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Chemical composition of rock-forming minerals and crystallization physicochemical conditions of the Middle Eocene I-type Haji Abad pluton, SW Buin-Zahra, Iran

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Abstract

The Haji Abad intrusion is a well-exposed Middle Eocene I-type granodioritc pluton in the Urumieh–Dokhtar magmatic assemblage (UDMA). The major constituents of the investigated rocks are K-feldspar, quartz, plagioclase, pyroxene, and minor Fe–Ti oxide and hornblende. The plagioclase compositions fall in the labradorite, andesine, and oligoclase fields. The amphiboles range in composition from magnesio-hornblende to tremolite–hornblende of the calcic-amphibole group. Most pyroxenes principally plot in the field of diopside. The calculated average pressure of emplacement is 1.9 kbar for the granodioritic rocks, crystallizing at depths of about 6.7 km. The highest pressure estimated from clinopyroxene geobarometry (5 kbar) reflects initial pyroxene crystallization pressure, indicating initial crystallization depth (17.5 km) in the Haji Abad granodiorite. The estimated temperatures using two-feldspar thermometry give an average 724 °C. The calculated average temperature for clinopyroxene crystallization is 1090 °C. The pyroxene temperatures are higher than the estimated temperature by feldspar thermometry, indicating that the pyroxene and feldspar temperatures represent the first and late stages of magmatic crystallization of Haji Abad granodiorite, respectively. Most pyroxenes plot above the line of $Fe^{3+} = 0$, indicating they crystallized under relatively high oxygen fugacity or oxidized conditions. Furthermore, the results show that the Middle Eocene granitoids crystallized from magmas with H_2O content about 3.2 wt%. The relatively high water content is consistent with the generation environment of HAG rocks in an active continental margin and has allowed the magma to reach shallower crustal levels. The MMEs with ellipsoidal and spherical shapes show igneous microgranular textures and chilled margins, probably indicating the presence of magma mixing. Besides, core to rim compositional oscillations (An and FeO) for the plagioclase crystals serve as robust evidence to support magma mixing. The studied amphiboles and pyroxenes are grouped in the subalkaline fields that are consistent with crystallization from I-type calc-alkaine magma in the subduction environment related to active continental margin. Mineral chemistry data indicate that Haji Abad granodiorites were generated in an orogenic belt related to the volcanic arc setting consistent with the subduction of Neo-Tethyan oceanic crust beneath the central Iranian microcontinent.

Keywords Thermobarometry . Mineral chemistry . Urumieh–Dokhtar magmatic arc . Haji Abad . Iran

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Introduction

The Haji Abad intrusion is hosted within the Urumieh– Dokhtar magmatic assemblage (UDMA) as part of the Zagros orogeny (Fig. [1\)](#page-3-0). Similar to other segments of the Alpine–Himalayan mountain chain, the Zagros orogeny formed as a consequence of closure of the Neo-Tethyan ocean and the continuing continental collision between Arabia and Eurasia (e.g., Berberian and Berberian [1981](#page-17-0); Berberian and King [1981](#page-17-0); Moine-Vaziri [1985;](#page-18-0) Arvin et al. [2007](#page-17-0); Allen [2009\)](#page-17-0) and is an outstanding natural laboratory for studying metamorphism and igneous rocks, continental orogenesis, and petrogenetic and geodynamic processes. Geologically, the Zagros

orogeny is made up of three NW–SE-trending parallel belts, which from north to south are the UDMA, Sanandaj–Sirjan structural zone (SSZ), and Zagros Fold–Thrust Belt (ZFTB) (Alavi [2004](#page-17-0)). UDMA which is 150 km wide is predominantly composed of tholeiitic, calc-alkaline, and K-rich alkaline intrusive and extrusive rocks with associated pyroclastic and volcanoclastic successions, and occurred along the active margin of the Iranian plate as an active continental magmatism (Alavi [2004](#page-17-0)). The intrusive rocks are dominantly composed of granite, granodiorite, and diorite that generally show calc-alkaline, metaluminous, I-type composition (e.g., Rezaei-Kahkhaei et al. [2011;](#page-18-0) Sarjoughian et al. [2012;](#page-19-0) Kananian et al. [2014;](#page-18-0) Kazemi et al. [2018\)](#page-18-0). Though many studies have been done on the petrogenesis of these rocks, there are few studies conducted on mineral chemistry in order to determine the emplacement conditions and physicochemical parameters of the parental magma of these rocks.

The mineral assemblage and compositions in igneous rocks can be used to evaluate the physicochemical conditions of magma crystallization during the emplacement of intrusive rocks (e.g., Abbott [1985](#page-16-0); Sarjoughian et al. [2015\)](#page-19-0). So, the compositions and structures of the various mineral phases (feldspar, amphibole, pyroxene, etc) can serve as ideal proxies for the determination of magmatic processes and physicochemical parameters, such as pressure and temperature of crystallization, oxygen fugacity, H_2O contents, and composition of parental magma (Zhang et al. [2006;](#page-19-0) Honarmand et al. [2012](#page-18-0); Murphy et al. [2012;](#page-18-0) Sepahi et al. [2012](#page-19-0); Sherafat et al. [2012;](#page-19-0) Ayati et al. [2013](#page-17-0); Sarjoughian et al. [2015\)](#page-19-0). Many researchers proposed that using estimated crystallization pressure can readily determine the depths of emplacement and provide insights into the denudation history (e.g., Hammarstrom and Zen [1986;](#page-17-0) Vyhnal et al. [1991](#page-19-0); Schmidt [1992](#page-19-0); Anderson [1996;](#page-17-0) Stein and Dietl [2001](#page-19-0); Zhang et al. [2006\)](#page-19-0). The estimation of the emplacement depth during the solidification of calc-alkaline intrusions is an indicator of characterizing the complex chemical evolution and tectonic processes in orogenic belts, thus also provides indirect evidence for the ascent or descent of exposed crustal sections through time (Rutter et al. [1989;](#page-18-0) Tulloch and Challis [2000](#page-19-0); Zhang et al. [2006](#page-19-0)).

