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Petrogenesis, mineral chemistry, and thermobarometry of back-arc basin metabasites from the Ghoulan area, East Azerbaijan, NW Iran

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Amphibolites from the Ghoulan area in the East Azerbaijan province, NW Iran are metabasites containing plagioclase and hornblende as main phases also rutile and opaque minerals as accessory phases. They are spatially associated with different magmatic intrusions from the Shahjahan batholith and their relationship is sharp. These metabasites are located between three main suture zones such as Sevan-Akera suture zone in Armenia, Bitlis-Portugal suture zone in Turkey and Zagros suture zone in Iran, so their geodynamic features will help us to reconstruction paleo-geodynamic of Neotethys Ocean especially in the North West of Iranian microplate. Based on whole rock, major and trace element geochemistry of the amphibolites, they are formed from sub-alkaline basalt to andesite-basalt with tholeiitic affinity which originated from high rate partial melting (more than 10%) of mantle with spinel lherzolite to spinel-garnet lherzolite composition, they do not show any negative Ti, Nb and Ta anomaly in the different normalized spider diagrams which indicate their generating is not related to the subduction tectonic setting but they are enrichment in large ionic lithophile and LREE elements such as Rb, Sr, U, Th and Cs rather than HREE and HFSE. The geochemical composition of studied metabasites show sialic back arc basin tectonic setting. Based on plagioclase and amphibole mineral chemistry, the amphibole minerals show metamorphic and calcic features also Edenite in composition and plagioclase are andesine in composition. Thermobarometry based on amphibole composition in amphibolites shows 697-778°C temperature and 3.5- 5.5 Kbar pressure for these metabasites which can be correlate with LP-HT metamorphic facies that confirm their generation in the extensional tectonic setting. Although any age dating on these metabasites is not reported yet but due to high similarities between these metabasites and studied metabasites in the Khoy metamorphic complex (NW Iran) from petrogenesis and geochemical viewpoints, we propose that these metabasites can be correlate together and generated from a single tectonic event at a same geological time, so we propose the Paleocene –Eocene possibility time for metamorphism of studied amphibolites and closure of the back arc basin.

Keywords: Amphibolite, LP-HT metamorphic facies, back-arc basin tectonic setting, Thermobarometry, Khoy metamorphic complex, Basalt

Introduction

Back-arc basins are formed by extensional processes similar to those occurring at mid-ocean ridges. They are typically very long and relatively narrow, often thousands of kilometers long while only being a few hundred kilometers wide at most. For back-arc extension to form, a subduction zone is required, but not all subduction zones have a back-arc extension feature⁴¹. Pearce and Stern (2006) concluded that the composition of basalts erupted in BABs (BABBs) can range from those resembling basalts created by melting of the depleted upper mantle at a mid-ocean ridge (mid-ocean ridge basalt (MORB)-like) to those resembling basalts created by the interaction of subducted lithosphere with the mantle wedge at a subduction zone (arc-like). Subduction-related components (i.e., fluids or melts derived from altered oceanic crust and/or subducted sediments) influence the geochemical signature of the back arc basin magmas⁵⁰. Since that, metabasites which generated and metamorphosed in the back arc basin tectonic setting are important to understand the tectonic evolution of orogenic belts. The Iranian plateau is a tectonically active region within the Alpine-Himalayan orogenic belt. It contains several fragments that have been welded together along suture zones of oceanic character. These fragments were controlled by the opening and closure of the Tethyan oceans during several successive stages¹⁶. Based on structural trends, Stöcklin and Nabavi (1973), divided the Iranian plateau into eight geological units (Figure. 1a): Zagros fold belt, Zagros thrust belt, Sanandaj-Sirjan Zone (SSZ), Urmieh-Dokhtar magmatic arc (UDMA), central Iran, Alborz– Azerbaijan magmatic belt (AAMB), Kopeh- Dag and eastern Iran which Ophiolites, ophiolitic mélange complexes and faults bordering some of these units, appear widely in the Iranian crust. The time of closure and the evolutionary history of the Neotethys Ocean in the Iranian domain still matters of controversy¹. The main suture of the Neotethys closure is along the Zagros orogen in Iran, which is continued to the Izmir-Ankara-Erzincan and Bitlis sutures in Turkey^{18, 32, 49}. Different ophiolite complexes are outcrop along these sutures (Figure. 1a). Also, Amassia-Sevan-Akera suture zone extends about 400 Km, from North West to South East of Armenia (Lesser Caucasus) and can be correlated with the Izmir-Ankara- Erzincan suture zone, however, their extension towards the south and possible relation with the ophiolites in the North West of Iran are still poorly understood⁹. The studied metabasites outcrop in NW Iran (~10 Km from Aras boundary river), near the Ghoulan village and mainly compose of amphibolites (Figure. 1b). Based on a 1:100000 geological map of the Siahroud area²⁸, these metamorphic rocks are known as the oldest unit in this area and the possibility Devonian age consider for these metamorphic rocks. There is no published account on petrography, geochemistry, geochronology, and tectonic setting of metabasites in this area. In this research we provide new petrography, whole- rock, trace element geochemistry and mineral chemistry data for studied metabasites, to understand the petrogenesis and tectonomagmatic features of their protolith also their thermobarometry based on standard equations. This information will help us to reconstruct the geodynamic evolution of the Neotethys Ocean in northwest Iran.

Figure. 1. (a) Distribution of ophiolites and ophiolitic mélanges in NW Iran, Armenia and Turkey (modified from Çolakoglu et al., 2014). (b) Simplified geological map of study area (red square), (After Mehrpartou, 1997).

