



Mineral chemistry and Petrology of the Andorian volcanic rocks: insight to the Ahar-Arasbaran magmatic zone, Northwestern Iran

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Abstract

The Neogene Andorian volcanic rocks, a part of the Ahar-Arasbaran magmatic zone, are situated in the northwest of Iran. These units are composed of a series of intermediate to acidic volcanic rocks including basaltic andesite, hornblende andesite, andesite, dacite, and rhyodacite. The basaltic andesite and hornblende andesite are mainly comprised of K-feldspar (Or_{10-63}), plagioclase (An_{5-37}), calcic amphibole, clinopyroxene ($En_{45-64} Wo_{29-54} Fs_{0-20}$), and biotite ($Mg\#: 0.70-0.82$). The compositions of biotite, clinopyroxene, and amphibole as well as whole rock chemistry of the Andorian volcanic rocks show calc-alkaline signatures. The amphibole-plagioclase thermometer and Al-in-hornblende barometer data yielded crystallization temperatures of 707–899°C and pressures of 0.5 to 2.9 kbar. The negative Nb, Ta, and Ti anomalies and large ion lithophile element (LILE; Rb, Ba, and Sr) enrichments relative to primitive mantle indicate a subduction setting. Furthermore, the chondrite-normalized rare earth element (REE) patterns show an LREE enrichment with no clear Eu anomaly. Amphibole and clinopyroxene compositions indicate crystallization under strongly oxidizing conditions.

Keywords Andorian · Ahar-Arasbaran magmatic zone · Calc-alkaline · Andesite

Introduction

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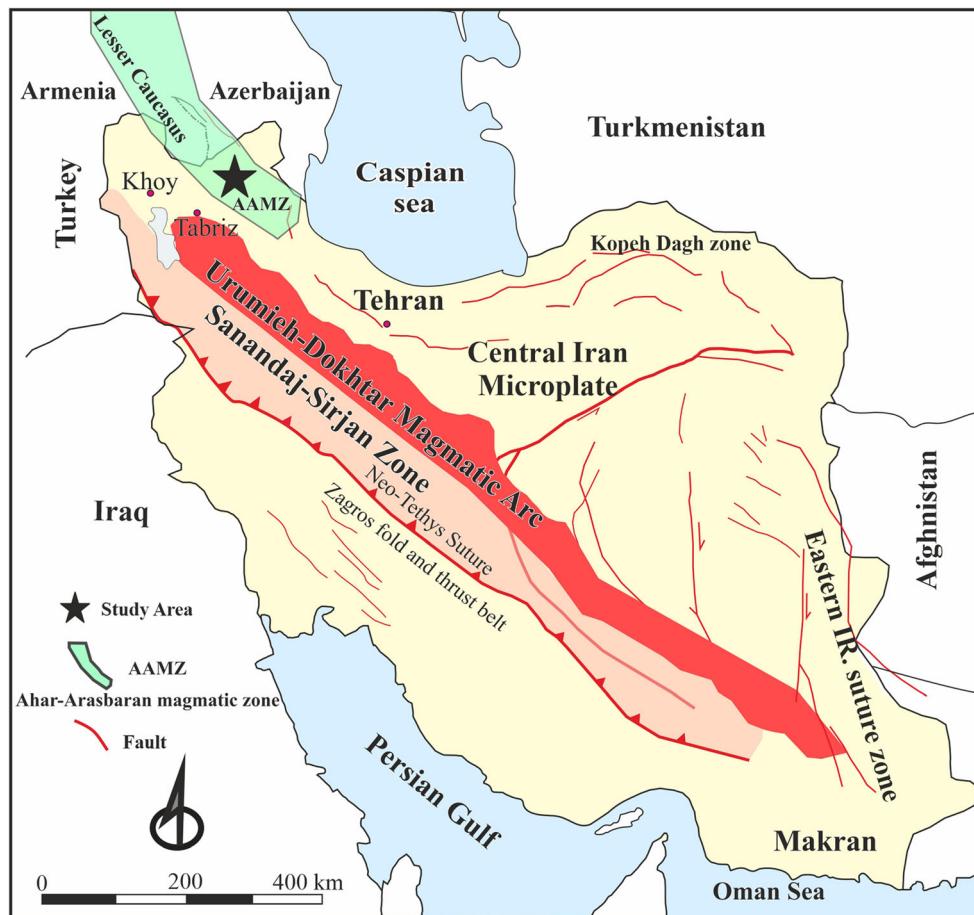
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The Ahar-Arasbaran magmatic zone (AAMZ) located in the southern part of the Lesser Caucasus (Fig. 1) with WNW–ESE trending. The position of the Lesser Caucasus provides a unique opportunity to understand the lateral connection of the central and western Tethyan metallogenic belt (Richards 2015). The AAMZ shows a complex geology and tectonic setting due to its proximity to the Arabia-Eurasian collision (Avagyan et al. 2018; Matossian et al. 2020). Lithospheric variations and faults are the main parameters affecting the tectonic evolution of the Lesser Caucasus (Avagyan et al. 2005). The AAMZ is situated in the hinterland of the Arabia–Eurasia collision zone and the edge of the Alpine-Himalayan tectonic belt (Dilek et al. 2010; Aghazadeh et al. 2012). This zone is 1500 km long and 150 to 200 km wide (more than 23000-km² area) and is exposed in the northwestern part of Iran and extends to Azerbaijan and Armenia (Castro et al. 2013; Hassanpour et al. 2015; Pazand and Hezarkhani 2018).

The AAMZ is limited by the Aras, Talesh, and Tabriz faults (Castro et al. 2013) and known as a high potential prospect for copper, gold, and molybdenum mineralization (Akbarpur 2007; Jamali et al. 2010; Moritz et al. 2011;

Fig. 1 Simplified structural map of Iran (modified from Stocklin 1968; Hassanpour 2017)



Maghsoudi et al. 2014; Hassanpour et al. 2015; Richards and Sholeh 2016; Moritz et al. 2016; Simmonds et al. 2017; Rabiee et al. 2019). The AAMZ shows extensive magmatic activity from the Upper Cretaceous to Quaternary with few time gaps (Ghorbani 2013; Simmonds et al. 2017). The following five magmatic episodes are recognized in the AAMZ:

- 1) Middle Cretaceous to Paleocene magmatic activity, where high-thickness (up to 1000 meters thick) Middle Cretaceous volcanic sequences underlay Late Cretaceous limestone units. These units consist of high-K calc-alkaline, calc-alkaline and tholeiitic lava flows, and pyroclastic rocks (Vincent et al. 2005; Aghazadeh et al. 2010; Hassanpour 2010; Jamali and Mehrabi 2015; Soltanmohammadi et al. 2018).
- 2) Eocene volcanic phase, which marks the peak of the volcanic activity in the AAMZ (with a climax in the Middle Eocene). The volcanic rocks of this sequence are mainly intermediate to acidic in composition while pyroclastic rocks (mainly tuff) of this sequence are predominantly acidic. This stage of volcanism is accompanied by widespread hydrothermal alteration and mineralization. This magmatic episode mostly includes alkaline and shoshonitic volcanic rocks, which are overlain by Late

Eocene flysch-type sediments and/or Late Miocene volcanic and sedimentary units (Dilek et al. 2010).