Feldspar and pyroxene thermobarometry have been widely used to estimate the crystallization pressure and temperature of igneous rocks, providing tools to determine the emplacement depth of rocks (Helz [1973;](#page-18-0) Fuhrman and Lindsley [1988](#page-17-0); Soesoo [1997](#page-19-0); Putirka et al. [2003;](#page-18-0) Putirka [2005,](#page-18-0) [2008](#page-18-0); Faak et al. [2013](#page-17-0)).

Amphibole-group minerals occur in a wide variety of igneous rocks formed in different tectonic environments and have an important influence in the subduction-related magmatic evolution (Anderson [1980](#page-17-0); Ernst [1999;](#page-17-0) Davidson et al. [2007](#page-17-0); Martin [2007;](#page-18-0) Larocque and Canil [2010;](#page-18-0) Ridolfi et al. [2010;](#page-18-0) Dessimoz et al. [2012;](#page-17-0) Krawczynski et al. [2012\)](#page-18-0). Mafic magmas that are related to the subduction tectonic environment are usually hydrous, and the increase in water contents of such magmas induces the late-stage metasomatic processes and formation of interstitial amphibole (Claeson and Meurer [2004\)](#page-17-0).

The Haji Abad intrusion is a well-exposed Middle Eocene I-type granodioritc pluton in the north of the Haji Abad village (Fig. [2\)](#page-4-0) and contains abundant globular or elliptical mafic microgranular enclaves (MMEs) of various sizes, that provide an excellent case to investigate the physicochemical conditions in terms of many parameters accompanying magma emplacement and crystallization.

The Haji Abad pluton was intruded into the volcanosedimentary rocks (Fig. [2](#page-4-0)) that mainly consists of granodiorite and diorite along with aplitic dikes (Tabbakh Shabani [1991;](#page-19-0) Safarzadeh et al. [2007;](#page-19-0) Kazemi et al. [2018\)](#page-18-0). This intrusive has been named granite in the geologic map of the Saveh quadrangle at 1:250,000 scale (Nogole-Sadat and Hoshmandzadeh [1984](#page-18-0)), but in the Danesfahan quadrangle map at 1:100,000 scale (Eghlimi [2000](#page-17-0)), it has been named as subvolcanic and plutonic rocks with diorite to granite suites. Kazemi et al. [\(2018](#page-18-0)) suggested that the Haji Abad granitoids are metaluminous, arc-related calc-alkaline, and Itype in composition. In addition, these researchers, based on field and petrographic characterization together with bulk rock geochemical and Nd–Sr isotopic data, suggested that host rocks and their MMEs originated by interaction between basaltic lower crust-derived felsic and mantle-derived mafic magmas in an active continental margin arc environment. The emplacement of the Haji Abad granitoid in the SW Buin-Zahra region took place ca. 40 Ma, representing an orogenic cycle in a preplate collision (Kazemi et al. [2018](#page-18-0)). Kazemi et al. [\(2018\)](#page-18-0) concluded that the angle of subduction of Neo-Tethyan oceanic crust beneath central Iran is less than 15° for Eocene magmatism in the central UDMA interior, consistent with flat or low-angle subduction.

The in situ microanalysis of minerals (such as feldspar, amphibole, and pyroxene) is our approach to reinvestigate this intrusion where major element compositions are used for (1) estimations of crystallization temperature, pressure, oxygen fugacity, and H_2O content using mineral chemical compositions of Haji Abad granitoid (HAG) rocks; (2) determination of chemical composition, nature, and tectonic setting of their formative magma; and (3) exploration of petrogenetic processes, such as magma mixing, responsible for the formation of I-type intrusive rocks, using chemical zoning in the plagioclase crystals and petrography observations.

Geological setting and field relations

The HAG is located about 20 km southwestern of Buin-Zahra City in the central part of the UDMAwithin the structural zone of central Iran (Figs. [1](#page-3-0) and [2\)](#page-4-0).

The area is dominated by Eocene magmatic rocks that are the thickest and largest exposed unit (Fig. [2\)](#page-4-0). The early Eocene volcanic rocks are the oldest geologic units in the study area and are traceable to the Oligocene, Miocene, Pliocene, and the Quaternary, that show facies variation from marine to continental eruptions.

The surrounding rocks in the Haji Abad intrusion are Eocene rhyodacitic tuff, dacitic pyroclastics, dacite-andesitic lava flows and breccia, basalt, andesitic basalt, dacitic ignimbrite, and tuffite (Fig. [2;](#page-4-0) Nogole-Sadat and Hoshmandzadeh [1984;](#page-18-0) Eghlimi [2000](#page-17-0); Dorouzi and Vosoughi Abedini [2009\)](#page-17-0).

Dacitic pyroclastics, mainly tuffs, are the oldest rocks, and they are mainly exposed in the southern and western parts of the Haji Abad granitoid and have the longest contact with the pluton. The northern and northeastern parts of the intrusion were emplaced into lower Eocene tuff, andesitic volcanics, and breccias, whereas the dacitic ignimberites are exposed in the south of the Haji Abad pluton. This pluton has a low height and hill morphology, while the surrounding volcanic rocks are higher.

