	35	30	19	33	71	60	62	56	140
Th	12	11	2	3	8	10	6	49	28	18	14	45	36	31	29	31	35	27	30	60	55
\mathbf{U}	15	18	11	5	9	5	6	20	18	12	10	20	14	17	19	19	18	24	19	25	25
Zr	239	61	1.51	220	112	154	149	240	342	21	299	186	328	182	157	208	328	402	335	203	532

In Figure 2, weight percent compositions of major oxides have been plotted against weight percent of SiO₂. The figure shows that a distinct gap would exist between gabbro-diorites and granites if the five samples of the transition zone were eliminated and that no differentiation relationship exists between the gabbro-diorites and the granites. Across the transition zone, SiO2 and K₂O increase as MgO, Fe₂O₃, CaO, TiO₂ and MnO decrease, correlating with the disappearance of ferromagnesian silicates and progressive appearance of microcline and quartz. From samples 013 and 010, Na₂O increases and then decreases in sample 009. This pattern corresponds to the retention of some Na in the recrystallized relatively sodic plagioclase (Collins, 1988). The trend for Al_2O_3 is somewhat irregular, first increasing and then decreasing. The early Al-increase occurs because the Al that is replaced from relatively calcic plagioclase is retained in biotite that replaces pyroxene. Later as the biotite is replaced by quartz, the Al content decreases (Replacement of biotite starts later than the replacement of plagioclase and pyroxene). After an increase of P₂O₅ in gabbro sample 012, a gradual decrease extends to the leucometasomatites and the Qooshchi granite.

The trace elements, Pb, Rb, and As follow the same trend as K_2O whereas Cu, Ni, Sc, V, Y, and Nb have similar trends to MgO and Fe₂O₃. Enrichment of Pb and Rb occur because of their similar ionic sizes to that of the K ion, which allow them to be retained in the microcline and biotite. After decreasing toward the monzonite, V increases in quartz monzonite and granite. After an early increase, Zn

decreases toward the granite, likely because Zn tends to concentrate in residual biotite. From gabbro toward quartz monzonite, Sr and Th increase and then decrease in granite. The Sr likely follows Ca, first being concentrated in residual Ca-bearing minerals, but then leaving the system with subtracted Ca. The elements Ba, Co, U, Ga, and Zr show no distinct trends. Ba, U, Ga, and Zr have increased in granite compared to gabbro whereas Co has decreased.



Figure 2. Percent composition of major oxides plotted against weight percent SiO2 for rocks of Qooshchi area. Solid line indicates the field of gabbro and diorites; dashed line, the granitic rocks; and dash-dot-dot indicates the samples of the transition zone. Gabbro and diorites are shown by solid squares, leucometasomatites by solid circles, and pink Qooshchi granites by open circles.

Distribution patterns of major and trace elements and their correlation with the mineralogic changes in the transition zone show that the expected relationship exists during replacement and that the mineralogical changes are consistent with the chemical changes.

Qooshchi Granite

Qooshchi granite with a rather large areal extent (Fig. 1) was intruded as an A-type within-plate granite (Jahangiri, 1990; Behnia, 1995). These granite types can appear within both continental and oceanic interiors of plates in a tensional anorogenic regime and even in an immediately post-orogenic environment (Pitcher, 1993) with alkaline and anhydrous imprints. A bimodal association of felsic and mafic rocks with no differentiational relationship has been reported in almost all cases. Crustal extension is supposed to be associated with a high heat flow, which is attributed by many workers to the rise of a mantle plume. Disagreement and debate exist for the origin of A-type granites and different sources and models have been proposed for their generation. For example Collins et al., (1982) and Clemens et al., (1986) have suggested high-temperature partial melting of meltdepleted I-type source rocks for the formation of A-type melts, whereas Creaser et al. (1991) propose a potentially more fertile source such as pre-existing tonalites and granodiorites, and Pitcher (1993) suggest that granites assembled early in the crust as a direct consequence of orogenesis should provide a potent source of new magma if remelted at a new, higher temperature. Magma mixing or assimilation has also been proposed (Foland and Allen, 1991; Jung et al., 1998). Jung et al., (1998) have attributed the A-type granites of Damara Belt in Namibia to partial melting of mantle derived tonalitic sources, limited crystal fractionation, and interaction of these magmas with crustal material. They (Jung et al., 2000) also suggested partial melting of metagranitoids? at temperatures in excess of 900°C for the formation of A-type granites in Oetmoed Granite–Migmatite Complex in Central Damara Orogen. This granite-migmatite complex consists mainly of garnet- and cordierite-bearing S-type granite and subordinate hornblende- and titanite-bearing A-type granite in the country rocks of cordierite-sillimanite-K-feldspar-garnet-bearing metasedimentary rocks and migmatite (Jung et al., 2000). They suggest that intrusion of hot, felsic magmas close to the inferred peak of metamorphism has probably caused, in part, the high temperature metamorphism and anatexis of the country rocks at relatively low pressures. Some workers (Taylor et al., 1980) have suggested that the peralkaline character of A-type granites may have developed in response to a volitile-rich (halogen and CO₂-rich) fluid phase during and after emplacement of the granite while others (Bailey, 1978) have suggested that the protolith has been metamorphosed before the generation of alkaline magma.