- 3) Late Eocene to Early Oligocene magmatic phase, is generally composed of small and large intrusions in the AAMZ area, generated various and wide hydrothermal alterations (Jamali et al. 2010; Hassanpour 2013; Ghorbani 2013). These intrusive bodies with NW-SE trend, which cut Middle Eocene volcanic rocks, comprise nepheline syenite, monzonite, granodiorite, quartz-diorite, and granite (Jamali et al. 2010). Locally, part of the intrusive rocks is covered by Oligo-Miocene red beds (Upper Red Formation) implying that they may Middle Oligocene or older in age.
- 4) The Middle Oligocene-Pliocene magmatic stage mainly consists of acidic volcanic domes and sub-volcanic rocks (Ghorbani 2013). According to Hassanpour et al. (2015), the development of the main porphyry Cu–Mo mineralization in the AAMZ is related to this phase (Early Miocene). Comparing with the second episode, this magmatic phase shows widely variable lithological characteristics.
- 5) The Quaternary alkaline basaltic and andesitic lavas (the last volcanic stage in the AAMZ) have been linked to the collision of the Afro-Arabian and Eurasian plates

(Kheirkhah et al. 2009; Dabiri et al. 2011). The rock composition indicates a subduction setting with a distinct enrichment in lithophile elements and a high La/Nb ratio (Kheirkhah et al. 2009). The volcanic rocks studied here are representative of the fourth magmatic episode. No detailed studies have been conducted on the Neogene volcanic rocks in the Andarian area. The main aim of this paper is to determine the geochemistry, petrogenesis, and nature of the magma source, as well as the tectonic setting characterized by the mineral composition and whole rock chemistry data for the Andarian volcanic rocks.

Geological setting

The Andarian region is situated in the East Azerbaijan province (NW Iran), about 51 km north of Tabriz city (Fig. 1). Andarian area exhibits a complex geology with a combination of intrusive igneous rocks, altered and mineralized rocks, low-metamorphic rocks, and volcanic rocks. Upper Cretaceous-Paleocene sedimentary rocks are exposed on the west of the Andarian village (Ghorbani 2019; Fig. 2). This sequence is generally composed of flysch deposits, thick sequences of limestones and marls, alternating with sandstones and siltstones. Sedimentary units, volcanic rocks, pyroclastic, and volcano-sedimentary rocks are the main constituent of Eocene outcrops in this area (Fig. 2). The Miocene Mivehrood pluton (Hassanpour et al. 2015; Fig. 2) comprises granodiorite, diorite, quartz-monzdiorite, and quartz-

monzonite with porphyritic to granular textures (Ferdowsi et al. 2015; Alirezaei et al. 2015). Contact aureoles (skarn and hornfels) formed by penetration of the pluton (stock) associated dykes and sills into the Upper Cretaceous sediments. Alirezaei et al. (2015) found that these skarns occur as a ring around the intrusive body. Hornfelses (with about 100 m thick) occurred in the contact with the skarns. The hornfelses show a dark color in hand specimens and consist of recrystallized feldspars and quartz, dolomite, calcite, micas, epidote, and wollastonite (Alirezaei et al. 2015). The Pliocene rocks (evidently Pliocene) consist of three units, a volcanogenic conglomerate, acidic to intermediate volcanic rocks (present work) and lava flows. These volcanic rocks overlay the Oligo-Miocene sedimentary beds (Qom Formation) near the Andarian village (Fig. 3a). Thus, field evidence suggests that the age of these volcanic rocks is late Miocene and younger (they are also known as post-Miocene volcanic rocks). In other parts of the AAMZ, the volcanic domes also crosscut the Oligo-Miocene sedimentary beds locally (Jamali et al. 2010). Intermediate volcanic rocks are more abundant than acidic ones and pyroclastic deposits are lacking.

In the study area, several major NW-SE reverse faults displaced the flysch deposits (Mehrpartou 1997). The second set of N-S trending faults separate the intrusive body from adjacent units and the major deformation occurred along these faults, causing displacement and fracturing of the pluton (Mehrpartou 1997; Ferdowsi et al. 2015).

In general, post-Miocene volcanic rocks are concentrated in the southwestern part of the AAMZ but distribution of them in other parts of this zone is rare (Jamali et al. 2010). Andesite, trachyandesite, trachydacite, dacite, and rhyolite rocks are the

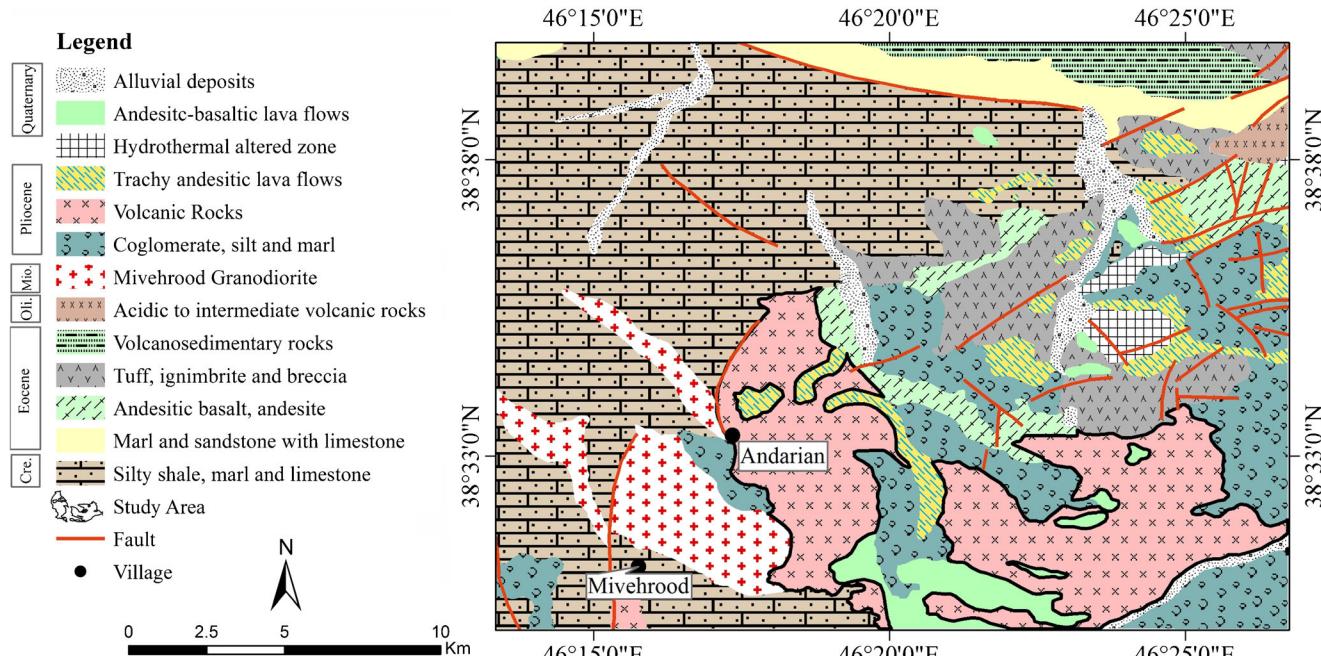


Fig. 2 Simplified geological map of the Andarian area after Mehrpartou (1997).

