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The mineralization of Titanium (Ti) and Iron (Fe) in gabbros of ophiolitic fanouj zone (Sistan & Baluchestan, Iran)

Majid Falaknazi, Mehrdad Karimi*

Department of Geology, Faculty of Sciences, Shiraz Branch, Islamic Azad University, Shiraz, Iran

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Key words: Fanouj, Ophiolite, Gabbro, Titanium mineralization.

Abstract

The ophiolitic complex of west Fanouj is located at 200km of southwest of Iran shahr and near Kheirabad village in Sistan & Baluchestan province. This Ophiolitic complex is in the obduction zone of oceanic crust of the Oman Sea between Makran coast faults and Fanouj fault (with east-west trend) and is often located in inverse status. Ophiolites of west Fanouj are composed of three units including gabbro, diabasic dikes, and a small amount of micro-diorite and peridotite. Ilmenite is the main mineral of titanium that is formed with magnetite as cross-crystal after crystallization of plagioclase, Olivine, and pyroxene and often combined with amphibole in gabbro ores. Under high oxygen fugacity condition, formation of extensive gabbro masses which is accompanied by crystallization of plagioclase and pyroxene has made a Ti-Fe-rich fluid formation while the main host of illmenite reserves, the ferro- gabbro ore is forming. Together with gradual crystallization process and reduction inconsistent elements such as Cr and Mg and increase in inconsistent elements such as Mn, Na, and Ti from lower part to upper parts of ophiolitic complex indicate formation of this complex by crystal subtraction process from Ti-rich tholeitic magma.

***Corresponding Author:** Mehrdad Karimi ✉ karimimehrdad63@yahoo.com

Introduction

Oceanic crust is composed of basalti clavas, peridotite, gabbro, and diabasic dikes together with pelagic limestones and radiolarites which during obduction over oceanic crust, all or part of it is drifted on the earth surface as tectonitic and in this case it is called ophiolite (Boulin, 1991, Boudier and Nicolas,1985, Knipper *et al*, 1986, Nicolas, 1989, Devaraju *et al*, 2014). Basic rocks with ultrabasic masses could be important in terms of Fe and Ti mineralization (Devaraju *et al*, 2014, Morisset *et al*, 2013, Mücke, 2003). Ophiolitic masses of Band-e-Ziarat and Fanouj in southern Iran have high potential of Fe and Ti mineralization (Rajabzadeh, 2011). Geologically, Fanouj complex occupied a part of an ophiolitic body (Fanouj and Rameshk) and it is located at south and southeast of Jazmoriyan desert and it is as old as upper cretaceous ophiolites in the Zagros at western Iran and other regions. From geological perspective, ophiolite complex of Fanoujis composed of sedimentary, igneous, and metamorphic rocks and a complete set of ophiolitic sequence. Sedimentary rocks are made of Cretaceous shallow-water limestones together with clastic sediments, intermediate-composition pillow lavas, meta-volcanic, phyllites, and schists. In fact, igneous rocks in west ofFanouj region constitute igneous part of the ophiolite complex which includes two sections, mafic and ultramafic masses and the entire region to be studied is composed of mafic masses. Most of the area under study at western Fanouj includes gabbro units which illmenite and magnetite mineralization occurred in two parts of it. Besides gabbro masses, diabasic dikes are also found which alteration occurred in some parts of it. These diabasic dikes are not Fe- and Ti-rich mineralized. So far, ilmenite gabbro masses for Kahnuj in Band-e-Ziarat complex located at Kerman province are considered the most important Titanium gabbros in Iran. However, according to the studies conducted for gabbro masses of ophiolites of Makran zone at south of Sistan & Baluchestan province, there are some evidences for west Fanouj that in terms of extent, reserves, and grade for such gabbro masses are evidently superior than those of gabbros of Kahnuj. This is the first scientific studies on titanium gabbros for ophiolites of Makran zone at Fanouj region. The aim of such studies was to examine mineralogical, extension, and geochemical characteristics of wide and high grade gabbro masses of west Fanouj and potential of valuable metal, titanium within these rock masses.