These rocks are dominantly composed of olivine, plagioclase, clinopyroxene, amphibole, biotite, K-feldspar, and quartz. Geochemically, the basalt, andesitic basalt, andesite, and dacite belong to the subalkaline series and show calcalkaline affinity. Based on their enrichment of LILE and LREE and relative depletion of HFSE, these rocks can be correlated with the subduction tectonic setting in an active continental margin (Dorouzi and Vosoughi Abedini [2009](#page-17-0)). The Oligocene starts with a clastic unit of conglomerate, sandstone, and marl of the Lower Red Formation followed by limestone marl and marl and finally changes to the periodicity of igneous and volcanoclastic units consisting of dacite, rhyolite, andesite, basalt, and ignimbrite. The younger geological units are marine and detrital sediments of Qom and Upper Red formations, which are deposited on top of the volcanic rocks during the Oligo-Miocene and Miocene, respectively.

Several plutonic bodies with K-Ar age of 39.2 ± 3.2 Ma (Caillat et al. [1978](#page-17-0)) in the vicinity of the Haji Abad granodiorite intruded the Eocene volcanosedimentary rocks that comprise gabbro, diorite, quart–diorite, quartz– monzodiorite, granodiorite, quartz–monzonite, and granite along with aplitic dikes (Tabbakh Shabani [1991](#page-19-0); Kazemi et al. [2018](#page-18-0)) with transitional contact. The Haji Abad pluton forms a large SE–NW elongated body, elongated parallel to the regional faults; is medium-grained, granular, and light gray; and exposed over an area of $> 40 \text{ km}^2$ that occurs at the intersection of the regional faults and shows weak contact metamorphism (Figs. [2](#page-4-0) and [3a](#page-5-0)). This pluton comprises of granodiorite and minor diorite. The dioritic rocks scattered as small outcrops through the southern part of the area. These rocks are fine-grained and have a seriate texture with feldspar megacrysts along the margins that

exhibit a chilled margin, but toward the center, gradually change to a granular texture. The study of Kazemi et al. [\(2018](#page-18-0)) revealed that the Haji Abad granitoids are mediumto high-K calc-alkaline, metaluminous, magnetite series and I-type igneous rocks.

It is notable that microgranular enclaves of various sizes are common throughout the Haji Abad granodiorites (Fig. [3b](#page-5-0)). They are globular or elliptical in shape, 2–30 cm in diameter, and display hypidiomorphic microgranular texture and sharp boundaries with their hosts. These enclaves are fine-grained and darker than their host rocks and comprised of diorite and gabbro-diorite. They are structurally massive with chilled margins toward the enclave rims.

Analytical methods

Electron probe microanalyses (EPMA) of mineral assemblages were carried out using a JEOL JXA-8230 Superprobe at Hefei University, China. The operating conditions were 15 kV accelerating voltage, 10 nA (K-feldspar and plagioclase) and 20 nA (amphibole and pyroxene) beam current, and 5 μm beam diameter. Structural formulae calculations of feldspars are based on eight atoms of oxygen. Structural formulae of amphibole are calculated on the basis of 23 oxygens. Pyroxenes are classified by using the total numbers of specified cations at the M sites based on the six oxygen atoms.

Field and petrography observation

The predominant intrusive rock of the investigated area is granodiorites that are gray and massive, and the diorites are scattered as separate and small outcrops throughout the southern part of the area and are fine-grained and seriate with feldspar megacrysts along the margins, but they increase in grain size and become granular toward the center. The major constituents of the investigated rocks are K-feldspar, quartz, plagioclase, pyroxene, and minor Fe–Ti oxide, and hornblende (Fig. [3](#page-5-0)c–f), and the accessory minerals (< 1%) include euhedral to rounded zircon, prismatic to acicular apatite, and titanite. Plagioclase occurs as euhedral to anhedral crystals, zoned and altered to sericite, epidote, and calcite, whereas the K-feldspars occur as anhedral grains. Plagioclase with sieve-textured and poikilitic texture (Fig. [3c](#page-5-0), e) are the common features in these samples. Some plagioclase crystals show rounding and corroded margins. Marginal comminution and the rounded corners of plagioclase grains can be an indicator of magma mixing (e.g., Zorpi et al. [1989](#page-19-0); Shelley [1993\)](#page-19-0). Pyroxene as euhedral to subhedral crystals is a dominant mafic phase in all the rocks of the HAG. Pyroxene crystals are partly to completely

Fig. 1 Simplified geology of the western Iran showing the Sanandaj–Sirjan zone (SSZ), main Zagros thrust (MZT), and Urumieh–Dokhtar magmatic arc (UDMA) (modified after Aghanabati [1998\)](#page-16-0)

transformed to actinolite as a result of hydrothermal alteration (Fig. [3](#page-5-0)c). Hornblende is commonly at interstitial phase and is rarely altered to tremolite hornblende, chlorite, and titanite. Quartz forms anhedral crystals or aggregates of several grains with irregular boundaries (Fig. [3e](#page-5-0)).

MME comprises mafic mineral assemblages, relatively fine-grained and commonly globular to ellipsoidal shaped having a typical igneous microstructure (e.g., Vernon [1990](#page-19-0); Barbarin [2005](#page-17-0)) with various sizes (Fig. [3](#page-5-0)b). These enclaves are present throughout the intrusion and are characterized by a hypidiomorphic microgranular texture and are structurally massive (Fig. [3](#page-5-0)f). The majority of the enclaves have chilled margins and sharp boundaries with their host granodiorite, although some MMEs have transitional contacts with their host rock. The MMEs mainly comprise of pyroxene, plagioclase, K-feldspar, quartz, and hornblende (Fig. [3](#page-5-0)f). The plagioclases occur as euhedral–subhedral tabular-prismatic shape. The pyroxenes are the most abundant dark mineral, followed by amphiboles.