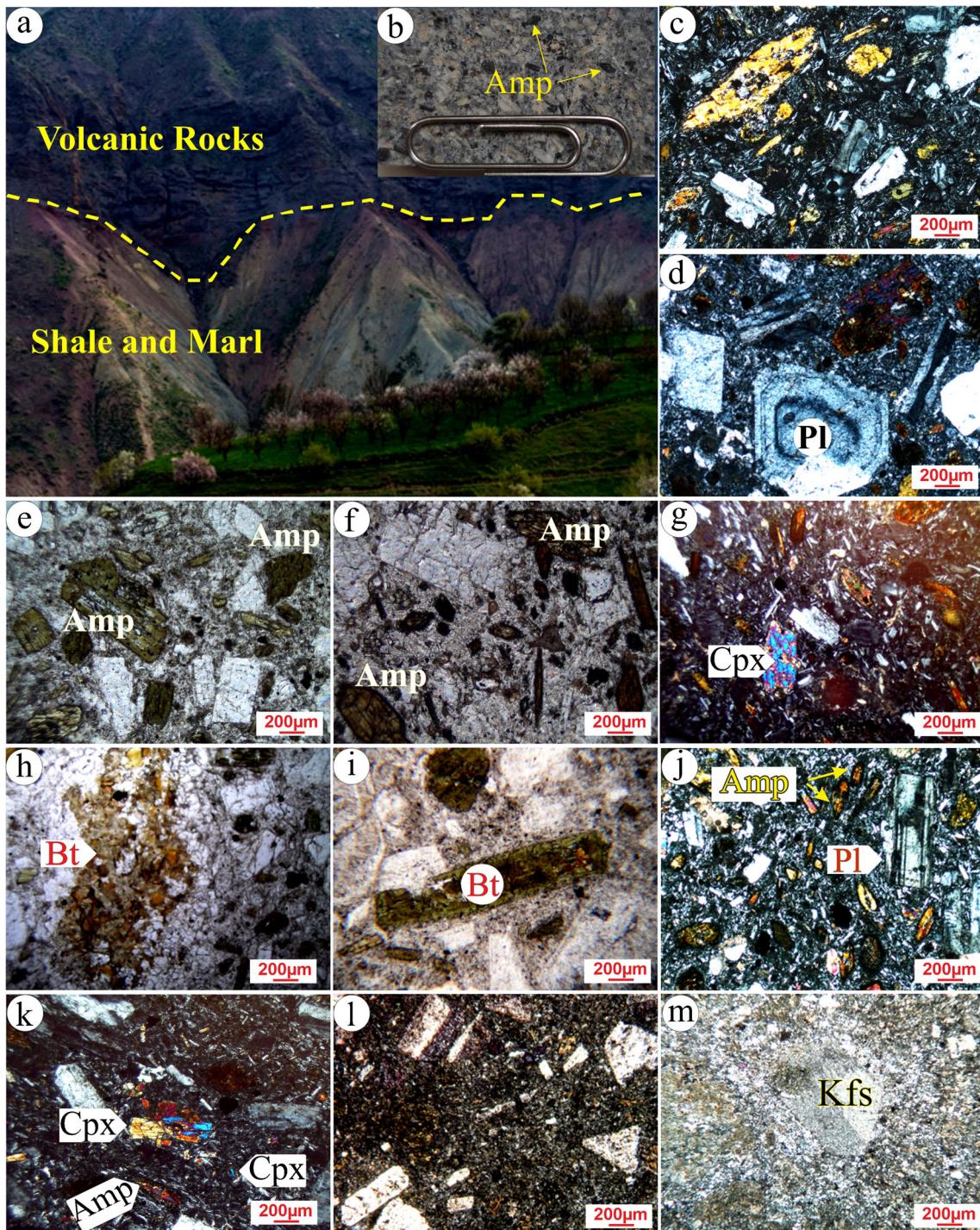


Fig. 3 **a** Stratigraphic contact of the Andarian volcanic rocks with the Oligo-Miocene sediments. **b** Handspecimen of hornblende andesite showing hornblende phenocrysts. **c** Microlitic porphyritic textures in hornblende andesite, crossed polarizers (XPL). **d** Zoned plagioclase phenocryst in hornblende andesite, XPL. **e** Semihedral green hornblende in hornblende andesite, parallel polarizers (PPL). **f** Brown hornblende in hornblende andesite, PPL. **g** Clinopyroxene phenocryst in the Andarian

hornblende andesite, XPL. **h** Secondary biotite in hornblende andesite, PPL. **i** Amphibole is replaced by biotite in hornblende andesite, PPL. **j** Porphyritic texture in basaltic andesite, XPL. **k** Clinopyroxene crystals in two forms of phenocryst and matrix component in basaltic andesite, XPL. **l** Porphyritic to semi-trachytic texture in andesite, XPL. **m** Porphyric texture in rhyodacite, XPL. Mineral abbreviations are from Whitney and Evans (2010)

main constituent of post-Miocene volcanic rocks. Jamali et al. (2010) concluded that there are no clear genetic relationships between the post-Miocene volcanic rocks and the

mineralization occurrences in the AAMZ. Based on extensive field observations, no mineralization associated with Neogene Andarian volcanic rocks has yet been reported.

Analytical method

The minerals were analyzed by using a fully automated JEOL JXA-8600 electron probe micro-analyzer at the Department of Earth and Environmental Sciences, Yamagata University, Japan. Selected points were analyzed using a 15-kV accelerating voltage and 20-nA beam current. The beam diameter was set to 5 μm and detection limits of 0.05 wt% with a maximum 40-s counting interval. Normalization for biotite, amphibole, plagioclase, and pyroxene was calculated on the basis of 24, 23, 8, and 6 oxygens per formula unit, respectively.

The volcanic rocks (8 samples) were powdered by agate mill for quantitative analysis of major and trace elements as well as rare earth elements. Major elements in samples were measured using an X-ray fluorescence spectrometer (XRF) using standard glass beads (these glass beads were prepared from whole rock powders) at SNU (Seoul National University). The glass beads that remain after measuring major element compositions using XRF were used to measure trace element compositions using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Trace and rare earth elements content of the volcanic rocks were determined by LA-ICP-MS at KBSI (Korea Basic Science Institute). Helium gas, the laser ablation source gas, was applied at a typical flow rate of 0.701 L/min. The collected ICP-MS data were operated in time-resolved analysis for 100s and in the peak-hopping mode with a dwell time of 20 ms. The Nd:YAG laser was acquired at a 20-Hz repetition rate, 110- μm spot size, and 70% energy level (20 J/cm²). More details of operating conditions of the laser source and ICP-MS were described in Kil and Jung (2015). Each bead was analyzed three times for monitoring the accuracy of data, and finally, the average was chosen as the analysis result. All data were normalized to calcium concentration, which was measured by the XRF as an internal standard.

Petrography of the volcanic rocks

The study area (Fig. 2) covered by the Pliocene volcanic rocks comprising basaltic andesite, andesite, hornblende andesite, and minor occurrences of dacite and rhyodacite.

Hornblende andesite

The hornblende andesite unit is one of the most widespread and dominant lithology in the Andarian area. The rocks show a porphyritic texture in hand specimens and contain visible phenocrysts of amphibole and plagioclase (Fig. 3b). Their color varies from greenish-gray to light gray. They are coarse- to medium-grained, with porphyritic and microlithic porphyritic textures (Fig. 3c). The hornblende andesites

contain 27–53% (mean 33%) groundmass, 24–48% (mean 37%) plagioclase, 15–28% (mean 21%) amphibole, less than 10% clinopyroxene and biotite, and less than 4% magnetite and K-feldspar. Plagioclase (mainly 0.6–0.8 mm in size, maximum 2.4 mm long) and hornblende (mostly between 0.6 and 0.7 mm, maximum 1.6 mm) are the most abundant phenocrysts.

Plagioclase crystals are mostly subhedral and zoned (Fig. 3d), whereas hornblendes are often subhedral to euhedral in shape. Hornblende phenocrysts show both deep green and brown color (Fig. 3e, f). Clinopyroxene crystals are only observed in few thin sections as phenocrysts (Fig. 3g), occasionally showing replacement by amphibole (see also in mineral chemistry evidence). Clinopyroxenes together with plagioclase grains developed glomeroporphyritic texture. The groundmass is composed of microlites but in some thin sections glass is preserved. Primary biotite is rare but it can be found as secondary biotite, which often replaces amphibole (Fig. 3h, i).

Basaltic andesite

Basaltic andesite is another major lithotype in the area. Coarse-grained plagioclase (mean 30%) together with hornblende (mean 13%) and clinopyroxene (mean 8%) and minor amount of fine-grained pyroxene and microlite in matrix (45%) yield a porphyritic texture (Fig. 3j, k). The subhedral to anhedral pale-green clinopyroxenes, variable in size, lack zoning. The hornblendes (mostly >400 μm) form elongated rod-shaped crystals (Fig. 3j), subhedral columnar, and large idiomorphic grains lacking a clear zoning. Plagioclase grains (>200 μm) sometimes exhibit zoning and tapered twins (lamellar becomes gradually thinner and narrower; Fig. 3j). Biotite, the less abundant ferromagnesian mineral, with brown to dark brown color is present in some cases and titanite is also observed as an accessory mineral.