Material and methods

Area under study

Mafic masses for west Fanouj (the study region)by an area of 60 Km are at 200 Km form southwest of Iran shahr in Sistan & Baluchestan and regarding geological situation they are located at ophiolitic complex over Makran zone south of Jazmoorian dimples (Fig. 1). Mafic masses of west Fanouj are on top of Makran coastal fault and under Fanouj fault. Ophiolitic masses of west Fanouj include variety of gabbros and diabasic dikes and lower masses of micr-odiorite and peridotite. Alluvial sediments related to quarterner surrounded these rock masses. Gabbro units for west Fanouj ophiolites are classified into three sections, lower, middle, and upper. Upper gabbros (gb) constitute north area. They are of low height and partially covered by alluvial sediments. Middle gabbros (gb_2) cover north area as several outcrops and lower gabbros (gb_1) are almost located at west area as upland. A set of diabasic dikes also outcrop in south and northeast the study area. It seems that the lower gabbros reach the highest level in this area due to the effects of tectonic factors or due to having larger thickness than the other parts of gabbro, and constituted the highest gabbro mass. Conversely, middle zone and upper zone gabbro masses drifted to the lower parts so that a large part of the gabbros are buried under alluvial sediments and some part could be seen at surface as outcrop (Fig. 2).

Research Method

Due to presence of placer ilmenite and magnetite sediments for west alluviums, to access the origin of coarse-grained placers alluvial sampling method was used to access the main source of this deposit.

Travelling not a very long distance, coarse-grained gabbro masses for west area were defined as origin of alluvial placers for western area. Because of low height and being covered by recent alluvial sediments, sampling from east area gabbros was done from surface outcrops. For the samples collected from the exploratory area, 20 thin sections and 18 polished sections, 13 XRD analyses, 12 ICP analyses, and 17 XRF analyses were performed in Zar Azma Persia Geochemical Laboratory.

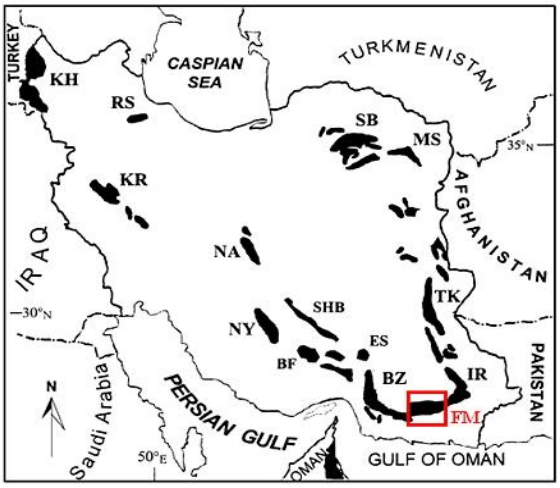

Fig. 1. Locations of major Iranian ophiolites. Khoy (KH), Kermanshah (KR), Neyriz (NY), Naien (NA), Shahr-e-Babak (SHB), Baft (BF), Esphandagheh (ES), Band-e-Zeyarat (BZ), Fanouj- Maskutan (FM), Iran shahr (IR), Tchehel Kureh (TK), Mashad (MS), Sabzevar (SB), Rasht (RS) (Ghazi *et al*, 2004).

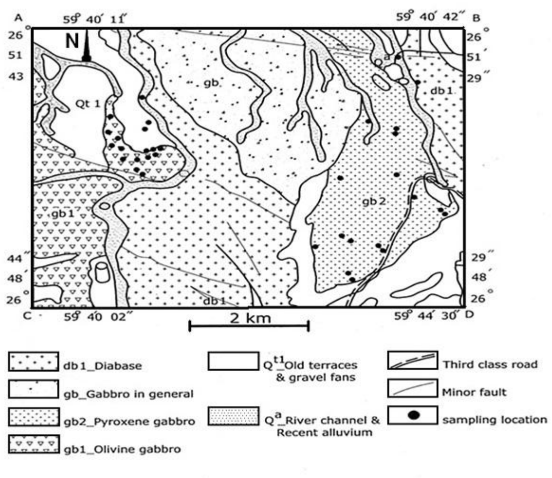

Fig. 2. Geological map for ophiolitic complex of west Fanoujadopted from [10].