Mineral chemistry

Feldspar

The results of EPMA analysis of plagioclases and Kfeldspar from the Haji Abad granodiorite are presented in Table [1](#page-6-0) and are shown in a Ab–An–Or ternary diagram (Fig. [4\)](#page-8-0). The compositions of K-feldspar crystals vary from Or_{77} to Or_{95} . The anorthite contents of plagioclases in the rocks range 9.8–60.2 mol%, and in the Ab–An–Or diagram (Deer et al. [1992\)](#page-17-0), all of them plot mainly in the labradorite, andesine, and oligoclase fields (Fig. [4\)](#page-8-0). Plagioclase crystals commonly show oscillatory zoning (Fig. [5\)](#page-8-0). The core to rim

EPMA analyses of three plagioclases, HG45-1-P, HG45-2- P, and HG45-4-P, all show oscillatory variations of An values from the center to the rime.

Pyroxene

The results of 25 point analyses performed on 15 representative clinopyroxene crystals from HAG are presented in Table [2](#page-9-0) and are plotted in the diagram of Wo–En–Fs (Fig. [6a](#page-10-0)). In the Wo–En–Fs diagram of Morimoto et al. [\(1988](#page-18-0)), most of them principally plot in the field of diopside and some in the augite field (Fig. [6a](#page-10-0)). They are classified as the "Quad" or Ca–Mg–Fe clinopyroxenes (Fig. [6b](#page-10-0); Morimoto et al. [1989\)](#page-18-0). Clinopyroxenes are rich in Ca (Wo_{46.67}) but poor in Na (Na₂O < 0.44). Their compositions range from $En_{38}Fs_9Wo_{43}$ to $En_{44}Fs_{15}Wo_{49}$.

Amphibole

The results of EPMA analysis of amphibole samples from the Haji Abad granodiorite are presented in Table [3](#page-11-0) and plotted on the BCa+BNa versus BNa diagram (Leake et al. [1997](#page-18-0)) (Fig. [7a](#page-13-0)). They range in composition from magnesiohornblende to hornblende and to tremolite–hornblende of the calcic-amphibole group [calculated Ca_B (B-site; apfuatoms per formula unit) is higher than 1.50 apfu, Ca_A is lower than 0.5 apfu, the $(Na+K)$ ^A (A-site) is lower than 0.5 apfu] following the nomenclature of Leake et al. [\(1997](#page-18-0)) (Fig. [7](#page-13-0)b). The chemical composition of amphibole in the HAG has wide Al_2O_3 and SiO_2 ranges from 2.87 to 4.16 wt% and from 49.57 to 53.1 wt%, respectively, while their Mg# (Mg/(Mg+Fe)) varies between 0.88 and 0.96 (Table [3](#page-11-0)).

Discussion

Estimation of pressure, temperature, oxygen fugacity, and water contents

Compositions of the mineral chemistry are used to determine the physicochemical crystallization conditions such as temperature, pressure, $H₂O$ contents, and oxygen fugacity. The estimations of crystallization temperature, pressure, H2O content, and oxygen fugacity using feldspar and pyroxene minerals of granitoid rocks were proposed by some researchers such as Helz [\(1973\)](#page-18-0), Fuhrman and Lindsley ([1988](#page-17-0)), Soesoo [\(1997](#page-19-0)), Putirka et al. ([2003](#page-18-0)), Putirka [\(2005](#page-18-0), [2008\)](#page-18-0), and Faak et al. [\(2013](#page-17-0)).

Fig. 3 Field photograph and thin section representative microphotographs (crosspolarized light) of the Haji Abad granitoids and their enclaves: a field photograph showing the Haji Abad granodiorite, b microgranular enclaves hosted by granodiorite, c granodiorite with granular texture including sieved plagioclase, d feldspar phenocrysts hosted by microgranular enclave, e poikilitic texture and resorption surface in the granodiorite, and f photomicrograph showing the relationship between microgranular enclave and host granodiorite. Abbreviations: Pl, plagioclase; Px, pyroxene; Qtz, quartz. Mineral abbreviations are from Kretz [\(1983\)](#page-18-0)