The geological background and field observations. The studied area is located at North West of Iran, near the Aras boundary river (between Iran and Armenia, Figure.1b). In this area several intrusions with gabbro, diorite, granodiorite, quartz–diorite, quartz-monzodiorite and tonalite compositions with Eocene to Oligocene relative age (based on ages reported in 1:100000 Jolfa geological map by the Geological Survey of Iran) which known as the Shahjahan batholith, intruded into the Upper Cretaceous – Paleocene flyschoid sediment, producing a low grade (albite-epidote hornfels facies) contact metamorphism (Figure. 2 a, b). The plutonic rocks subsequently experienced propylitic alterations⁵⁴. Flyschoid sediments have been precipitated in an environment with high subsidence, probably corresponding to a pull-apart basin. They include alteration of limestone, sandy limestone, shale (containing *Globotruncana* and *Heterohelix* microfossils with Cretaceous age), and submarine tuff (Figure. 2b) also extended toward adjacent area such as Tabriz to the South and Jolfa to the West.

Due to the presence of an extensional condition during the formation of such a basin, submarine basic magmatism accompanied the sediments. Accordingly, basaltic and andesitic lavas are alternatively observed in the northern parts of the host flyschoid association, which show the moderate to intense alteration. In the eastern part of the magmatic units, the metamorphic rocks, including amphibolites, metagabbro and metatuff with NW-SE structural trends, outcrop which amphibolites are more abundant in this area and are in sharp contact with intrusive rocks (Figure. 2c). Amphibolites are dark green color and medium-grained foliated to the fine-grained massif in appearance (Figure. 2d). Different felsic dikes and veins with mainly NW-SE trends cross-cut the metamorphic rocks and show the moderate to intense alteration (Figure. 2e). At the Eastern part of studied area, low grade and alternated meta- igneous rocks (meta- andesite) outcrop and cover a wide range of studied area (Figure. 2f). Based on field observations, we infer that the metamorphic grade decrease from West to East.

Figure. 2. Photographs of field observations (a) outcrop of diorite intrusions (part of Shahjahan batholith) (b) Flyschoid sediments with upper-cretaceous age (c) outcrop of amphibolite (d) hand specimen of amphibolite with dark amphibole minerals (e) felsic dikes which intruded into the amphibolites (f) low grade and alternated igneous rocks (meta-andesite) at the eastern part of study area.

Petrography. Amphibolite is the dominant lithology in the studied area, forming a rough topography (Figure. 2c). It is composed of plagioclase and amphibole as the main mineral phases with a subordinate amount of quartz, rutile and opaque minerals which displaying nematoblastic texture (Figure. 3a, b). Plagioclase is subhedral, medium- to fine-grained (1-2 mm), with poorly polysynthetic twinning, which makes ~40-50 modal % of the rock. Amphibole (~40-45 modal %, 2-2.5 mm) is fine- to medium-grained, fresh and euhedral to subhedral with green pleochroism which shows a foliation (Figure. 3c, d). Quartz (~5-6 modal %) is anhedral, fine-grained (< 2 mm), rutile (~3-4 modal %) is spine- shape and mainly presence in the amphibole mineral (Figure. 3a, b) and Opaque minerals (~5-7 modal %, < 1 mm) are anhedral to subhedral and disseminated throughout the rock. The studied metabasites show simple petrography without any garnet, epidote or calcite minerals.

Figure. 3. Photomicrograph of studied amphibolites. (a, b) Medium-grained and sub-hedral amphibole with rutile minerals, also medium to fine-grained plagioclase. (c, d) subhedral Amphibole and fine-grained plagioclase minerals. Abbreviation mineral names are from Whitney and Evans (2010).

Materials and methods

After detail microscopical studies, fourteen samples of amphibolites with minimum alteration effects, were selected for analyses by X-Ray fluorescence Spectroscopy (XRF) for major oxides and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for trace and rare earth elements in the Actlabs research Laboratory (Canada). Samples were cut by a diamond – bonded brass saw blade, crushed in a steel jaw crusher that was cleaned extensively with deionized water before each course, and milled in an agate mortar to minimize the potential contamination of transitional metals. 5g of each sample pulp was pulverized to 100-mesh size and then about 1 g was dried at 110 °C and heated to 1000 °C for 3 hours for chemical preparation. A 200 mg fraction of each sample was then mixed with 900 mg lithium tetraborate in a vitreous graphite crucible and fused at 1000 °C in a silica muffle furnace under an atmospheric pressure of argon for 30 min. after cooling; the obtained glass was directly dissolved in the crucible containing dilute 100 mL of 4% HNO₃ and glycerin. This solution was then analyzed by inductively coupled plasma-mass spectrometry. For XRF analysis, 900 gr of each sample was added to 9 g of lithium borate flux (50 %-50 % Li₂Br₄O₇-LiBO₂), mixed well, and fused in an auto flux between 1050-1100 °C. A flat molten glass disc was prepared from the resulting melt. Then the disc was analyzed by X-Ray fluorescence spectrometry. Detection limits for all oxides were about 0.01%. Representative data of major oxide and trace elements shown in Tables 1 and 2. Also two thin sections of amphibolites were selected for Electron microprobe analyses (JEOL JXA-8200) under 15 kv and 20 nA conditions which 10 points of Amphibole and 11 points of plagioclase minerals were analyzed in the Korean Basic Science research laboratory (KBSI), South Korea, the results shown in Table 3 and 4.