Results and discussions

Mineralization in the Study Area

For ophiolites of west Fanouj, there are three litho strati graphical gabbro units that two middle and lower units have ilmenite and magnetite mineralization, however, upper gabbros are barren and without deposit creation economically. Geochemically, Ti-rich ophiolites are highly identical to the main oceanic basins and/or back arc basins that are created during intermediate and final stages of disruption of back arc basins while Ti-poor ophiolites are created by magmatic crystallization indicating first stages of rifting (Anant *et al*, 2011, The studies on microscopic sections indicate that western are agabbros are more coarse-grained and high-graded so that the sizes of ilmenite crystals tend to be 1 cm for rock masses (Fig. 3A). For all microscopic ilmenite samples are next to magnetite (Fig. 3B) and it represents that titanium reserves of west Fanouj are ortho magmatic genesis. Of course, growth of ilmenite blade and drop and creation of exsolution (Fig. 3C) and emolsoid (Fig. 3D) textures prove this reserve to be ortho magmatic.

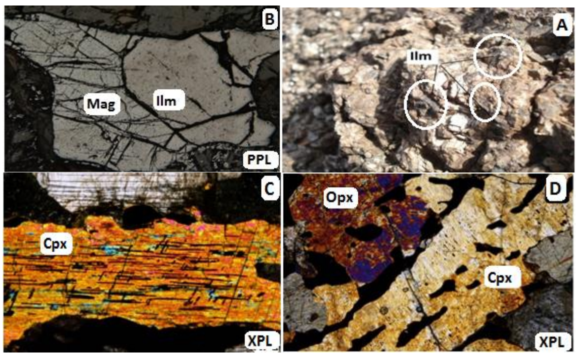

Fig. 3. (A) aview of coarse-grained and high-grade gabbros for western area in manual sampling, (B)Intergrowthilmenite and magnetite for Fanoujgabbros, (C) formation of magnetite-ilmeniteore as thin blades along augite cleavages. It represents almost simultaneous formations of these two minerals and creation of magmatic magnetite – ilmenite ore and pyroxene simultaneously, (D) long drop-like minerals forIlmenite-Magnetite in pyroxene that indicates emolsoid texture and outlier of this mineral during cooling of the initial gabbro rock.

To study and determine mineralogical composition of crystalized samples in deposits of the study area, sampling and analysis were done by using x-ray diffracto meterin laboratory of Zar Azma Persia Research Company. In this method, chemical compositions of samples, number of mineralogical phases, and percenage for each of them in the samples collected from two rock units and placers related to alluvial rivers including minerals were evaluated. Table 1 show presents the results of XRD analysis.

Index minerals for gabbro rocks include anorthite, augite, and albite. Anorthite and the other basic plagioclases (labradorite and bitonite) are Ca-rich. Minor minerals include chlorite, prehnite, magnetite, and ilmenite. For some partially altered samples, secondary clay minerals such as illite and montmorillonite have also been created (Table 1). The results of mineralogical analysis by XRD method indicate that important metal minerals for mineralization zones include ilmenite and magnetite.

Table 1. Results from Analysis by XRD Method.