Andesite

The andesites display porphyritic to semi-trachytic textures (Fig. 3l). Plagioclase (mean 45%, mainly 0.4–0.6 mm) and hornblende phenocrysts show some orientation probably related to the lava flow. Andesites are slightly altered as most of the plagioclases show weak sericitic-kaolinitic alteration. Hornblende crystals are partially altered to chlorite and aggregate clusters of secondary biotite. K-feldspar crystals are only observed in few thin sections.

Dacite and rhyodacite

The dacite and rhyodacite hand specimens are milky to cream in color. Because of the apparent similarity of the two rock

types, dacites and rhyodacites are difficult to discriminate in hand specimen. The rhyodacite shows a porphyritic texture and mainly consists of quartz, alkali feldspar, biotite, and minor amounts of zircon, Fe–Ti oxides, and secondary biotite (Fig. 3m). Some samples display signs of chloritization and sericitization. The dacites contain amphibole and plagioclase phenocrysts in a groundmass of quartz and feldspar. Completely unaltered samples of dacite and rhyodacite were not observed, most of them partially altered.

Result

Mineral composition

In this section, we present mineral composition of feldspar, amphibole, clinopyroxene, and biotite that were analyzed in representative samples of hornblende andesite and basaltic andesite rocks.

Feldspar

Representative feldspar analyses and their normalized values of two types of rock samples are presented in Tables 1 and 2. Plagioclases in the hornblende andesites show a compositional range from albite to andesine ($An_{5.1-33.8}$; majority recognized as oligoclase). This range overlaps with that of basaltic andesite plagioclases ($An_{11.9-37.0}$; Fig. 4a). The point analyses of K-feldspar crystals suggest sanidine and anorthoclase variants (Fig. 4a).

As mentioned in the petrographic section, zoning in plagioclase crystals is common. All the zoning in the studied phenocrysts shows some coarse oscillations ($>10 \mu\text{m}$) with moderate anorthite variation ($\sim 4 \text{ mol\%}$; Fig. 4b; Table 2).

Amphibole

The chemical composition, normalized to 23 oxygens, of the analyzed amphiboles from the hornblende andesites and basaltic andesites is listed in Table 3. Based on BSE images, amphiboles are often found as unaltered phenocrysts and microcrysts and there is no clear zoning in them. Almost all of the amphiboles are primary and have high TiO_2 content (1.01–3.77 wt% in the hornblende andesite and 1.12–3.70 wt% in the basaltic andesite). Based on the Leake et al. (2004) classification, all amphiboles of the volcanic rocks have $\text{Ca} + \text{Na} > 1.00$ implying that they are calcic amphiboles. Regarding calcic amphibole classification (Leake et al. 2004; Hawthorne et al. 2012), most of the amphiboles are edenite and pargasite/hastingsite. Few samples also show magnesioc-hornblende and tschermakite by plotting their composition (Fig. 5).

Pyroxene

The result of point analysis of the hornblende andesite and basaltic andesite samples is reported in Table 4. The clinopyroxene compositions are plotted in the quad field (Morimoto 1988; Fig. 6a). Figure 6 b presents the Wo–En–Fs diagram suggesting diopside and augite species for clinopyroxenes (Morimoto 1988).

Mica

As mentioned earlier, the amount of mica crystals in the studied volcanic rocks is insignificant. The result of the point analyses of mica is reported in Table 5. Al_2O_3 and TiO_2 contents of mica vary between 12.97 to 17.90 wt% and 0.49 to 4.87 wt% respectively (Table 5). Based on Al versus $\text{Fe\#} = \text{Fe}/(\text{Fe} + \text{Mg})$ diagram (Foster 1960), all biotites from the hornblende andesite and basaltic andesite are plotted in the phlogopite field (Fig. 7a). Furthermore, using ternary classification diagram of biotite (Foster 1960), all analyses are plotted either in or at the border of the phlogopite field (Fig. 7b).

Thermobarometry

Experimental investigation demonstrates that amphibole and clinopyroxene composition can be used to estimate the P-T condition of the volcanic rock crystallization (Johnson and Rutherford 1989; Putirka 2008; Ridolfi et al. 2010; Neave and Putirka 2017).

The thermobarometry equations (Ridolfi et al. 2010; Ridolfi and Renzulli 2012) which were developed for calcic amphiboles of volcanic calc-alkaline rocks are used in this paper. In the equations, the amphiboles with less than 10% CaO are assumed as low calcic amphiboles that are not able to measure the temperature and pressure. According to these thermobarometric equations (Ridolfi et al. 2010), the amphibole composition of the hornblende andesite suggests an estimated range of temperatures of 809–1013°C (mean = $914 \pm 47^\circ\text{C}$) and pressures of 0.77–3.81 kbar (mean = 2.04 ± 0.22 kbar; Fig. 8a, Table 3). The P-T diagram of Ridolfi et al. (2010) has been divided into four domains (Fig. 8a): (1) ($\text{Mg-Hbl} \pm \text{Pl} \pm \text{Opx} \pm \text{Mgn} \pm \text{Ilm} \pm \text{Bt}$), (2) ($\text{Tsc-Prg} \pm \text{Pl} \pm \text{Cpx} \pm \text{Opx} \pm \text{Mgn} \pm \text{Ilm}$), (3) ($\text{Tsc-Prg} \pm \text{Pl} \pm \text{Ol} \pm \text{Cpx} \pm \text{Opx} \pm \text{Mgn} \pm \text{Ilm}$), and (4) ($\text{Cpx} \pm \text{Mgn} \pm \text{Ol} \pm \text{Pl}$). The samples plot within domains 1 to 3, so that all of the minerals with the exception of orthopyroxene, olivine, and ilmenite are also observed in petrographic studies. The equation of Ridolfi et al. (2010) yields estimated temperatures of 853–1014°C (mean = $946 \pm 46^\circ\text{C}$) and pressures of 0.89 to 3.87 kbar (mean = 2.41 ± 0.26 kbar) for the basaltic andesite samples (Fig. 8a).