Sample	SiO ₂	Al ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	FeO	Fe ₂ O ₃	L.O.I	Total
ZAJ-9	50.46	15.58	0.195	7.05	9.47	3.31	0.21	1.75	0.31	9.0	1.45	1.78	100.6
ZAJ-5	48.43	15.32	0.171	9.49	10.28	2.46	0.71	1.34	0.20	6.7	2.83	2.81	100.8
ZAJ-10	49.08	16.18	0.198	6.6	10.02	3.06	0.15	1.76	0.30	8.8	1.40	1.69	99.3
ZAJ-21	57.36	14.20	0.25	3.64	8.05	2.9	0.98	1.32	0.21	8.6	1.84	1.53	100.9
ZAJ-24	49.37	16.83	0.181	6.54	11.33	2.81	0.70	1.25	0.16	6.9	2.65	2.1	100.8
ZAJ-18	46.82	16.13	0.177	7.71	11.55	2.35	0.27	1.40	0.17	7.5	2.82	2.85	99.76
ZAJ-22	49.11	15.77	0.183	8.37	10.24	2.78	0.18	1.60	0.28	9.1	1.19	1.87	100.7
ZAJ-23	48.81	17.31	0.158	7.8	11.21	2.63	0.16	1.26	0.14	7.8	0.96	1.9	100.1
ZAJ-7	48.85	14.91	0.181	9.89	11.16	2.07	0.41	1.36	0.20	6.9	2.45	2.27	100.7
ZAJ-4	49.20	16.54	0.167	6.21	11.11	3.24	0.45	1.64	0.31	8.7	1.22	2.03	100.8
ZAJ-6	48.31	17.34	0.148	8.21	9.95	3.61	0.23	1.21	0.11	6.4	3.04	1.93	100.5
ZAJ-20	48.47	16.35	0.161	7.67	10.5	2.59	1.17	1.23	0.14	7.0	2.97	2.42	100.7
ZAJ-19	52.02	15.18	0.182	7.11	11.59	2.79	0.32	1.40	0.24	6.2	1.98	1.61	100.6
ZAJ-41	47.77	16.33	0.154	7.89	10.45	3.2	0.63	1.20	0.3	9.1	1.16	2.60	100.8

Table 1. Representative whole rock analyzes (XRF) for the studied metabasites (Wt %).

Sample	Sc	Be	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Rb	Sr	Y	Zr	Nb
ZAJ-9	35	< 1	288	150	37	70	40	90	18	2	< 5	2	242	31	130	8
ZAJ-5	32	< 1	241	400	46	180	70	80	17	2	< 5	22	372	21	91	6
ZAJ-10	32	< 1	266	140	38	70	40	90	18	1	< 5	< 2	232	31	131	9
ZAJ-21	34	< 1	302	< 20	22	< 20	< 10	90	18	2	< 5	20	187	31	100	6
ZAJ-24	36	< 1	293	160	37	70	70	70	16	1	< 5	15	353	18	68	4
ZAJ-18	41	< 1	336	180	39	80	80	70	16	1	< 5	5	377	20	62	2
ZAJ-22	35	< 1	280	170	42	100	50	80	18	2	< 5	2	265	30	129	7
ZAJ-23	35	< 1	269	200	35	90	60	70	16	1	< 5	2	262	20	62	3
ZAJ-7	33	< 1	235	390	45	180	50	70	15	2	< 5	11	337	22	90	6
ZAJ-4	37	< 1	316	120	33	50	50	90	19	2	< 5	7	311	27	119	12
ZAJ-6	41	< 1	269	290	41	110	30	50	16	2	< 5	4	262	21	86	2
ZAJ-20	39	< 1	269	210	37	90	10	60	17	2	< 5	38	222	16	70	1
ZAJ-19	31	< 1	263	210	26	90	< 10	70	16	2	< 5	5	342	23	118	10
ZAJ-41	40	1	343	190	39	100	50	80	16	1	< 5	10	451	18	64	4

Table 2. Representative trace elements analyzes (ICP-MS) for the studied metabasites (ppm).

Sample	Mo	Ag	In	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
ZAJ-9	< 2	0.5	< 0.2	1	< 0.5	< 0.5	65	10.5	27.8	3.98	19.4	5.3	1.68	5.9	1	6.2
ZAJ-5	< 2	< 0.5	< 0.2	1	< 0.5	0.8	111	9.4	23.1	3.15	14.4	3.8	1.47	4.4	0.8	4.6
ZAJ-10	< 2	0.5	< 0.2	1	< 0.5	< 0.5	61	11.1	29.5	4.25	19.9	5.4	1.85	6.1	1	6.5
ZAJ-21	< 2	< 0.5	< 0.2	1	< 0.5	0.5	142	11.7	26.3	3.47	15.4	4.3	1.42	5.2	0.9	5.9
ZAJ-24	< 2	< 0.5	< 0.2	1	< 0.5	0.5	189	6.4	16	2.25	10.7	2.9	1.1	3.5	0.6	3.7
ZAJ-18	< 2	< 0.5	< 0.2	1	< 0.5	< 0.5	60	4.4	12	1.79	9.3	2.8	1.11	3.5	0.6	3.9
ZAJ-22	< 2	< 0.5	< 0.2	1	< 0.5	< 0.5	76	9.7	25.3	3.64	17.4	4.7	1.56	5.6	0.9	5.8
ZAJ-23	< 2	< 0.5	< 0.2	1	< 0.5	< 0.5	74	4.9	13	1.98	9.6	2.9	1.09	3.7	0.6	4.1
ZAJ-7	< 2	< 0.5	< 0.2	1	< 0.5	1	209	9.1	22	3.06	14.2	4	1.33	4.2	0.7	4.3
ZAJ-4	< 2	0.5	< 0.2	1	< 0.5	< 0.5	167	14.3	33.1	4.34	19.6	5	1.64	5.4	0.9	5.6
ZAJ-6	< 2	< 0.5	< 0.2	1	< 0.5	< 0.5	55	4.5	12.4	1.92	10.1	3.2	1.12	3.7	0.6	4
ZAJ-20	< 2	< 0.5	< 0.2	1	< 0.5	0.7	141	3.3	9.6	1.55	8.2	2.6	0.95	3.2	0.6	3.6
ZAJ-19	< 2	0.5	< 0.2	1	< 0.5	< 0.5	75	10.4	24.8	3.2	15	4	1.31	4.4	0.8	4.9
ZAJ-41	< 2	< 0.5	< 0.2	1	< 0.5	< 0.5	172	13.1	29.5	3.99	18.1	4.7	1.47	4.4	0.7	3.9