Sample	Major phase	Minor phase	Trace phase
Fn1	Anorthite-Augite	Magnetite-Chlorite-Hornblende	-----------
Fn2	Albite- Augite	Chlorite	Ilmenite- Hornblende
Fn3	Albite	Chlorite- Augite-Prehnite	Hornblende
Fn4	Albite- Augite	Chlorite	Ilmenite
Fn5	Albite- Augite	Chlorite- Hornblende	----------
Fn7	Anorthite- Montmorillonite	Magnetite-Illite- Augite- Ilmenite	Chlorite- Hornblende- Magnetite
Fn8	Albite	Augite-Chlorite-Hornblende- Montmorillonite	Magnetite- Ilmenite
Fn11	Anorthite-Augite	Magnetite- Chlorite- Montmorillonite	----------
Fn13	Magnetite- Ilmenite– Augite	Chlorite- Hematite- Albite	----------
Fn14	Magnetite- Ilmenite- Hematite	-----------	Quartz
Fn15	Anorthite-Augite	Chlorite- Ilmenite- Magnetite	---------
Fn16	Anorthite-Augite	Chlorite- Ilmenite- Magnetite- Magnesite	Hematite- Hornblende
Fn17	Albite- Augite-Ilmenite	Magnetite- Chlorite- Hornblende	Hematite

Geochemistry of Rocks

Samples of rock units that are constituents of west Fanoujophiolites were analyzed by ICP and XRF methods and results of chemical data analysis are given in Table 2.

Table 2. Results for main oxides obtained from XRF analysis and element analysis by ICP method. medium-tofine-grained ferro-gabbrosat east of the area (Fn1,….Fn5), Altered diabasemasses (Fn6), Fine-grained alluvium placers (Fn7…..Fn10), Coarse-grained alluvium placers (Fn11….Fn14), Coarse-grained and high-grade gabbros(Fn15, Fn16, Fn17).

Sample%	Fn1	Fn2	Fn3	Fn4	Fn5	Fn6	Fn7	Fn8	Fn9	Fn10	Fn11	Fn12	Fn13	Fn14	Fn15	Fn16	Fn17
SiO_2	46.6	43.81	42.31	40.55	43.04	51.64	43.33	44.09	45.81	45.04	11.58	11.19	8.72	2.41	36.09	36.49	29.32
TiO_2	2.98	2.53	3.9	4	3.58	1.77	4.46	4.52	3.98	3.81	15.07	15.05	16.56	18.59	8.4	7.37	11.76
FeO	13.07	13.88	17.97	19.14	18.05	10.77	20.21	19.05	16.17	16	62.71	63.35	66.71	75.3	25.65	26.45	37.55
Al_2O_3	15.04	14.57	14.52	12.24	12.41	14.69	13.15	13.31	16.3	14.23	4.13	4.19	3.2	1.69	9.89	13.06	8.92
CaO	10.65	11.16	11	11.02	11.53	5.42	8.76	8.94	8.07	10.18	3.17	3	1.93	0.56	9.78	8.18	7.02
K_2O	0.18	0.07	0.13	0.14	0.13	0.24	0.17	0.14	0.28	0.14	0.05	0.05	0.05	0.05	0.11	0.14	0.11
MgO	4.95	7.14	3.64	5.26	6.37	5.56	3.88	3.75	2	4.57	1.68	1.64	1.69	0.55	5.41	3.26	2.93
MnO	0.21	0.15	0.17	0.21	0.18	0.22	0.25	0.25	0.17	0.18	0.5	0.49	0.41	0.49	0.28	0.26	0.28
Na_2O	3.33	2.57	2.98	2.55	2.54	5.16	3.61	3.75	4.86	3.54	0.53	0.53	0.62	0.12	1.92	2.96	2.09
CuO	……	……	……	……	……	3.03	……	……	……	……	……	……	……	……	……	……	……

Sample%	Fn1	Fn2	Fn3	Fn4	Fn5	Fn6	Fn7	Fn8	Fn9	Fn10	Fn11	Fn12	Fn13	Fn14	Fn15	Fn16	Fn17
LOI	2.55	3.97	3.23	4.52	2	4.2	1.9	1.89	1.57	2.1	<0.01	<0.01	<0.01	<0.01	2.31	1.37	<0.01
Total	97.01	95.88	96.62	95.23	97.83	98.5	97.88	97.8	97.37	97.69	99.42	99.49	99.98	99.76	97.37	98.17	99.98
ppm																	
Cr	51	42	34	96	2076	17	72	41	102	125	136	97	81	132	142	111	73
Co	38	41	46	49	62	67	47	41	35	48	48	52	90	63	61	50	54
V	233	341	501	427	577	178	325	412	355	369	518	3986	4315	3577	201	354	306
Ni	27	38	39	50	73	24	68	21	14	23	24	57	46	86	44	41	10
Cu	64	48	73	130	121	20810	51	46	1115	76	78	112	98	81	152	140	279
P	0.15	0.02	0.02	0.12	0.02	0.1	0.08	0.09	0.3	0.05	0.02	0.05	0.02	0.02	0.02	0.16	0.02
S	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