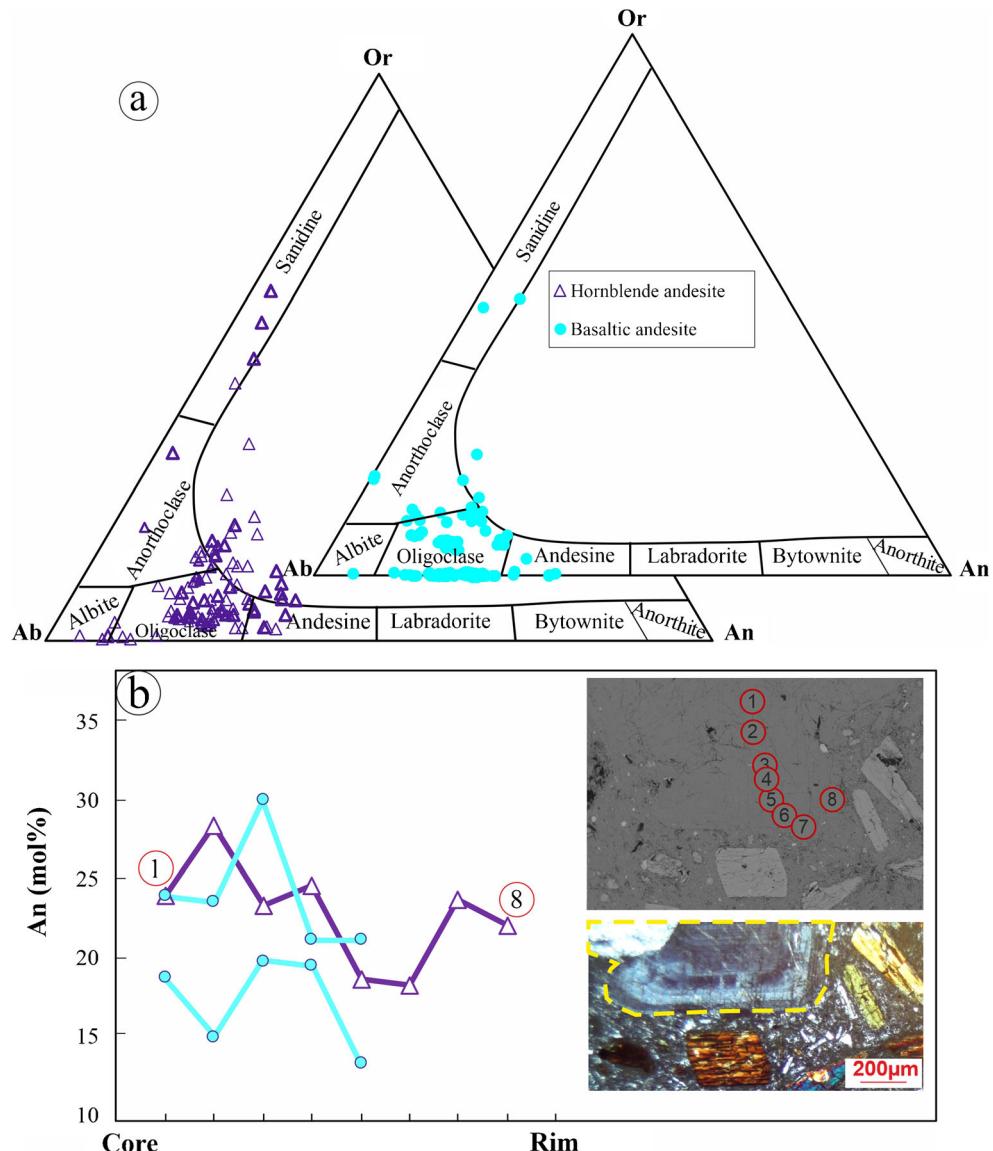
Moreover, amphibole-plagioclase geothermometry (Holland and Blundy 1994) and Al-in-hornblende

Table 1 Representative chemical compositions and calculated mineral formulae of the feldspars from the Andarian volcanic rocks. Oxides are in wt% and elements are in a.p.f.u., bd /below detection limit

Table 2 Chemical compositions and calculated mineral formulae of the feldspars from the Andarian volcanic rocks. Bold values are representative points of plagioclase zoning

Sample number	AN-46-7-3	AN-46-9-3	AN-46-23	AN-46-24-2	AN-48-12-2	AN-48-13-2	AN-48-24-6-1	AN-48-24-6-2	AN-48-24-6-3	AN-48-24-6-4	AN-48-24-6-5	AN-48-24-6-6	AN-49-13-2	AN-49-4-3	AN-49-4-2	AN-49-4-1	AN-49-20-3	AN-49-49-20-3	AN-49-49-20-3
SiO ₂	60.41	63.19	58.04	63.22	60.78	58.85	59.60	59.75	57.72	60.93	59.97	62.22	57.69	56.94	58.63	60.21	60.19	59.02	60.86
TiO ₂	bdl	bdl	0.10	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.06	bdl	bdl	bdl	bdl	bdl	
Al ₂ O ₃	24.23	22.05	28.54	22.29	23.79	25.21	24.47	24.16	25.94	22.79	23.71	22.44	24.67	25.29	23.92	24.92	23.01	23.52	23.09
FeO*	0.24	0.30	0.25	0.70	0.21	0.16	0.20	0.20	0.23	0.25	0.25	0.24	0.34	0.23	0.28	0.24	0.33	0.41	
MnO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.15	bdl	0.12	bdl	0.08	0.08	bdl	bdl	
MgO	bdl	bdl	bdl	bdl	0.90	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	
CaO	4.63	2.71	7.51	3.56	5.36	7.01	6.16	5.67	7.72	4.77	5.15	3.89	6.43	7.52	6.35	6.16	4.69	5.81	4.97
Na ₂ O	10.33	10.92	7.99	6.12	9.86	9.11	9.60	8.97	8.77	9.43	10.57	9.30	8.53	9.41	8.92	9.45	9.34	9.81	
K ₂ O	0.85	1.56	0.38	4.45	bdl	bdl	bdl	0.06	0.09	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	
Total	100.69	100.72	102.71	101.34	100.00	100.34	100.03	100.03	100.03	100.47	97.59	98.50	99.49	98.34	98.70	98.54	100.67	97.67	99.14
Normalization based on 8 O																			
Si	2.399	2.509	2.259	2.495	2.431	2.346	2.383	2.417	2.296	2.497	2.435	2.501	2.345	2.306	2.379	2.392	2.465	2.408	2.454
Ti	bdl	bdl	bdl	0.004	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.002	bdl	bdl	bdl	
Al	1.283	1.167	1.481	1.173	1.269	1.340	1.305	1.303	1.375	1.245	1.283	1.203	1.337	1.366	1.294	1.320	1.256	1.279	1.241
Fe _{total}	0.019	0.024	0.019	0.055	0.017	0.013	0.016	0.016	0.018	0.018	0.020	0.020	0.020	0.028	0.018	0.022	0.020	0.027	0.033
Mn	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.012	0.000	0.010	bdl	0.007	bdl	0.006	0.006	bdl	bdl
Mg	bdl	bdl	bdl	0.071	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.003	bdl	bdl	bdl	
Ca	0.368	0.215	0.584	0.281	0.429	0.559	0.492	0.459	0.614	0.391	0.418	0.313	0.523	0.609	0.515	0.489	0.384	0.474	0.401
Na	1.640	1.734	1.244	0.966	1.576	1.453	1.535	1.452	1.395	1.430	1.531	1.700	1.512	1.382	1.527	1.418	1.548	1.524	1.582
K	0.135	0.248	0.060	0.702	bdl	0.06	0.00	0.00	0.009	0.014	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	
Or	6.28	11.27	3.16	36.03	0.06	0.00	0.48	0.69	0.11	0.00	0.01	0.12	0.21	0.10	0.46	0.00	0.02	0.21	
Ab	76.55	78.94	65.89	49.56	78.56	72.22	75.71	75.62	68.94	78.44	78.55	84.46	74.21	69.27	74.71	74.01	80.12	76.26	79.61
An	17.17	9.79	30.95	14.42	21.37	27.78	24.29	23.90	30.36	21.45	25.67	15.53	25.19	30.52	25.19	25.53	19.88	23.72	20.18
Location	rim	rim	core	core	core	core	core	core	rim	core	core	core	rim	core	core	rim	core	rim	

Fig. 4 **a** Composition of feldspars of the Andrian volcanic rocks in the Ab-Or-An diagram (Deer et al. 1992). **b** Representative core to rim profiles of An (mol%) for the plagioclase phenocrysts with the photomicrograph and BSE image



geobarometry (Anderson and Smith 1995) give temperatures from 710 to 892 °C (mean = 816 °C) and pressures of 0.8–2.9 kbar (mean = 1.7 kbar) for the hornblende andesites. These equations yield temperatures of 707–899 °C (mean = 826 °C) and pressures of 0.5 to 2.8 kbar (mean = 1.6 kbar) for the basaltic andesite samples (Table 6). We also applied classic thermobarometry (e.g., Saki et al. 2021) using the Ti-in-hornblende thermometric (Otten 1984) and the Al [VI]-in-hornblende (Larocque and Canil 2010) barometric equations. Pressures calculated with the calibration of Larocque and Canil (2010) are from 0.5 to 3.4 kbar (mean = 1.5 kbar) and 0.4–3.5 kbar (mean = 1.7 kbar) for the hornblende andesites and basaltic andesites, respectively. The obtained temperatures range from 762 to 957 °C (mean = 879 °C) and 774–959 °C (mean = 872 °C) using calculation of Otten (1984) for

the hornblende andesites and basaltic andesites, respectively (Table 6).