Table 2. Continued.

Sample	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Tl	Pb	Bi	Th	U	LOI
ZAJ-9	1.3	3.6	0.51	3.4	0.51	3.5	0.5	< 1	< 0.1	< 5	< 0.4	0.6	0.2	0.77
ZAJ-5	0.9	2.6	0.38	2.6	0.39	2.5	0.4	< 1	0.2	< 5	< 0.4	0.8	0.2	2.06
ZAJ-10	1.3	3.7	0.54	3.6	0.53	3.7	0.5	< 1	< 0.1	< 5	< 0.4	0.6	0.2	0.7
ZAJ-21	1.2	3.5	0.54	3.7	0.54	2.7	0.4	< 1	< 0.1	< 5	< 0.4	2.1	0.5	0.56
ZAJ-24	0.7	2.1	0.3	2.0	0.31	1.9	0.3	< 1	< 0.1	6	< 0.4	0.3	0.1	1.33
ZAJ-18	0.8	2.3	0.33	2.1	0.32	1.7	0.1	< 1	< 0.1	< 5	< 0.4	0.3	0.1	2.01
ZAJ-22	1.1	3.3	0.48	3.1	0.49	3.1	0.4	< 1	< 0.1	< 5	< 0.4	0.5	0.2	0.85
ZAJ-23	0.8	2.4	0.35	2.3	0.34	1.8	0.1	< 1	< 0.1	< 5	< 0.4	0.2	< 0.1	1.02
ZAJ-7	0.9	2.4	0.35	2.2	0.33	2.5	0.4	< 1	< 0.1	< 5	< 0.4	0.8	0.3	1.49
ZAJ-4	1.1	3.2	0.47	3.0	0.45	3.2	0.6	< 1	< 0.1	< 5	< 0.4	0.9	0.4	0.55
ZAJ-6	0.8	2.3	0.33	2.2	0.35	2.2	0.1	< 1	< 0.1	< 5	< 0.4	0.3	0.1	1.21
ZAJ-20	0.7	2.1	0.3	1.9	0.29	1.9	0.1	2	0.1	< 5	< 0.4	0.3	0.2	1.63
ZAJ-19	1	2.8	0.41	2.8	0.41	3.0	0.6	1	< 0.1	< 5	< 0.4	1.1	0.4	0.92
ZAJ-41	0.8	2	0.31	2.0	0.28	2.0	0.2	< 1	< 0.1	< 5	< 0.4	2.0	0.7	1.59

Table 2. Continued.

Results

Petrogenesis and tectonic setting. The applicability of whole-rock chemistry of metabasic rocks to determine the magmatic nature and tectonic setting of the parental magma has been debated. Different elements behave differently during metamorphism of mafic rocks. Some elements are mobile and some others act as relatively immobile elements in this regard. For instance K, Na, Si, and Ca are mobile during metamorphism while P, Al, and Ti are relatively immobile. Elements such as Zr, Sc, and Y are practically immobile^{13, 39}. White (2001) considers alkali elements with high ionic potential such as K, Ba, Sr, Cs, and Rb as mobile elements, also Seewald and Seyfried (1990) believe that transitional elements Co, Cr, V, Ni, Nb, Ta, and REE are immobile during metamorphism. Overall it is possible to use immobile elements such as P and Ti and rare elements such as Zr, Ta, Nb, V, Cr, Y, and REE to distinguish the magmatic nature of the protolith of metamorphosed mafic rocks at greenschist to amphibolite facies. Results from whole-rock and trace elements geochemistry of Ghoulan amphibolites with emphasis on immobile elements are used to put constraints on the petrological features and tectonomagmatic aspects of the parental magma (protolith) which forming the studied amphibolites. Major and trace element composition of the Ghoulan amphibolites indicates that they are products from metamorphism of the former igneous rocks (ortho-amphibolite) (Figure. 4a, b). The evidence for this is the high Cr and low K₂O and Na₂O contents of the rocks pointing to igneous source material. To identify the original rock type, Zr/Ti versus Nb/Y also Zr/TiO₂ versus SiO₂ diagrams⁵³, immobile elements) are used (Figure. 4 c, d). As it is evident from these diagrams, the protolith has basalt to andesite magmatic composition. SiO₂ versus Na₂O+K₂O²³ and SiO₂ versus FeO (t)/MgO diagrams²⁹ show the tholeiitic feature for parental magma (Figure. 4 e, f). To find out the paleotectonic setting of the protolith of the Ghoulan amphibolites, discriminant diagrams for different tectonic settings of mafic rocks are used. In Ti/100-Zr-Sr/2 triangle diagram (Pearce and Can, 1973) and DF₁-DF₂ diagram² the studied samples plot in the both mid-oceanic basalt (MORB) and Island arc basalts (IAT) fields (Figure. 5a and f) which these two tectonic settings together show back-arc basin setting¹². Also FeO (T)/MgO versus TiO₂ diagram⁴⁴ shows a back-arc basin setting for studied samples (Figure. 5b). The V (ppm) versus Ti (ppm) diagram from Shervais (1982) studied samples plot between Ti/V=20 to Ti/V=50 field which is related to the mid-oceanic basalt (MORB) and back-arc basin basalts (Figure. 5e). Also in the Ti (ppm) versus Zr (ppm) diagram³⁴ all of the studied samples show MORB tectonic setting (Figure. 5d, c). To separate the rocks formed at supra subduction zone (SSZ) tectonic setting and mid-ocean basalts, FeO (T)/MgO versus TiO₂³⁶ is used (Figure. 5g). Based on this diagram most of the samples are plotted in the MORB setting. To understand the mantle source and partial melting rate of basaltic magma, La/Sm versus Lu/Hf diagram³⁸ is used. This diagram shows that basaltic magma which generated the studied amphibolites, formed from spinel-peridotite source with about ten Percent partial melting rate (Figure. 5i, h). Also (Ce/Yb)_N < 5 in the studied samples confirms the spinel-peridotite source¹⁴. Since, Spinel is resistant at less than 60 Km depth, so the basaltic magma which mentioned as protolith for studied amphibolites, generated from less than 60 Km depth.