Pressure and temperature conditions of crystallization

The plagioclase and pyroxene compositions are sensitive to variations in the chemistry of magma and the pressure and temperature crystallization conditions. The pyroxene crystallization pressures obtained from granodiorite using the X_{PT} and Y_{PT} parameters are shown in Fig. [8](#page-13-0)a (Soesoo [1997](#page-19-0)). X_{PT} and Y_{PT} parameters were calculated using the following methods:

```
X_{\text{PT}} = 0.446\text{SiO}_2 + 0.187\text{TiO}_2 - 0.404\text{Al}_2\text{O}_3 + 0.346\text{FeO}^{\text{tot}} - 0.052\text{MnO} + 0.309\text{MgO} + 0.431\text{CaO} - 0.446\text{Na}_2\text{O}
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Y_{PT} = -0.369SiO_2 + 0.535TiO_2 - 0.317A1_2O_3 + 0.323FeO<sup>tot</sup> + 0.235MnO - 0.516MgO - 0.167CaO - 0.153Na_2O
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Table 1 (continued)

The results illustrate clearly that all the pyroxenes fall within the < 2-kbar pressure.

Putirka ([2008](#page-18-0)) proposed a geobarometry base on clinopyroxene compositions that can be used in granitic rocks. According to the proposed barometers (equations 30 and 32c: Putirka [2008\)](#page-18-0), the averages of calculated pressures are 1.9 and 1.8 kbar, respectively. The highest calculated pressure using the clinopyroxene geobarometry is 5 kbar, which reflects initial pyroxene crystallization pressure, indicating initial crystallization depth (17.5 km) in the Haji Abad granodiorite.

Assuming that 1 kbar is comparable to ca. 3.5 km of the crust, they were emplaced at ca. 6.6 km in depth. Petrographic and textural pieces of evidence such as medium- to finegrained and sharp angular contacts to the uppermost crustal country rocks where low-grade metamorphic aureole, hydrothermal alteration, and cognate volcanic rocks nearby were exposed suggest high-level emplacements in the granodiorite rocks that are in good agreement with the abovementioned results (Clarke [1992](#page-17-0)). The calculated pressure (1.9 kbar) for the HAG is compatible with suggested thicknesses (ca. 3 – 9 km) of Paleogene volcanic and sedimentary rocks in the Urumieh–Dokhtar magmatic assemblage (e.g., Förster et al. [1972;](#page-17-0) Morley et al. [2009](#page-18-0)). Moreover, the estimated pressures from the other plutonic rocks in UDMA, such as lower Eocene Kuh-e Dom pluton (1.3 kbar; Sarjoughian et al. [2012](#page-19-0)), Natanz pluton (2.1 –2.5 kbar; Honarmand et al. [2012](#page-18-0)), Oligo-Miocene Nabar pluton (2-2.15 kbar; Abbasi et al. [2014\)](#page-16-0), and Miocene Niyasar plutonic complex (0.2 –1.7 kbar; Honarmand et al. [2016\)](#page-18-0), are in good agreement with the pressure of HAG, indicating that most of the Paleogene granitoids in the UDMA intruded into the Eocene volcanic rocks. The mentioned discussions suggest that these shallow intrusions formed under overburden pressures of < 3 kbar.

Several models of two- and three-feldspar thermometry have been proposed (e.g., Nekvasil and Burnham [1987](#page-18-0); Fuhrman and Lindsley [1988](#page-17-0); Elkins and Grove [1990\)](#page-17-0). The estimated temperatures using ternary-feldspar thermometry (Fuhrman and Lindsley [1988\)](#page-17-0) range from 518 to 649 °C, with average 585 ± 40 °C. But it should be noted that this thermometry probably displays the subsolidus temperature that is lower than the actual feldspar crystallization temperature.

Two-feldspar thermometry (Putirka [2008](#page-18-0): Eq. 27a) is the other thermometry that we use for the estimation of crystallization temperature. This thermometry shows relatively higher temperature than the previous geothermometer, with an average value of 724 ± 23 °C.

Plagioclase and pyroxene are commonly coexisting minerals in igneous rocks in a wide range of temperature and compositions and are used for geothermometry (Faak et al. [2013\)](#page-17-0). Clinopyroxene –plagioclase thermometry was developed by Faak et al. ([2013](#page-17-0)) based on experiments in the temperature-sensitive exchange of Mg between clinopyroxene

Fig. 4 Compositions of feldspars of the Haji Abad pluton on the Ab–An– Or diagram (Deer et al. [1992\)](#page-17-0). Or, potassium feldspar; Ab, albite; Ol, oligoclase; And, andesine; La, labradorite; By, bytownite; An, anorthite

and plagioclase, according for different anorthite contents in plagioclase (X_{An}) and various silica activities (a_{SiO2}) in the system:

$$
T[K] = (-9219 + 2034X_{An}) / (1n K_{Mg}^{p1/Cpx} - 1.6 - 1n a_{SiO2}).
$$

Using this geothermometry, the calculated temperatures range from 633 to 822 °C (with an average of 741 \pm 20 °C). The estimated temperature corresponds well with the twofeldspar thermometry results.

Furthermore, we used the X_{PT} versus Y_{PT} diagram of Soesoo [\(1997\)](#page-19-0) for determination of the pyroxene crystallization temperature (Fig. [8b](#page-13-0)). It suggests that the pyroxenes crystallized under the temperature of 1150–1200 °C. Likewise, two methods from Putirka [\(2008](#page-18-0)) (equations 32d and 34) are used for the estimation of temperature conditions of clinopyroxene crystallization. According to equations 32d and 34, the calculated temperatures for clinopyroxene crystallization range from 1009 to 1144 °C (with an average of 1090 °C) and 947 to 1171 °C (with an average of 1014 °C), respectively. These temperatures are higher than the estimated temperature by feldspar thermometry, indicating that the pyroxene and feldspar temperatures represent the first and late stages of magmatic crystallization of Haji Abad granodiorite, respectively.

Oxygen fugacity (fO_2) , H₂O contents, and density