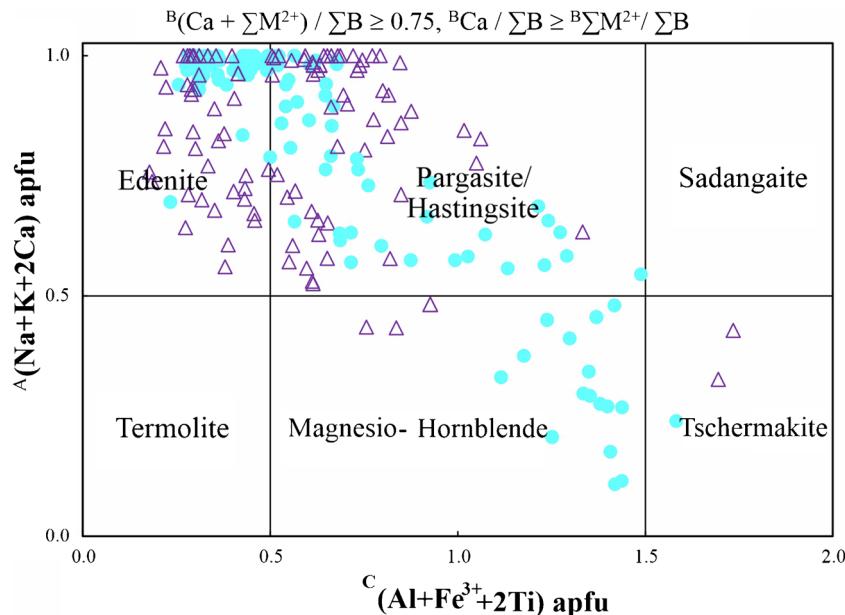
A qualitative estimate of clinopyroxene crystallization pressure can be obtained using the Al^{IV} vs. Al^{VI} diagram (Aoki and Shiba 1973). All the samples are clustered in the low- to medium-pressure field (Fig. 8b). The XPT vs. YPT diagram of Soesoo (1997) suggests quantitative temperature of 1175–1250 °C for clinopyroxene (Fig. 8c).

The occurrence of remarkably high amounts of amphibole in the studied andesites indicates that the Andrian volcanic rocks crystallized from a relatively water-rich magma. Ridolfi et al. (2010) provide a method for estimating the water contents on the basis of the amphibole composition. These estimates indicate water contents of magma up to 4.89 wt% for the hornblende andesite and up to 3.61 wt% for the basaltic

Table 3 Representative chemical compositions and calculated mineral formulae of the amphiboles from the Andonian volcanic rocks

Sample number	AN-50-11	AN-72-16	AN-72-11-1	AN-43-10-2	AN-40-10-3	AN-50-23	AN-50-24-2	AN-40-41-9	AN-41-10	AN-41-10-1	AN-43-16	AN-50-14	AN-50-14-2	AN-41-1-3	AN-72-3-2	AN-72-3-4	AN-41-7-4		
SiO ₂	41.81	47.74	48.94	41.37	42.40	42.16	48.88	47.87	40.90	44.09	41.24	40.48	41.12	43.20	43.18	46.97	47.84	41.94	
TiO ₂	3.77	1.40	1.11	3.03	2.83	2.91	1.27	1.51	3.13	2.33	2.91	3.63	3.33	3.14	2.17	1.34	1.31	1.62	2.95
Al ₂ O ₃	12.18	7.69	6.35	11.79	11.73	11.47	5.65	6.75	11.61	9.16	11.87	11.38	11.56	10.24	11.10	7.64	7.29	6.99	12.16
Cr ₂ O ₃	bdl	0.05	bdl	bdl	0.07	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.07	bdl	bdl	bdl	bdl	
FeO*	11.60	12.24	11.60	8.41	7.50	10.30	10.66	11.15	10.49	13.35	9.06	10.23	12.36	10.99	10.84	12.05	11.95	9.47	11.99
MnO	0.17	0.31	0.24	0.10	0.18	0.11	0.34	0.39	0.13	0.20	0.11	0.05	0.18	0.15	0.11	0.29	0.23	0.19	
MgO	13.08	14.53	16.18	16.32	16.64	15.60	16.26	16.00	15.14	14.18	15.73	14.80	13.22	14.81	15.20	15.56	15.36	15.68	14.86
CaO	11.07	11.69	11.73	11.85	11.55	12.01	11.77	11.64	11.50	11.80	11.63	12.73	12.32	11.84	11.70	11.63	12.55	11.68	
Na ₂ O	4.30	2.77	2.53	3.20	3.34	3.64	2.51	2.84	3.52	3.09	3.17	3.54	4.09	3.68	3.25	2.67	2.41	2.54	3.68
K ₂ O	0.65	0.47	0.45	1.57	1.24	0.93	0.43	0.54	0.82	0.75	1.35	0.82	0.83	0.64	0.78	0.59	0.49	0.47	0.95
F	0.54	0.49	0.49	0.38	0.45	0.68	0.31	0.76	0.31	0.37	0.13	0.97	0.32	0.18	0.26	bdl	0.11	0.38	bdl
Cl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	
Total	99.17	99.39	99.63	98.03	97.90	99.63	98.40	99.59	97.70	99.02	97.36	97.51	99.73	99.34	98.80	98.81	98.35	97.81	100.40
Normalization based on 23 O																			
Si	6.045	6.779	6.968	6.044	6.150	6.101	7.061	6.877	6.014	6.432	6.054	6.029	6.062	6.297	6.252	6.747	6.851	6.953	6.000
Ti	0.410	0.150	0.119	0.333	0.309	0.317	0.138	0.163	0.347	0.255	0.321	0.406	0.369	0.344	0.237	0.144	0.142	0.178	0.318
Al _{IV}	1.955	1.221	1.032	1.956	1.850	1.899	0.939	1.123	1.986	1.568	1.946	1.971	1.938	1.703	1.748	1.253	1.149	1.047	2.000
Al _{VI}	0.120	0.065	0.033	0.073	0.154	0.057	0.023	0.020	0.025	0.006	0.108	0.026	0.071	0.056	0.147	0.040	0.088	0.151	0.051
Cr	bdl	0.006	bdl	bdl	0.008	bdl	0.008	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.008	bdl	bdl	bdl	bdl
Fe ³⁺	0.000	0.443	0.397	0.307	0.314	0.344	0.131	0.261	0.439	0.441	0.327	0.242	0.000	0.000	0.390	0.470	0.421	0.000	0.533
Fe ²⁺	1.406	1.011	0.984	0.720	0.596	0.902	1.156	1.079	0.850	1.188	0.785	1.032	1.524	1.340	0.923	0.977	1.019	1.151	1.901
Mn	0.021	0.037	0.029	0.012	0.022	0.014	0.041	0.047	0.016	0.024	0.014	0.006	0.023	0.018	0.014	0.036	0.028	0.032	0.022
Mg	3.034	3.288	3.435	3.554	3.598	3.365	3.502	3.427	3.319	3.084	3.443	3.286	2.905	3.218	3.282	3.331	3.299	3.398	3.170
Ca	1.838	1.779	1.790	1.855	1.795	1.835	1.859	1.811	1.834	1.797	1.856	1.856	2.011	1.924	1.836	1.801	1.795	1.955	1.790
Na	1.228	0.763	0.699	0.907	0.938	1.021	0.704	0.791	1.004	0.873	0.903	1.021	1.169	1.040	0.914	0.743	0.673	0.716	1.022
K	0.120	0.086	0.082	0.293	0.229	0.172	0.080	0.100	0.153	0.140	0.252	0.157	0.156	0.118	0.143	0.108	0.090	0.087	0.173
F	0.245	0.218	0.222	0.176	0.205	0.312	0.140	0.345	0.145	0.172	0.059	0.455	0.151	0.083	0.120	bdl	0.050	0.176	bdl
Mg/(Mg+Fe)	0.683	0.765	0.777	0.831	0.858	0.789	0.752	0.761	0.796	0.722	0.814	0.761	0.656	0.706	0.781	0.773	0.764	0.747	0.779
T (°C)	995	838	814	1013	1001	991	809	839	1008	909	1012	1008	979	952	877	854	834	857	1002
P (MPa)	381	126	89	356	343	320	77	99	346	185	368	339	354	242	100	123	114	109	367
logfO ₂	-10.13	-12.01	-11.83	-8.88	-9.00	-9.47	-11.98	-11.55	-9.35	-10.93	-9.06	-9.56	-10.43	-10.38	-10.49	-11.26	-11.65	-11.44	-9.54
H ₂ O melt (wt.%)	3.42	4.05	2.85	1.29	2.27	4.89	2.48	2.42	2.94	2.88	2.19	2.74	3.22	2.95	2.65	3.05	3.59	3.88	3.05
Location	rim	core	rim	core	core	core	core	core	core	core	core	core	core	core	core	core	rim	rim	