Figure. 4. Chemical classification of studied rocks (a) FeO-MgO-CaO triangle diagram (Walker et al., 1960), (b) Cr versus TiO_2 diagram (Leake, 1964) (c) Zr/Ti versus Nb/Y diagram (Winchester and Floyd, 1997) (d) SiO_2 versus Zr/TiO_2 diagram (Winchester and Floyd, 1997) (e) $\text{Na}_2\text{O} + \text{K}_2\text{O}$ versus SiO_2 diagram (Irvin and Baragar, 1971) (f) $\text{FeO}(t)/\text{MgO}$ versus SiO_2 diagram (Miyashiro, 1974) which shows tholeiitic magmatic series for studied samples.

Figure. 5. Geotectonic classification of the studied samples (a) Ti/100-Sr/2-Zr triangle diagram (Pearce and Can, 1973) (b) TiO₂ versus FeO^T/MgO diagram (Shuto et al., 2006) (c) Th/Ta versus Yb diagram (Schandl and Gorton, 2002) (d) Ti versus Zr diagram from Pearce (1982) (e) V (ppm) versus Ti (ppm) (Shervais, 1982) (f) DF1-DF2 diagram (Agrawal, 2008). (g) FeO/MgO versus TiO₂ diagram (Pearce, 2003) (h) Ce/Yb versus Sm/Yb diagram (Coban, 2007) (i) Lu/Hf versus La/Sm diagram (Regelous et al., 2003).

Spider diagrams. All of the studied samples in the N-MORB ⁴⁶ and chondrite normalized diagrams ⁴⁸ display enrichment of large ionic lithophile elements (LILE) which include Rb, Sr, Ba, Th, U, and K. Also LREE are enriched relative to the high field strength elements (HFSE) like Ta, Nb, Ti, Zr, Hf, Y and heavy rare earth elements (HREE). The studied samples do not show Ti-Nb-Ta negative anomalies (known as TNT negative anomaly) which confirm that their source is not related to the subduction zone (Figure. 6 a, b). Negative Nb anomaly also positive K, U, Ba, and Sr anomalies probably show the contamination with crustal materials in the studied metabasites ⁴⁷.

Figure. 6. Normalized Spider diagrams for studied samples. (a) N-MORB normalized spider diagram (Sun and McDougall, 1989) (b) Chondrite normalized spider diagram (Thompson, 1982).

Mineral chemistry

Mineral chemistry of the Amphibole bearing metabasites. The complex chemical composition of members of the amphibole group can be expressed by the general formula $A_{0-1}B_2C_5T_8O_{22}(OH, F, Cl)_2$, where $A = Na, K$; $B = Na, Zn, Li, Ca, Mn, Fe^{2+}, Mg$; $C = Mg, Fe^{2+}, Mn, Al, Fe^{3+}, Ti, Zn, Cr$; and $T = Si, Al, Ti$. Nearly complete substitution may take place between sodium and calcium and among magnesium, ferrous iron, and manganese (Mn). There is limited substitution between ferric iron and aluminum and between titanium and other C -type cations. Aluminum can partially substitute for silicon in the tetrahedral (T) site. Partial substitution of fluorine (F), chlorine, and oxygen for hydroxyl (OH) in the hydroxyl site is also common. The complexity of the amphibole formula has given rise to numerous mineral names within the amphibole group. In 1997 Leake presented a precise nomenclature of 76 names that encompass the chemical variation within this group. The mineral nomenclature of the amphiboles is divided into four principal subdivisions based on B -group cation occupancy: 1) the iron-magnesium-manganese amphibole group; 2) the calcic amphibole group; 3) the sodic-calcic amphibole group, and 4) the sodic amphibole group ²⁷.

To separate metamorphic amphiboles from igneous type, Al_(IV) versus Al_(VI)²⁶ and Si (a.p.f.u) versus Ti (a.p.f.u)⁵⁵ diagrams were used (Figure.7 a, b), according to these diagrams, most of the studied amphiboles are metamorphic type. To determine the amphibole mineral groups in metabasites of the study area, chemical composition of the amphiboles analyzed plotted on B (Na) on B (Ca) + BNa diagram (Figure. 7c). According to this diagram, the amphiboles in studied metabasites are a member of the calcic group and based on the Mg/ (Mg + Fe²⁺) on Si (a.p.f.u) diagram²⁷ the studied amphiboles are Edenite type (Figure. 7d).