Oxygen fugacity has an important influence on the liquidus temperature, melt and crystal composition, magmatic process control, crystallization sequence, and types of crystallized minerals (Botcharnikov et al. [2005;](#page-17-0) France et al. [2010](#page-17-0)). Schweitzer et al. ([1979](#page-19-0)) suggested that the $Fe³⁺$ content of

Fig. 5 Measured EPMA profiles for representative plagioclase crystals from the Haji Abad granodiorite, indicating oscillatory zoning

the pyroxenes depends on the oxygen fugacity of their generation environment, and is shown on the $Al^{IV} + Na$ versus $Al^{VI} +$ 2Ti+Cr plot. Papike and Cameron ([1976\)](#page-18-0) have mentioned distances of the plotted samples from the line of $Fe³⁺$ and suggested that the more distance of samples from the line is indicative of a higher amount of oxygen fugacity in their formation environment. When the samples of granodiorite are plotted on the diagram, most of them plot above the line of $Fe³⁺ = 0$, indicating that they crystallized under relatively high oxygen fugacity or oxidized conditions (Fig. [8](#page-13-0)c).

The water contents have a considerable influence on plagioclase-melt equilibria (e.g., Kudo and Weill [1970;](#page-18-0) Housh and Luhr [1991;](#page-18-0) Panjasawatwong et al. [1995\)](#page-18-0). Putirka [\(2005\)](#page-18-0) proposed a hygrometric formulation for the calculation of water contents based on plagioclase-melt compositions. According to the plagioclase-melt hydrometer of Putirka [\(2005\)](#page-18-0), the average of water contents in the Haji Abad granodiorite is about 3.2 wt%. The calculated water content is consistent with the generation environment of HAG rocks in an active continental margin and has allowed the magma to reach shallower crustal levels.

Because of released water from the subducted oceanic slab and its transfer to a higher level and eventually the role of released fluids in the production of magma, this leads to the

Fig. 6 a En–Wo–Fs ternary (Morimoto et al. [1988](#page-18-0)) and b Q=Ca+Mg+Fe²⁺ versus J=2Na diagrams (Morimoto et al. [1989\)](#page-18-0) for the determination of clinopyroxene compositions

hydration of igneous rocks in the subduction zone environment (Sarjoughian [2012](#page-19-0)).

The abovementioned pieces of evidence indicate that the Haji Abad intrusion had probably been saturated with water before the final solidification. $H₂O$ is the main volatile phase dissolved in natural aluminosilicate melts and strongly affects the physicochemical attributes of melts such as phase relationships, viscosity, density, and diffusivity. Therefore, dissolved water can control magma's ability to separate from the source and melt crystallization (Snelling and Woodmorappe [1998\)](#page-19-0) and distribution of enclaves within the host rocks. As Mcbirny [\(2007\)](#page-18-0) proposed, density reduces throughout the entire calc-alkaline series due to the steady reduction in iron and increase in silica. The calculated density by the method of Bottinga and Weill [\(1970\)](#page-17-0) for granodioritic magmas gives an average 2392 kg/m^3 .

Mineralogical evidence for magma mixing

The magma forming the Haji Abad granodiorites evolved by magma mixing, in particular mixing of mafic and felsic melts. This can be proved by the following evidence in terms of petrography and mineralogy: The widespread occurrences of ellipsoidal and spherical MMEs in the Haji Abad granodiorite with igneous microgranular textures, distinct contacts with their host rocks (Fig. [3b](#page-5-0), f), chilled margins against the host granodiorite, and with no sign of recrystallization, deformation, and metamorphic or residual sedimentary fabrics support a magmatic origin resulting from interactions between basic and felsic magmas (e.g., Vernon [1984](#page-19-0); Didier and Barbarin [1991;](#page-17-0) Baxter and Feely [2002;](#page-17-0) Grogan and Reavy [2002](#page-17-0); Perugini et al. [2003](#page-18-0); Sarjoughian et al. [2012](#page-19-0); Yang et al. [2015](#page-19-0)) and preclude the possibility that the enclaves are fragments of recrystallized, refractory metamorphic rocks or of melt residues from the granite sources (e.g., Chappell et al. [1987,](#page-17-0) [2000](#page-17-0); White et al. [1999\)](#page-19-0), fragments of cumulates from the host magma (e.g., Noyes et al. [1983](#page-18-0); Chen et al. [2009](#page-17-0); Shellnutt et al. [2010](#page-19-0); Huang et al. [2014](#page-18-0)), or xenoliths of mafic rock (e.g., Bonin [2004;](#page-17-0) Yang et al. [2004,](#page-19-0) [2006\)](#page-19-0). Furthermore, the presence of K-feldspar and plagioclase megacrysts and acicular apatite in the MMEs, feldspars, and quartz that were entrained from the host granitoids to the enclaves (Fig. [3](#page-5-0)d) and the sieve texture in corroded, partially resorbed plagioclases are pieces of evidence suggesting a hybrid system formed by mixing of two distinct end-member magma compositions (e.g., Yang et al. [2015](#page-19-0)), during which the mafic magma was injected into the felsic magma and crystallization under rapid cooling in a quenched environment occurred as a result of mingling of small volumes of hot mafic melt with cooler granitoid magma (e.g., Vernon [1984](#page-19-0); Chen et al. [2009](#page-17-0), [2016](#page-17-0)).