According to Na_2O+K_2O/SiO_2 diagram (Rickwood, 1989) rocks of this region are included within sub-alkaline (Fig. 4A).

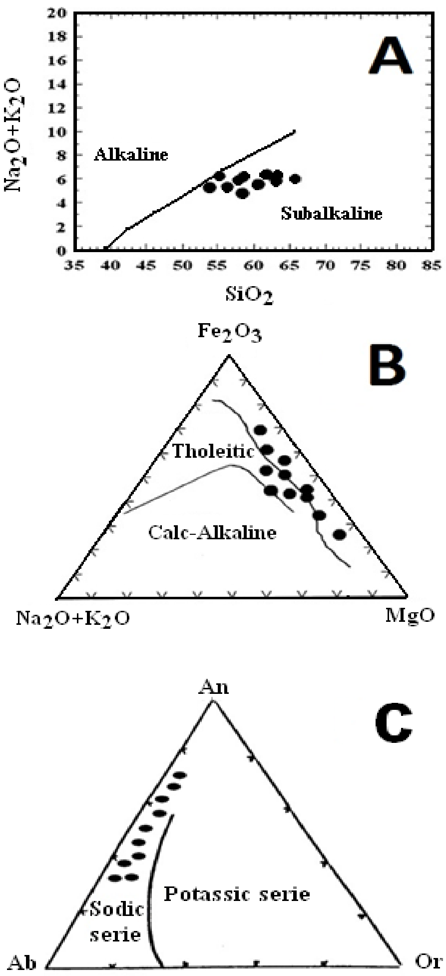

Fig. 4. A. Na_2O+K_2O/SiO_2diagram for gabbro masses, B. determination of intrusive magmatic series based on $Fe_2O_3/MgO/Na_2O+K_2O$ diagram, C determination of Fanoujgabbro masses onAn, Ab and Or diagram.

Sub-alkaline rocks could be calc-alkaline or tholeitic. To separate calc-alkaline rocks from tholeitic rocks, diagram for $Fe_2O_3/MgO/$ Na_2O+K_2Oratio is used. According to this diagram, rocks of this region are classified as tholeiti crocks which indicates their tholeitic parent magma (Fig. 4B). For tholeitic magma, with increase in subtraction process, SiO_2 percentage in remaining liquid increases gradually and also becomesmore FeO- and TiO_2- rich. Gradual increases in FeOandTiO_2 are quite apparent. According to An-Ab-Or diagram (Rickwood, 1989), rocks of the exploratory area at west Fanouj are classified as ferro-gabbros and in sodic to calcic series (Fig. 4C). The diagram indicates that potassium feldspars have no role in these rocks so the compositions tend to be plagioclases.

Host rocks of ilmenite and magnetite in this area include ferrogabbros and rocks such as norite, gabbro-norite, and pegmatite ferrogabbro all of which are included withingabbros' family. The fact that mineralogy of pegmatite gabbros is identical to that of their own gabbro hosts (Fig. 5A), could demonstrate that they are formed in a place in which they have been in balance with their gabbro hosts (Beard and Day, 1986). Within the area studies except gabbro units, diabasic dikes are also extended at south and northeast. These diabasic masses seem to be younger than gabbro units and because they are semi-deep that have a partially fine-grained texture and do not have economical deposit creation of titanium and iron types (Fig. 5B). For altered zones of diabasic dikes, we could only see iron sulfide, oxide, and hydroxides and sometimes traces of copper minerals. Due to formation at lower temperatures, iron oxides and hydroxides have box-work (Fig. 5C) and collo form (Fig. 5D) textures. However, iron sulfides are euhedral to subhedral in shapes and sometimes marginally they are changing into iron oxides and hydroxides (Fig. 5E). Reason for such alteration for pyrite minerals is the primary formation of sulfide minerals under regenerative and deep conditions and change in regenerative conditions into oxidant due to different reasons and transportation of sulfide minerals from depth to surface parts.