Mineral chemistry of the Plagioclase bearing metabasites. To determine the plagioclase mineral groups in metabasites of the study area, chemical composition of the plagioclases analyzed plotted on Ab-An-Or diagram¹⁰. According to this diagram, the plagioclases are mainly andesine (Figure. 7e).

	Amp1	Amp2	Amp3	Amp4	Amp5	Amp6	Amp7	Amp8	Amp9	Amp10
SiO ₂	45.31	45.95	46.05	45.92	44.66	46.86	45.91	46.76	46.68	46.18
TiO ₂	1.03	1.10	1.07	1.29	1.17	1.20	1.18	1.02	1.15	1.28
Al ₂ O ₃	10.03	9.84	10.20	10.27	10.68	9.03	9.58	10.23	9.82	10.48
FeO	15.56	14.73	15.18	15.01	14.84	15.40	15.75	14.15	14.38	14.05
MnO	0.24	0.26	0.28	0.26	0.27	0.33	0.34	0.29	0.31	0.29
MgO	12.06	11.52	11.11	11.28	11.28	11.48	10.90	11.27	11.50	11.61
CaO	10.20	10.82	10.70	10.67	10.52	10.39	10.42	10.51	10.62	10.24
Na ₂ O	1.68	1.65	1.69	1.68	1.71	1.62	1.70	1.58	1.58	1.68
K ₂ O	0.22	0.20	0.19	0.21	0.21	0.20	0.24	0.23	0.25	0.22
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.32	96.07	96.47	96.58	95.34	96.51	96.02	96.05	96.29	96.03
a.p.f.u based on (23 O)										
Si	6.611	6.782	6.775	6.739	6.630	6.870	6.798	6.871	6.853	6.761
Ti	0.113	0.122	0.118	0.142	0.130	0.132	0.131	0.113	0.127	0.141
Al	1.725	1.711	1.769	1.777	1.869	1.560	1.672	1.772	1.699	1.809
Fe	1.898	1.818	1.868	1.842	1.842	1.888	1.950	1.739	1.766	1.720
Mn	0.030	0.033	0.035	0.032	0.034	0.041	0.043	0.036	0.039	0.036
Mg	2.623	2.534	2.435	2.468	2.495	2.508	2.406	2.468	2.516	2.533
Ca	1.594	1.711	1.687	1.678	1.673	1.632	1.653	1.655	1.671	1.606
Na	0.476	0.473	0.482	0.478	0.493	0.460	0.489	0.450	0.449	0.477
K	0.041	0.038	0.035	0.039	0.040	0.038	0.045	0.043	0.046	0.041
Sum	15.110	15.222	15.204	15.194	15.206	15.131	15.187	15.148	15.166	15.124
Mole Fraction										
T: Si	6.611	6.782	6.775	6.739	6.630	6.870	6.798	6.871	6.853	6.761
Al(IV)	1.389	1.218	1.225	1.261	1.370	1.130	1.202	1.129	1.147	1.239
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
T-Sum	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
C: Al(VI)	0.336	0.493	0.544	0.516	0.499	0.430	0.470	0.644	0.553	0.570
Ti	0.113	0.122	0.118	0.142	0.130	0.132	0.131	0.113	0.127	0.141
Fe ³⁺	1.123	0.549	0.554	0.588	0.732	0.673	0.628	0.457	0.504	0.657
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Mg	2.623	2.534	2.435	2.468	2.495	2.508	2.406	2.468	2.516	2.533
Fe²⁺	0.776	1.269	1.313	1.254	1.110	1.216	1.322	1.282	1.262	1.063
Mn	0.030	0.033	0.035	0.032	0.034	0.041	0.043	0.036	0.039	0.036
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C-Sum	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
B: Ca	1.594	1.711	1.687	1.678	1.673	1.632	1.653	1.655	1.671	1.606
Na	0.406	0.289	0.313	0.322	0.327	0.368	0.347	0.345	0.329	0.394
B-Sum	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
A: Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.070	0.184	0.169	0.156	0.166	0.093	0.142	0.105	0.120	0.083
K	0.041	0.038	0.035	0.039	0.040	0.038	0.045	0.043	0.046	0.041
A-Sum	0.110	0.222	0.204	0.194	0.206	0.131	0.187	0.148	0.166	0.124
(Na+K)A	0.110	0.222	0.204	0.194	0.206	0.131	0.187	0.148	0.166	0.124

Table 3. Electron probe microanalysis results for amphibole in the studied metabasites.