Chemically oscillatory zoning in plagioclase has been widely observed in magmatic rocks (e.g., Tepley et al. [2000;](#page-19-0) Davidson et al. [2001](#page-17-0); Halama et al. [2002](#page-17-0); Tepley and Davidson [2003](#page-19-0); Chen et al. [2015\)](#page-17-0), especially fluctuating An and FeO contents in plagioclase that are a widespread phenomenon in subduction-related magma systems (e.g., Hattori and Sato [1996;](#page-18-0) Tepley et al. [2000](#page-19-0); Davidson et al. [2001](#page-17-0); Ruprecht and Wörner [2007](#page-18-0); Andrews et al. [2008](#page-17-0); Shcherbakov et al. [2011](#page-19-0); Cao et al. [2014\)](#page-17-0) and are an indicator to identify magmatic processes. Plagioclase crystals with oscillatory zoning in the form of anorthite fractions (Fig. [5](#page-8-0)) likely indicate the mixing of coexisting mafic and felsic magmas. Ustunisik et al. [\(2014](#page-19-0)) suggested that temperature, total pressure, and water content of the melts are important factors controlling compositional zoning in plagioclase, although lithospheric pressure will have a little real effect on plagioclase at a given liquid composition (Housh and Luhr [1991;](#page-18-0) Lange et al. [2009\)](#page-18-0). Oxygen fugacity has obvious effects on Fe content, but not for other elements, such as partitioning of Ca between plagioclase and melt

Note: Formula based on 23 oxygens

Note: Formula based on 23 oxygens

Fig. 7 a BCa+BNa versus BNa diagram, indicating that studied amphiboles belong to the calcic group (Leake et al. [1997](#page-18-0)). b Composition of amphiboles of the Haji Abad granodiorite plotted on the Si versus Mg/(Mg+Fe⁺²) diagram (Leake et al. [1997](#page-18-0))

(Phinney [1992;](#page-18-0) Wilke and Behrens [1999](#page-19-0)). Although An and FeO values display similar trends within the core–mantle–rim of these crystals, they do not show synchronous variations (Fig. [5\)](#page-8-0). These trends indicate that oxygen fugacity variations have no important role in the observed oscillations, but these oscillations are indeed caused by changes to the melt composition, while asynchronous variations (decreasing An without decreasing FeO) suggest the effect of plagioclase crystallization which depleted Ca in the melt (Cao et al. [2014\)](#page-17-0). As a result, strong correlations between An and FeO contents in plagioclase

Fig. 9 a TiO₂ versus K₂O and b TiO₂ versus MgO diagrams using amphibole compositions for discrimination of geochemical affinity and tectonic environment (Molina et al. [2009\)](#page-18-0)

(Fig. [5](#page-8-0)) from the Haji Abad granitoid indicate that mixing or recharging of magma took place under open-system conditions (Ruprecht and Wörner [2007\)](#page-18-0). Zoned plagioclases in HAG show wide compositional oscillations from An_{10} to An_{60} and usually well-developed dissolution surfaces that can be an indicator of large-scale turbulences of the magma chamber occurring in open-system conditions, such as during magma mixing or contamination that both of them can effectively change the temperature and chemical composition (e.g., Singer et al. [1995;](#page-19-0) Hattori and Sato [1996](#page-18-0); Davidson and Tepley [1997](#page-17-0); Tepley et al. [1999](#page-19-0), [2000;](#page-19-0) Davidson et al. [2001](#page-17-0)). The oscillatory patterns of chemical compositions from the core to the rim are commonly interpreted as an indicator of magma mingling in silicaintermediate rocks (Stamatelopoulou-Seymour et al. [1990](#page-19-0)).

According to the petrography and plagioclase chemistry descriptions mentioned above, it can be concluded that

Fig. 11 a $SiO_2/100-TiO_2-Na_2O$ ternary diagram using pyroxene composition (Beccaluva et al. [1989\)](#page-17-0). b Plotted pyroxene data on the Ti versus Ca diagram (Sun and Bertrand [1991](#page-19-0)) fall in the orogenic field. c

Amphiboles in Haji Abad granodiorite are plotted in the field of subduction amphibole on the Na₂O versus SiO₂ diagram (Coltorti et al. 2007)

Fig. 12 Schematic model of the generation of the Haji Abad granitoids and their mafic enclaves in the UDMA during the Middle Eocene

chemical and/or thermal changes occurred in the chamber magma during crystal growth as a result of magma mixing (Baxter and Feely [2002](#page-17-0); Grogan and Reavy [2002](#page-17-0); Yang et al. [2015](#page-19-0)).

Nature of magma and tectonic environment

The mineral chemistry of ferromagnesian minerals (such as pyroxene, amphibole, and biotite) is a function of chemical composition and tectonic setting of their formative magma and can provide valuable information about tectonic setting and petrogenesis of the granitoid rocks (Maulana et al. [2012\)](#page-18-0). According to many researchers (Chappel and White [1974](#page-17-0); Wyborn et al. [1981;](#page-19-0) White and Chappell [1983;](#page-19-0) Clemens and Wall [1984\)](#page-17-0), the presence of calcic amphiboles in granitoid rocks indicates that these rocks belong to the I-type granitoids (Stein and Dietl [2001\)](#page-19-0), because the abundance of CaO in these granites leads to hornblende crystallization.

Molina et al. [\(2009\)](#page-18-0) suggested that the incorporation of K, Mg, and Ti into the amphibole structure depends of the nature of magma, as the amphiboles in the subalkaline series have lower TiO₂ (<2 wt%) and K₂O than those found in alkaline series. According to Molina et al. (2009) (2009) (2009) , on the TiO₂ versus $K₂O$ and TiO₂ versus MgO discrimination diagrams (Fig. [9\)](#page-14-0), the studied amphiboles are grouped in the subalkaline fields that are consistent with crystallization from I-type calc-alkaline magma in a subduction environment related to active continental margin. Clinopyroxene compositions, especially element contents such as Ti, Al, Na, Cr, and Si, can be used to identify the magmatic affinity and geotectonic environment (e.g., Le Base [1962](#page-18-0); Leterrier et al. [1982;](#page-18-0) Sun and Bertrand [1991\)](#page-19-0). Le Base [1962](#page-18-0) has believed that it is possible to separate peralkaline, alkaline, and subalkaline magmatic series using the SiO_2 , Al_2O_3 , and TiO_2 contents in the chemical composition of pyroxene. Pyroxene in granodiorites is rich in Si and poor in Ti and Al and, in the SiO_2 and TiO_2 versus Al_2O_3 diagrams (Fig. [10](#page-14-0)), plots in the fields of subalkaline and calc-alkaline, respectively. The above results are in agreement with geochemical data (Tabbakh Shabani [1991;](#page-19-0) Safarzadeh et al. [2007](#page-19-0); Kazemi et al. [2018](#page-18-0)). As Kazemi et al. [\(2018](#page-18-0)) suggested, these rocks are metaluminous and calc-alkaline in character with low A/CNK (molar $Al_2O_3/(CaO+Na_2O+K_2O))$ ratios from 0.69 to 1.03 and A/NK (molar Al_2O_3/Na_2O+K_2O) ratios from 1.37 to 2.54, indicative of an I-type affinity for these rocks.