Fig. 5 Amphibole classification diagram (Hawthorne et al. 2012) of the Andrian volcanic rocks. Symbols as in Fig. 4



andesite. These findings appear to support the hypothesis that primary melt was water-rich.

Oxygen fugacity and magma source

The amphibole composition can reflect the physico-chemical conditions of the magma (Ridolfi et al. 2010). Anderson and Smith (1995) proposed that the Fe# ($Fe/Fe + Mg$) of amphibole reflect the oxygen fugacity of the melt. Since $Fe/Fe + Mg$ ratios of the Andrian amphibole are less than 0.6, it is inferred that amphiboles crystallized at highly oxidizing conditions (Fig. 9a). Quantitative calculation of oxygen fugacity from the amphiboles was conducted using Ridolfi et al.'s (2010) equation. Log fO_2 values for the hornblende andesite and basaltic andesite range from -8.8 to -12 and -8.7 to -11.1 bars, respectively. The distribution of these samples in temperature vs. log fO_2 diagram indicates that all samples plot between NNO and NNO+2 buffers and follow their trend (Fig. 9b).

The clinopyroxene data of the Andrian volcanics are placed above the line of $Fe^{3+} = 0$ on the $Al^{VI}+2Ti+Cr$ vs. $Na + Al^{IV}$ diagram of Schweitzer et al. (1979), meaning that the pyroxenes have been formed at high oxygen fugacity (Fig. 9c). This result is also confirmed by the oxygen fugacity estimation using amphibole chemistry.

The plot of the amphibole data on the Al_2O_3 vs. TiO_2 magma source discriminator diagram (Changyi and Sanyuan 1984) suggests a mantle and crust-mantle as the likely source for the Andrian volcanic rocks (Fig. 10a). In addition, MgO vs. $FeO^*/(FeO^* + MgO)$ diagram for biotite (Zhou 1986) shows the mantle source for these samples (Fig. 10b).

Whole rock geochemistry

Table 7 illustrates the whole rock analysis data for major and trace elements of 8 volcanic rocks from the Andrian region. Although in the major element analyses of volcanic rocks the total volatile content has been reported as loss on ignition (LOI), the elimination of volatile content in order to monitor alteration effect is normal (Gill 2010). All data have been recalculated into the volatile free form before plotting on the related diagrams.

Based on petrographic studies and LOI content, the samples are classified to fresh ($LOI < 1\%$), relatively fresh ($LOI < 2\%$), or slightly altered ($2 < LOI < 5\%$). Analyzed samples are characterized by relatively moderate amounts of SiO_2 (60.88–70.75 wt%), limited range of Al_2O_3 (15.12–16.58 wt%), low TiO_2 (0.43–0.84 wt%), high Na_2O (4.50–5.20 wt%), and variable contents of Fe_2O_3 and MgO (2.13–5.06 wt% and 1.56–3.86 wt% respectively). The relatively low LOI content (mean~2.4) reflects a relatively low effect of alteration in these samples.

In the Zr/TiO_2 vs. SiO_2 diagram (Winchester and Floyd 1977), the Andrian volcanic rocks plot in the fields of andesite and rhyodacite-dacite, whereas in Ti vs. Zr plot (Hallberg 1984) all samples fall into the andesite field (Fig. 11a, b). The geochemical classification diagrams mostly match classifications obtained by using petrographic nomenclature, except for rhyodacite samples which classify as andesite in the Ti vs. Zr graph (Hallberg 1984).

As mentioned in the petrographic section, the rhyodacitic samples are more or less affected by hydrothermal alteration. Since REEs are not completely immobile (e.g., Zhiwei and Zhenhua 2003; Dongen et al. 2010; Hikov 2011), they may

Table 4 Representative chemical compositions and calculated mineral formulae of the clinopyroxenes from the Andonian volcanic rocks