	PI1	PI2	PI3	PI4	PI5	PI6	PI7	PI8	PI9	PI10	PI11
SiO₂	56.02	56.10	55.77	55.63	56.91	55.99	56.61	57.11	56.49	56.32	56.11
TiO₂	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.00	0.01	0.00	0.00
Al₂O₃	27.99	27.78	28.09	28.50	27.08	28.18	27.68	27.68	27.44	27.83	27.65
FeO	0.13	0.11	0.15	0.16	0.12	0.12	0.13	0.13	0.14	0.10	0.14
MnO	0.02	0.01	0.00	0.00	0.00	0.01	0.04	0.00	0.01	0.01	0.00
MgO	0.00	0.00	0.00	0.00	0.02	0.01	0.01	0.02	0.00	0.00	0.01
CaO	9.63	9.81	9.77	9.62	9.61	9.78	9.30	9.24	9.86	9.42	9.74
Na₂O	6.25	6.16	6.12	6.31	6.93	6.26	6.42	6.40	6.20	6.28	6.12
K₂O	0.04	0.05	0.04	0.05	0.09	0.04	0.04	0.05	0.07	0.05	0.03
Total	100.09	100.03	99.96	100.29	100.77	100.40	100.24	100.63	100.22	100.01	99.80
Oxygen	8	8	8	8	8	8	8	8	8	8	8
Si	2.517	2.522	2.510	2.496	2.545	2.509	2.536	2.546	2.535	2.529	2.527
Al	1.482	1.472	1.490	1.507	1.427	1.489	1.462	1.455	1.452	1.473	1.468
Ti	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.005	0.004	0.006	0.006	0.004	0.004	0.005	0.005	0.005	0.004	0.005
Mn	0.001	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000
Mg	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.001	0.000	0.000	0.001
Zn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca	0.464	0.473	0.471	0.463	0.460	0.470	0.446	0.441	0.474	0.453	0.470
Na	0.544	0.537	0.534	0.549	0.601	0.544	0.558	0.553	0.540	0.547	0.534
K	0.002	0.003	0.002	0.003	0.005	0.002	0.002	0.003	0.004	0.003	0.002
Total	5.015	5.011	5.013	5.025	5.044	5.019	5.012	5.005	5.010	5.009	5.007
Or	0.227	0.283	0.228	0.282	0.481	0.225	0.227	0.285	0.394	0.286	0.171
Ab	53.889	53.040	53.009	54.122	56.343	53.546	55.414	55.464	53.015	54.521	53.115
An	45.884	46.677	46.763	45.596	43.176	46.228	44.359	44.251	46.591	45.193	46.713

Table 4. Electron probe microanalysis results for plagioclase in the studied metabasites

Figure. 7. Amphibole and plagioclase nomenclature diagrams (a) Al_(IV) versus Al_(VI) (Leak et al., 1965) (b) Si (a.p.f.u) versus Ti (a.p.f.u) diagram (Fleet and burnet, 1978) (c) B (Na) on B (Ca) + B(Na) diagram (Leak et al., 1997) which shows calcic feature for studied amphibolites (d) Mg/(Mg+Fe) versus Si (a.p.f.u) diagram (Leak et al., 1997) shows Edenite composition for amphibole minerals (e) Ab-Or-An diagram (Deer et al., 1991) shows andesine composition for studied plagioclase minerals.

Pressure-Temperature estimation for metabasites. In general, the calculation of pressure-temperature (P-T) conditions of metamorphism of the Ghoulan metabasites are hampered by the absence of suitable mineral phases such as garnet. However, some conventional quantitative geothermometers and geobarometers are available including amphibole geobarometers which proposed by Schmidt (1992), Hammarstorm and Zen (1986), Hollister et al., 1987 and Johnson and Rutherford (1989) as equations 1 to 4.

$$P (\pm 0.6 \text{ kbar}) = -3.01 + 4.76 \text{ Al}^t \quad \text{Schmidt (1992)} \quad \text{Eq.1}$$

$$P (\pm 3 \text{ kbar}) = -3.92 + 5.03 \text{ Al}^t \quad \text{Hammarstorm and Zen (1986)} \quad \text{Eq.2}$$

$$P (\pm 1 \text{ kbar}) = -4.76 + 5.64 \text{ Al}^t \quad \text{Hollister et al., 1987} \quad \text{Eq.3}$$

$$P (\pm 0.5 \text{ kbar}) = -3.46 + 4.23 \text{ Al}^t \quad \text{Johnson and Rutherford (1989)} \quad \text{Eq.4}$$

To estimate the temperature of metamorphism, we used of amphibole geothermometers which proposed by Humphreys et al., 2009, Otten (1984) and Vyhnal et al., 1991 as equations 5 to 7.

$$T = 479.8(\text{Na}+\text{K})_A + 643.5 \quad R^2=0.63 \quad \text{Humphreys et al., 2009} \quad \text{Eq.5}$$

$$(T < 970 \text{ } ^\circ\text{C}) = 1204 (\text{Ti}) + 545 \quad \text{Otten (1984)} \quad \text{Eq.6}$$

$$T (^\circ\text{C}) = 25.3P + 645.9 \quad R^2=0.845 \quad \text{Johnson and Rutherford (1989)} \quad \text{Eq.7}$$

Based on the mineral chemistry of amphibole and standard equations, 697-778 °C temperature and 3.5- 5.5 Kbar pressure estimated for metamorphism of studied amphibolites as shown in Table 5, which indicate high temperature – low pressure (HT-LP) metamorphic facies.

	P (Kbar) Schmidt (1992)	P (Kbar) Hammarstorm & Zen (1986)	P (Kbar) Hollister etal., 1987	P (Kbar) Johnson &Rutherford (1989)	T (°C) Humphreys et al (2009)	T (°C) Otten (1984)	T (°C) Vyhnal et al (1991)
Amp-1	5.199	4.754	4.966	3.835	696.501	681.066	777.437
Amp-2	5.134	4.686	4.890	3.777	749.791	691.719	775.806
Amp-3	5.408	4.976	5.215	4.021	741.423	687.383	782.743
Amp-4	5.448	5.017	5.261	4.056	736.737	716.408	783.735
Amp-5	5.885	5.479	5.779	4.444	742.206	701.704	794.801
Amp-6	4.414	3.925	4.036	3.137	706.336	703.756	757.584
Amp-7	4.949	4.491	4.671	3.613	733.386	703.196	771.126
Amp-8	5.425	4.994	5.235	4.036	714.392	680.701	783.166
Amp-9	5.078	4.927	4.824	3.728	723.249	697.851	774.398
Amp-10	5.598	5.177	5.440	4.190	703.021	714.660	787.550
Average	5.254	4.813	5.032	3.884	724.704	697.844	778.834
Max	5.885	5.479	5.779	4.444	749.791	716.408	794.801
Min	4.414	3.925	4.036	3.137	696.501	680.701	757.584

Table 5. Pressure and temperature estimation results based on amphibole geothermobarometry in the studied amphibolites.