The frequency of elements such as Al, Ti, Cr, Na, and especially Si in the chemical composition of pyroxene is an indicator of their nature and tectonic setting (Le Base [1962;](#page-18-0) Leterrier et al. [1982](#page-18-0); Sun and Bertrand [1991](#page-19-0)). As shown in Fig. [11a](#page-14-0), low contents of Ti and high $SiO₂$ contents in the studied pyroxene structure are characteristic of arc volcanic igneous rocks (Beccaluva et al. [1989\)](#page-17-0). Furthermore, the plotted pyroxene data on the Ti versus Ca diagram (Sun and Bertrand [1991](#page-19-0)) indicates that the HAG rocks were generated in an orogenic belt (Fig. [11b](#page-14-0)). The studied amphiboles have low contents of Na_2O and TiO_2 . Coltorti et al. [\(2007](#page-17-0)) proposed that suprasubduction amphiboles (S-Amph) generally show lower contents of $Na₂O$ and $TiO₂$ than intraplate amphiboles (I-Amph). Also, amphiboles in Haji Abad granodiorite are plotted in the field of subduction amphibole on the $Na₂O$ versus $SiO₂$ diagram (Fig. [11](#page-14-0)c; Coltorti et al. [2007](#page-17-0)). As shown in Fig. [10,](#page-14-0) the low content of Ti and the high content of $SiO₂$ in the pyroxene structure indicate the characteristics of pyroxenes in igneous rocks associated with volcanic arc (Beccaluva et al. [1989\)](#page-17-0). A subduction zone setting for the studied intrusion is also supported by geochemical data (Tabbakh Shabani [1991;](#page-19-0) Safarzadeh et al. [2007;](#page-19-0) Kazemi et al. [2018](#page-18-0)). Many researchers proposed the Neo-Tethyan subduction beneath central Iran as the interpretation of the origin of magmatism in the UDMA (Rezaei-Kahkhaei et al. [2011](#page-18-0); Honarmand et al. [2012](#page-18-0); Sarjoughian et al. [2012](#page-19-0); Kananian et al. [2014;](#page-18-0) Sarjoughian et al. [2018\)](#page-19-0). For instance, Honarmand et al. [\(2012](#page-18-0)) using clinopyroxene and biotite composition suggested that Natanz pluton formed from a calc-alkaline magma in a subduction zone setting. Also, Sarjoughian et al. [\(2018\)](#page-19-0) based on geochemical data proposed that Zafarghand igneous complex in the UDMA formed in an active continental margin setting, which was emplaced during subduction of Neo-Tethyan oceanic crust beneath the Sanandaj–Sirjan and central Iran zones. Consequently, the HAG represents an orogenic cycle, and the mixing processes possibly took place in an active continental margin during northeastward subduction of Neo-Tethyan oceanic crust underneath the central Iranian microcontinent (Fig. [12\)](#page-15-0).

Conclusions

- 1. The Haji Abad intrusion is a well-exposed I-type granodioritc pluton in the central part of the UDMA. Two-feldspar and clinopyroxene thermometers yield crystallization temperatures with an average of 724 and 1090 °C. The calculated pyroxene and feldspar temperatures represent the first and late stages of magmatic crystallization of Haji Abad granodiorite, respectively.
- 2. Meanwhile, the calculated average pressures of emplacement are 1.9 kbar for the granodioritic rocks, which is equal to depths of about 6.7 km based on the two barometer equations of clinopyroxene. The highest calculated pressure (5 kbar) reflects initial pyroxene crystallization

pressure, indicating initial crystallization depth (17.5 km) in the Haji Abad granodiorite.

- 3. The oxygen fugacity estimates according to pyroxene are above the line of $Fe^{3+} = 0$, indicating that the Haii Abad magmas were characterized by relatively high oxygen fugacity or oxidized conditions. Furthermore, the results show that the rocks crystallized from magmas with H_2O content of 3.2 wt%. The calculated water content is consistent with the generation environment of HAG rocks in active continental margins.
- 4. The widespread ellipsoidal and spherical MMEs with igneous micogranular textures and chilled margins in the Haji Abad granodiorite; the presence of K-feldspar and plagioclase megacrysts and acicular apatite in the MMEs, feldspars, and quartz that were entrained from the host granitoids to the enclaves; and sieve texture in corroded, partially resorbed plagioclases, together with An and FeO oscillatory patterns in the plagioclase, suggest a hybrid system formed by mixing of two distinct end-member magma compositions, during which the mafic magma was injected into the felsic magma, and crystallization under rapid cooling in a quenched environment occurred as a result of mixing/mingling of hot mafic melt with cooler granitoid magma, since chemical and/or thermal changes occurred in the chamber magma during crystal growth as a result of magma mixing.
- 5. The studied amphiboles and pyroxenes are grouped in the subalkaline fields that are consistent with crystallization from I-type calc-alkaline magma in a subduction environment related to active continental margin, indicating the generation of HAG in an orogenic belt related to the volcanic arc setting consistent with the subduction of Neo-Tethyan oceanic crust beneath the central Iranian microcontinent.

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