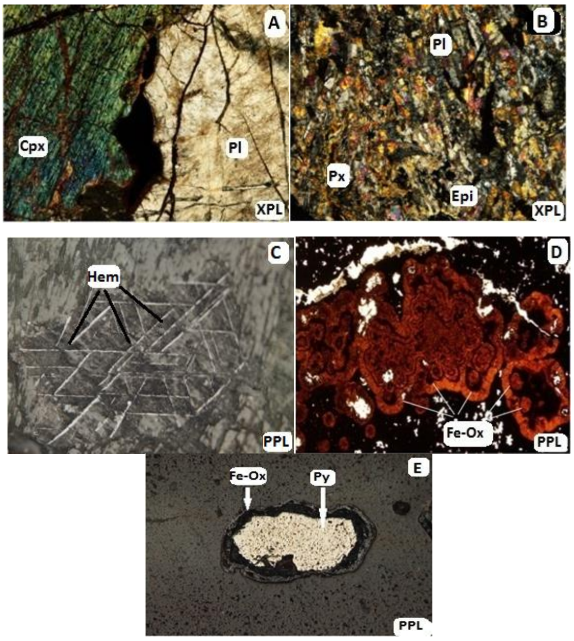

Fig. 5. A. Plagioclase and clinopyroxine minerals and opaque mineral in pegmatite ferro-gabbro, B. Decomposition of the main ore minerals into epidote in diabase rock, C. Stockwork texture in hematite minerals representing formation at low temperature, D. Formation of ferrous hydroxides at low temperature and creation of a coloform texture, E. Decomposition of shaped pyrites from margin into the ferrous oxide and hydroxides.

The most important titanium reserves within the area studies are related to two lower and middle gabbro units of west and east area and alluvial placers of west of the exploratory area. As result of erosion and destruction of dense (heavy) minerals and deposition of ilmenite and magnetite, these placer deposits have concentrated there (Robb, 2005). According to frequency chart of TiO_2 (Fig. 6A), for samples of middle- to fine grained gabbros in east area (gb_2), the amount of TiO_2 does not exceed 4% because of high percentage for SiO_2 as compared to coarse-grained gabbros of western area (gb_1) and the least amount of this oxide is 2.5% for this region. As could be seen in this diagram, for the altered regions the least amount of TiO_2diabasic dikesis 1.8%. Diabasic masses in ophiolites of west Fanouj could not be a good host for ilmenite and magnetite reserves of the area due to being semi-deep and Ti and Fe ions not to be transferred. However, the samples for fine-grained placers originated from coarse-grained gabbros of western area and coarse-grained placers that are near to gabbros of western area have different grades so that fine-grained placers and those with far distance from its own main origin have TiO_2grades between 3.8 and 4.6%. However, coarse-grained placers in which sometimes size of ilmenite crystals is 3 cm (Fig. 6B) have very higher grade than fine-grained placers so that grade of TiO_2 is variable from 15 to 18.6%. If placer deposits are low-grade and as their constituent materials are loose, they could be easily extractable (Guilbert and Park, 1997). Samples for coarse-grained gabbros of west of the exploratory area collected from 15 meter height of this gabbro unit have higher grades than those of the other gabbros and this point is considered the main source of Ti placer reserve in alluvial sediments of western area. According to TiO_2frequency chart (Fig. 6A), grade of lower gabbros in the exploratory area ranges from 7.4 to 11.8%. This range is unique for gabbro masses in Iran and yet such ilmenite reserve histed by gabbro has not been reported for any part of Iran. Because ilmenite and magnetite are observed together, a very strong correlation could be seen between FeO and TiO_2 (Fig. 6C). Frequency chart for FeO is exactly similar to that for TiO_2 (Fig. 6D) so that for all samples with low TiO_2, amount of FeO is also low and the same procedure could be seen reversely for these two oxides in this chart. For both charts, minimum values for FeO and $TiO_2$are related to the altered masses in diabasic dikes and maximum values for them are related to coarse-grained placers. Comparing frequency charts for TiO_2 and FeO with frequency chart for SiO_2, we observe that where TiO_2 and FeO have minimum amounts, the amount of SiO_2 is high (Fig. 5E).