Discussions

Geotectonic model. The time of opening, closure and the evolutionary history of the Neotethys Ocean in the Iranian domain is still a matter of controversy. These uncertainties led different authors to suggest various theories for the evolution of the Neotethys basin. Berberian and King (1981) and Ghasemi and Talbot (2006) proposed a single-stage subduction scenario for the Neotethys oceanic crust beneath central Iran, whereas, Glennie (2000) advocates a double- stage subduction for the Neotethys, considering the opening of two parallel oceanic basins. Some authors such as Azizi and Jahangiri (2008) proposed single stage subduction for Neotethys Ocean beneath the Central Iran microplate but they consider the subduction of back arc basin which generated after Urmieh-Dokhtar magmatic arc, toward the North East and beneath the Alborz- Azerbaijan microplate caused magmatism and plutonic intrusions in the Alborz-Azerbaijan. Moayyed (2002) proposed the generation of back arc basin at Jurassic – lower Cretaceous behind of the Urmieh-Dokhtar magmatic arc and its closure at Eocene to Lower-Miocene by fault which caused the emplacement of Khoy metamorphic complex in the North West of Iran.

Based on the geochemical data and interpretations which mentioned in this research, we infer that after the Neotethys oceanic lithosphere subduction beneath the central Iran microplate, the Urmieh-Dokhtar magmatic arc with Eocene – Oligocene intrusive age was generated as one of the

subduction results (Figure. 8a), after that the extensional forces happened in the central Iran microplate and the progressive of these forces caused the rifting in the Central Iran microplate and behind of the Urmieh-Dokhtar magmatic arc and caused the back-arc basin tectonic setting (Figure. 8a). Due to the decrease of pressure on the lithospheric mantle, partial melting with high rate (more than 10 percent) of lithospheric mantle with spinel lherzolite to rarely spinel- garnet lherzolite was happened and basalts emplaced in the back-arc basin tectonic setting which show the tholeiitic magmatic series. This back-arc basin started to extend and probably at the Paleocene to Eocene, this back – arc started to close by function of faults in this area and caused the metamorphism of tholeiitic basalts to the amphibolite facies which are the studied amphibolites in the Ghoulan area, North West Iran (Figure. 8b). According to the geochemical data, all of the studied metabasites do not show Ti, Nb and Ta negative anomalies which infer that the studied samples did not generate at subduction environment. Also the P-T estimation for them show high temperature- low pressure metamorphic facies that confirms the extensional tectonic setting.

The comparison of studied amphibolites with simple ortho-amphibolites (without any garnet minerals) in the Khoy region, North West Iran, which studied in detail by different authors, such as Hassanipak and Ghazi (2000), Khalatbari-jafari et al. (2004), Azizi et al. (2005), Moazzen and Oberhänsli (2008), Faridazad et al. (2010), Azizi et al. (2011) and Ebadi et al. (2019) show similar geochemistry and geotectonic evidences and we infer that these amphibolites can be correlate together and caused by single tectonic event at a same time. Also because of the simple petrography of Ghoulan amphibolites, their geotectonic and geochemical features we propose that these metamorphic rocks are not related to the basement and perhaps will show young metamorphism age (Such as Eocene age). However understanding the exact metamorphism age for studied amphibolites needs geochronological data on amphibole minerals which not reported yet.

Figure 8. Proposed geotectonic model for studied metabasites in the Ghoulan area, NW Iran.

Conclusion

Metabasites from the Ghoulan area in the East Azerbaijan province, NW Iran are mainly amphibolites which consist of plagioclase and amphibole minerals as main phases also rutile, quartz and opaque minerals as accessory phases with nematoblastic texture. They have a sharp contact with Shahjahan batholith intrusions (Eocene-Oligocene intrusive age) and different felsic dikes intruded into these metamorphic units. Geochemical data show their protolith is mainly basalt with sub-alkaline and tholeiitic affinities (ortho-amphibolites) that formed in a back-arc basin tectonic setting. They do not show any subduction characteristics such as negative Ti, Nb and Ta anomalies, however the studied samples show LREE and LILE are enrichment rather than HREE and HFSE. Amphibole mineral chemistry and Thermobarometry show calcic and Edenite composition for this mineral that formed under 697-778 °C temperature and 3.5-5.5 Kbar pressure conditions. These conditions are in a good agreement with LP-HT geothermal gradient in an extensional tectonic setting. Also the main composition of plagioclase minerals is andesine. Although any age dating not reported for these metamorphic rocks yet but based on previous studied in the Khoy metamorphic complex (especially simple amphibolites in this complex), NW Iran which is near the studied amphibolites, and their geochemical similarities with studied metabasites, we propose a possibility same tectonic setting and tectonic event for both of them. According to these interpretations we infer the generation of sialic back-arc basin behind of the Urmieh-Dokhtar magmatic arc which closed without any subduction and just by fault function probably at Paleocene to Eocene time.

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