Plots of chemical data for seven samples of Qooshchi granite in the quartz-feldspar-water system (Winkler, 1976; Behnia, 1995) suggest that this rock crystallized in a temperature range of 700-760°C. Contact metamorphism would be expected in the wall rocks because of the high temperatures of the intrusive rocks, but faulting, or soil and vegetation cover has removed the evidence.

Although pink Qooshchi granite has formed from a magma, it may have achieved its felsic composition by a prior history of metasomatism. This Section suggests the leucometasomatites as the possible source rock for Qooshchi granite. In the field, the southern portion of the Qooshchi granite has entirely magmatic characteristics. Northward is a border zone containing leucometasomatites within the granite. The samples collected from the marginal parts of Qooshchi pluton (samples P3.1, P3.2, and P4.4) show characteristics of both pink Qooshchi granite and leucometasomatites and can be considered as transitional rocks between these two rock types. These samples, although having granophyric texture, contain replacement textures of leucometasomatites as well. The existence of gradational changes between gabbros, leucometasomatites, and Qooshchi granite suggest that both granitic rocks were formed by K- and Si-metasomatism of the gabbros with the aid of hydrous fluids. After achieving a leucocratic composition, sufficient rise in temperature could cause large portions of the metasomatized rocks to melt and subsequently recrystallize as the pink Qooshchi granite.

It seems that pink Qooshchi granites are more felsic products compared to leucometasomatites yet they are indistinguishable on the basis of their major elements. In order to show trace element distribution in these granites, the mean value of some trace elements

(arithmetic means out of six pink granite and eight leucometasomatite samples have been normalized to those of gabbors (three samples). Figure 3 shows that both granites have been enriched in Rb, Th, and Zr but depleted in Sr, Ti, V, Zn, Cu, Ni, and Cr compared to gabbro. Nb shows a positive anomaly in pink granites whereas in leucometasomatites its content is almost the same as its normalized value. Generally, pink granites relative to leucometasomatites have been enriched in Nb, Th, Y, U, Rb, and Zr, but have less Ba, Sr, Ti, Cu, Cr, Pb, and Zn, and almost the same amounts of Ni. Incompatible elements such as K, Rb, Ba, and Sr, which are considered as large ionic lithophile elements (LILEs) or low field-strength (LFSEs) are mobile and behave differently from immobile high field-strength (HFSEs) like Th, U, Nb, Zr, Y and Ti. Concentration of LFS elements may be a function of the behavior of a fluid phase, whereas HFS element concentrations are controlled by the chemistry of the source and the crystal/melt processes which take place during the evolution of the rock (Rollinson, 1993). If pink granites have been formed by melting of leucometasomatites, it would be natural if they have higher concentrations of HSF elements relative to leucometasomatites. Except for Ti, this is true for other HFS elements; i.e., Th, Zr, U, and especially for Nb and Y (Fig. 3). Figure 4 shows parts per million compositions of Nb against Th for rocks from the Ghoosgchi area. In this figure three distinct fields can be recognized (I-III). The higher concentration of Nb in pink granites differentiates them easily from leucometasomatites.

The lower concentration of Ti in pink granites may be due to its compatibility to a particular mineral. For example the mineral/melt partition coefficient (Kd) of Ti in magnetite relative to a rhyolitic melt is 12.5 (Pearce and Norry, 1979). So, although Ti is an incompatible element, it may react as a compatible element.