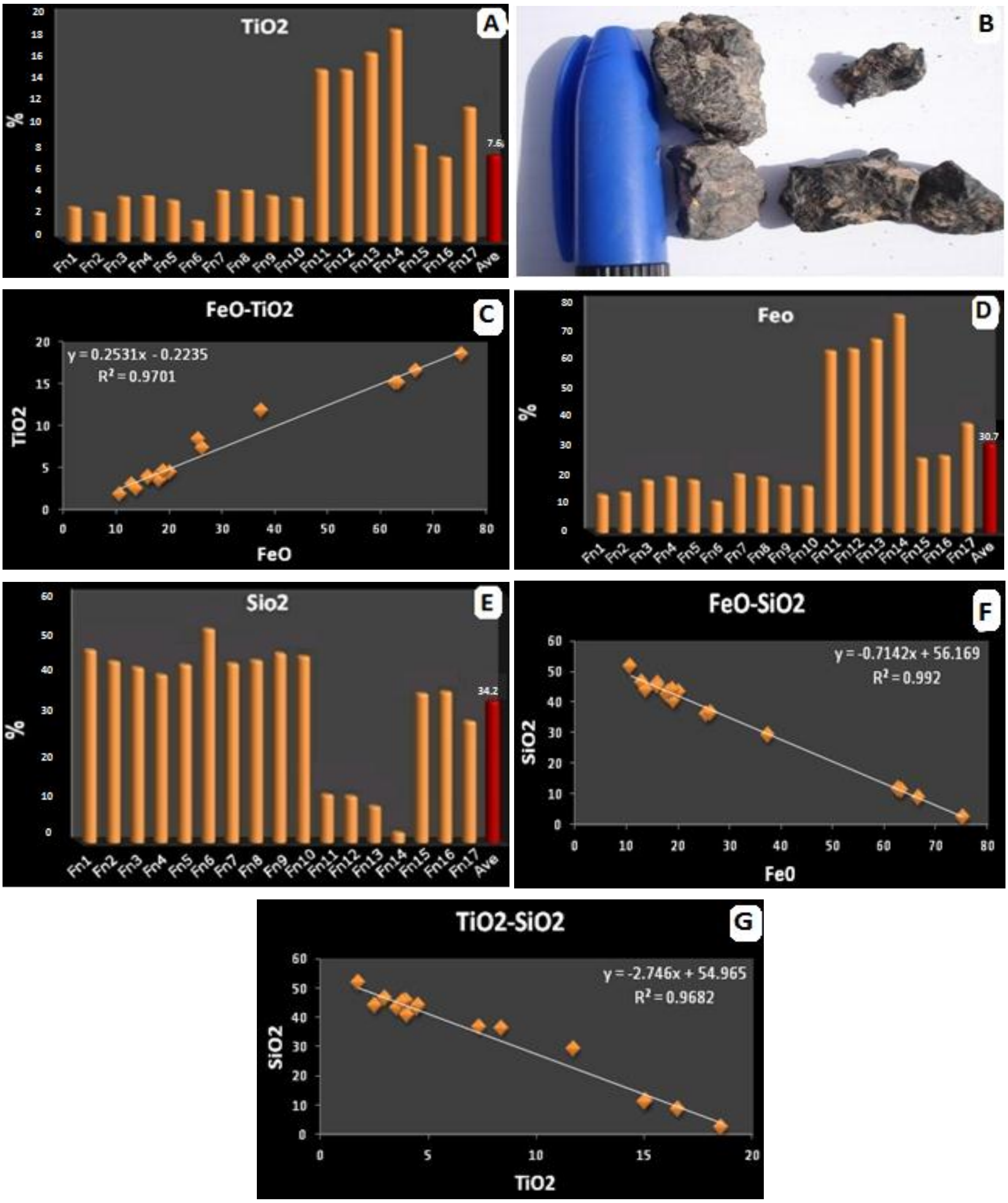

Fig. 6. A. Frequency chart of TiO_2 within the area under study, B. Coarse placers in alluvial deposits of west of the area, C. Correlation chart for TiO_2-FeO, D. Frequency chart for FeO in the area, E. Frequency chart for SiO_2 in the area, F. Correlation chart for SiO_2-FeO, (G) correlation chart for SiO_2-TiO_2.

It suggests a strong negative correlation between SiO_2 and FeO (Fig. 6F) and TiO_2 and SiO_2 (Fig. 6G). Therefore, such SiO_2-rich rocks have lower TiO_2. For light and medium to fine-grained gabros of east area the amount of $SiO_2$is above 40% whereas SiO_2 frequency for coarse-grained gabbros of western area is lower than 37%. Lower amount of SiO_2 for coarse-grained and high-grade gabbros of western area indicate that such rock mass is formed at more deep parts. Results of XRF analysis demonstrate that by gradual separation of magma and more Si entering composition of middle gabbros, these three gabbro units for this area have more SiO_2 from depth to surface and as a result lower FeO and TiO_2. Maximum amount of SiO_2 is related to the altered diabase masses and minimum amount of $SiO_2$is related to coarse-grained placers. High amount of SiO_2 for the altered regions of diabasic dikes are due to presence of quartz-rich veins. These veins are created as a result of magmatic separation and Si separation from rock-forming silicate minerals by hot magmatic solutions and their injection on the surface.

Conclusions

Fe and Ti mineralization is formed in gabbro rocks of Fanoujophiolitic mass. Variety in structures and textures of gabbro rocks is due to slow magmatic-basaltic crystallization with low viscosity in plutonic environments. Lower (gb_1) and middle (gb_2) ferrogabbros are important in terms of presence of ilmenite and magnetite minerals. These two metal minerals in gabbro masses are formed in two types of independent and present in ferro-magnesium minerals of pyroxene and amphibole. Although for some samples, vanadium element along with Fe and Ti show a considerable grade in ferro-magnesium minerals. Behavior of V parallel with Ti during crystallization process is also a good sign for Ti distribution within ilmenite or titanomagnetite without being affected by secondary alterations. High grades of ilmenite and magnetite in western areagabbros are due to presence of more ferro-magnesium minerals than plagioclases and as a result, genetic dependence of ilmenite to Fe and Mg minerals that were separated from them during becoming outlier (exsolution). Results from studies on thin sections indicated that moving from depth to surface with reduction in ferro-magnesium minerals against increase in plagioclase in gabbro masses, the amonuts of Ti and Fe decrease whereas the amounts of Si and Al increase. That is why the highest grades for ilmenite and magnetite are found in lower and coarse-grainesgabbros (gb_1) that their crystallization occurred very slowly. However, by magmatic separation and gradual crystallization of pyroxene and Ca plagioclases, the remaining magma of Al and Si become richer and formed the middle gabbros (gb_2). For this low-grade gabbro unit, ratio of plagioclase to pyroxene is higher. They are also rich and economical because of presence of ilmenite and magnetite, however, they have lower grade (a grade between 2.9 and 11.8%) than western areagabbros due to presence of higher Si and Al. thus, gabbro unit (gb_2) and gabbro unit (gb_1) are considered the most important gabbro units of west Fanoujophiolites in terms of extent and high grade (7.4 -11.8), respectively. For both units, ilmenite is regarded as the most important mineral economically while magnetite could also be Extractablean economical and by-product beside ilmenite. Because of high extension and high grade of titanium, gabbros for westFanoujophiolitic masses are the greatest titanium deposit in Iran and one of the most important deposits in the world.

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