The lower concentration of Ba and Sr (and little depletion of Pb) in pink granites can be also described according to the mineral/melt partition coefficient of their host minerals relative to a rhyolitic melt. Ba is similar to K in ionic radius so Ba appears in biotite and Kfeldspar as a captured element. The Kd of Ba in K-feldspar relative to a rhyolitic melt has been reported to be 6.12, 11.45, and 4.30 (Arth, 1976; Nash and Crecraft, 1985; Michael, 1988 respectively). This coefficient in biotite is 9.7, 23.533 and 5.367 (Arth, 1976; Nash and Crecraft, 1985; Michael, 1988 respectively). So Ba may act as a compatible element.



Figure 3. Plot of trace element distribution patterns of leucometasomatites and pink Qooshchi granites normalized to the trace element composition of gabbros. Solid circles are from leucometasomatites; open circles, from pink Qooshchi granites.



Figure 4. Plot of Nb ppm against Th ppm, showing three distinct fields. Symbols are the same as those in Fig. 2.

Sr substitutes for Ca and K usually in plagioclase and K-feldspar. The mineral/melt partition coefficients reported for Sr in plagioclase

relative to a rhyolitic melt are 4.40, and 15.633 (Arth, 1976; Nash and Crecraft, 1985, respectively) and in the case of K-feldspar are 3.870, 5.400, and 3.760 (Arth, 1976; Nash and Crecraft, 1985; Michael, 1988 respectively), which is indicative of its compatibility. The lower concentrations of compatible elements, such as Cr, Cu, and Zn, are also expected. The only exception is V, which has higher content in pink granites relative to leucometasomatites.

Generally, trace element distribution in granites of the area agrees with the possibility that pink granites could be formed by melting of leucometasomatites. There is also a correspondence between field observation and petrology with trace-element data. Figure 5 shows Sr ppm plotted against Rb ppm for the rocks of the area. The Sr content, after an early increase in the transition zone (between gabbros and leucometasomatites) decreases from leucometasomatites toward pink granites. Data from samples collected from marginal parts of Qooshchi pluton, which have a transitional texture between leucometasomatites and pink granite (samples P3.1, P3.2, and P4.4), plot in a transitional position between these two rock types (Fig. 5). This suggests that there is also a transition zone between leucometasomatites and pink granite as well as the gabbro-diorites and leucometasomatites.

Figure 5. Plot of Sr ppm versus Rb ppm. Sr content shows an early increase and decreases then in leucometasomatites to reach the minimum pink in Qooshchi granites. Samples P3.1, P3.2, and P4.4 (shown as black and white circles), which show transitional features in



microscopic studies, plot in the transition zone between leucometasomatites and pink granites. The symbols are the same as those in Fig. 2.

Conclusions

On the basis of field observation, and microscopic and geochemical studies it is concluded that an intensive metasomatism has overprinted the country rocks especially the gabbros, transforming them into a felsic composition. The resulting leucometasomatites, which appear as apophyse-like bodies within gabbros and in the marginal parts of the Qooshchi granite, preserve distinct metasomatic features.

Qooshchi granite has been intruded as an anorogenic, A-type within plate granite. According to the intensive K- and Si-metasomatism affecting the gabbro and diorites. and the existence of with distinct replacement textures leucometasomatites and a gradational change between pink Qooshchi granites and leucometasomatites, it is suggested that the Qooshchi granite may have achieved its leucocratic A-type composition by a prior history of metasomatism. Any further rise in the temperature could have melted the metasomatized rocks and their subsequent recrystallization as pink Qooshchi granite.

The heat and hydrous fluids are most probably from a deep mantle source moving up in an extensional regime. Penetration of the hot hydrous fluids, rich in Si and K, into the solidified, cooler gabbro lowered their temperatures. At the lower temperatures the resulting early metasomatic products were below melting conditions. However, where the original gabbro was changed into the composition of granite by metasomatism, the temperatures eventually could become hot enough to cause melting. Compositions of metasomatic minerals in granite were likely at or near the eutectic. The cause of the temperature rise, of course, is unknown and results from heat and heated fluids moving up from some deep mantle source. Further detailed isotopic studies are needed to support this hypothesis.

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