Sample number	AN-42-5	AN-42-	AN-42-	AN-42-	AN-42-	AN-42-	AN-44-	AN-46-21-3												
SiO ₂	50.82	50.01	51.62	51.21	51.51	51.49	51.16	52.01	49.32	50.88	49.31	51.72	50.14	49.68	50.83	54.14	53.90	54.45	53.03	52.93
TiO ₂	0.85	1.12	0.29	0.19	0.54	0.37	0.61	0.41	1.11	0.27	0.83	0.52	0.64	0.81	0.58	0.61	0.58	0.24	0.54	0.69
Al ₂ O ₃	2.30	3.44	1.15	1.06	1.93	1.61	1.87	2.12	4.23	1.01	3.94	1.88	2.88	3.51	2.31	2.35	3.48	2.91	3.78	3.81
Cr ₂ O ₃	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.59	0.07	bdl	0.83	0.40	0.41	0.10	bdl	0.05	0.39	0.19	bdl
FeO*	6.81	6.13	9.28	8.84	5.54	8.35	5.95	4.46	6.20	8.35	4.56	5.17	4.94	5.58	6.48	6.07	5.38	4.00	5.88	6.06
MnO	0.16	0.07	0.22	0.32	0.11	0.19	0.08	bdl	bdl	0.08	bdl	bdl	bdl	bdl	bdl	0.41	0.15	bdl	0.09	bdl
MgO	16.15	15.25	14.80	14.25	17.09	15.81	16.99	17.63	15.24	14.78	15.85	17.77	15.86	16.06	17.19	16.02	16.43	17.16	15.00	15.54
CaO	22.48	23.49	21.91	22.09	22.20	21.96	22.63	22.26	23.23	21.76	23.14	22.03	23.30	22.65	21.37	17.87	18.20	17.21	18.72	17.72
Na ₂ O	0.57	0.78	0.92	1.08	0.48	0.69	0.43	0.70	0.52	1.02	0.68	0.43	0.66	0.66	0.52	0.76	0.69	1.09	0.82	0.78
K ₂ O	bdl	0.07	bdl	bdl	bdl	bdl	0.61	0.41	1.11	0.27	0.83	0.52	0.64	0.81	0.58	bdl	bdl	bdl	bdl	
Total	100.14	100.36	100.19	99.04	99.40	100.47	100.33	100.59	101.03	98.42	99.97	100.44	99.46	100.17	99.96	98.23	98.86	97.45	98.05	97.53
Normalization based on 6 O																				
Si	1.861	1.825	1.905	1.911	1.889	1.887	1.859	1.787	1.904	1.795	1.871	1.837	1.808	1.872	2.020	1.990	2.020	1.982	1.981	
Ti	0.023	0.031	0.008	0.005	0.015	0.010	0.017	0.011	0.030	0.008	0.023	0.014	0.020	0.022	0.016	0.024	0.021	0.010	0.023	
Al _{IV}	0.141	0.142	0.100	0.090	0.110	0.120	0.141	0.139	0.212	0.100	0.193	0.126	0.160	0.187	0.130	0.098	0.031	0.000	0.042	
Al _{VI}	0.004	0.006	0.050	0.040	0.030	0.050	0.062	0.061	0.030	0.051	0.040	0.053	0.151	0.040	0.040	0.002	0.119	0.127	0.129	
Cr	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.017	0.002	bdl	0.024	0.011	0.008	0.012	0.010	bdl	0.001	0.011	bdl
Fe total	0.208	0.187	0.286	0.276	0.170	0.256	0.181	0.134	0.188	0.261	0.139	0.156	0.165	0.170	0.161	0.190	0.171	0.123	0.184	
Mn	0.005	0.002	0.007	0.010	0.004	0.006	0.002	bdl	0.003	bdl	bdl	bdl	bdl	bdl	bdl	0.010	0.005	0.003	0.001	bdl
Mg	0.881	0.830	0.814	0.793	0.934	0.863	0.921	0.947	0.823	0.824	0.860	0.959	0.848	0.870	0.951	0.890	0.922	0.950	0.841	0.873
Ca	0.882	0.918	0.866	0.883	0.872	0.862	0.881	0.859	0.902	0.873	0.903	0.854	0.876	0.883	0.834	0.710	0.719	0.682	0.750	0.710
Na	0.041	0.055	0.066	0.078	0.034	0.049	0.030	0.049	0.036	0.074	0.048	0.030	0.049	0.047	0.036	0.048	0.053	0.081	0.062	
K	bdl	0.003	bdl	bdl	bdl	bdl	bdl	0.028	0.019	0.051	0.013	0.039	0.024	0.035	0.038	0.027	bdl	bdl	bdl	
Wo	49.11	52.53	48.90	50.53	47.66	48.15	48.90	47.58	52.28	50.30	51.20	47.11	51.37	50.35	47.25	39.80	40.22	38.93	42.37	40.20
En	49.08	47.47	45.97	45.37	51.04	48.22	51.10	52.42	47.72	47.52	48.80	52.89	48.63	49.65	52.75	49.64	50.51	54.01	47.24	49.07
Fs	1.81	0.00	5.13	4.10	3.63	0.00	0.00	0.00	2.18	0.00	0.00	0.00	0.00	0.00	0.00	10.56	9.28	7.06	10.38	10.73
Location	core	core	core	core	rim	core	rim	core	core	core	core	core	rim							

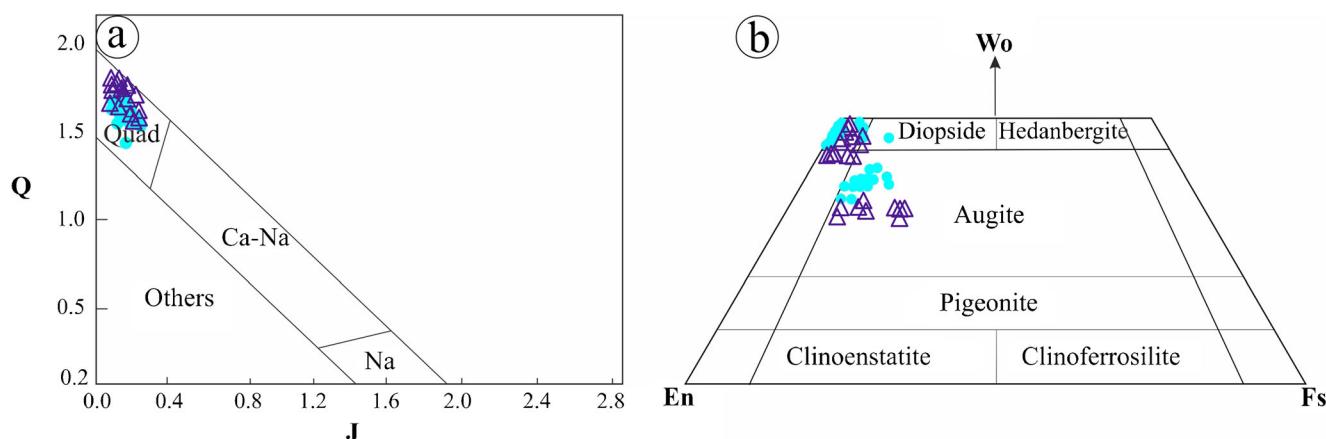


Fig. 6 **a** Classification of clinopyroxene from the Andrian volcanic rocks in Q–J diagram ($J = 2\text{Na}$, $Q = \text{Ca} + \text{Mg} + \text{Fe}^{2+}$) (Morimoto 1988). **b** Clinopyroxenes classification in wollastonite (Wo)-ferrosilite (Fs)-enstatite (En) diagram (Morimoto 1988). Symbols as in Fig. 4

Table 5 Chemical compositions and calculated mineral formulae of the biotites from the Andrian volcanic rocks (*H.A* hornblende andesite, *B.A* basaltic andesite)

Sample number	An-41-10-1	AN-41-11-2	AN-41-12	AN-41-13	AN-41-14	AN-41-15	AN-41-16	AN-43-17	AN-43-18	An-44-28	An-44-28-2	An-44-28-3	An-49-12	An-49-12-2
	H.A	H.A	H.A	H.A	H.A	H.A	H.A	H.A	H.A	B.A	B.A	B.A	B.A	B.A
SiO ₂	33.65	35.67	32.29	34.45	34.54	35.59	35.42	36.01	35.17	37.40	37.72	37.71	36.12	36.93
TiO ₂	3.27	2.70	0.49	0.68	0.63	0.74	1.22	1.28	1.17	4.50	4.77	4.87	4.55	4.31
Al ₂ O ₃	14.32	14.96	17.77	16.69	17.90	16.93	16.30	16.14	16.57	13.42	13.53	13.27	12.97	13.44
Cr ₂ O ₃	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.05	bdl	bdl	0.05	bdl
FeO*	12.31	11.96	11.78	11.90	11.29	11.72	11.55	11.09	11.69	8.92	7.92	8.52	11.86	9.84
MnO	0.10	0.13	0.15	0.11	0.15	0.16	0.10	0.15	0.15	2.71	2.20	2.23	0.67	1.85
MgO	16.51	17.58	16.71	18.61	17.34	18.01	17.80	17.78	17.86	20.21	20.95	20.17	17.29	17.97
CaO	4.27	0.53	0.72	0.78	0.21	0.52	0.60	0.43	0.49	bdl	bdl	bdl	0.71	0.15
Na ₂ O	0.48	0.48	0.40	0.29	0.75	0.45	0.56	0.49	0.36	1.34	1.09	1.06	0.89	0.69
K ₂ O	7.27	7.45	7.16	6.82	8.75	7.66	7.84	8.05	6.45	4.50	4.77	4.87	4.55	4.31
F	0.70	0.87	0.17	0.58	0.56	1.49	0.57	0.53	0.46	2.71	2.20	2.23	0.67	1.85
Cl	0.10	0.09	0.11	0.05	0.06	0.06	0.09	0.10	0.11	0.80	0.68	0.63	0.43	0.55
Total	92.98	92.42	87.75	90.96	92.18	93.33	92.05	92.05	90.48	96.56	95.83	95.56	90.76	91.89
Normalization based on 24 O														
Si	5.204	5.450	5.172	5.312	5.291	5.403	5.411	5.483	5.414	5.507	5.516	5.550	5.562	5.632
Ti	0.381	0.310	0.059	0.079	0.072	0.085	0.140	0.146	0.135	0.499	0.525	0.539	0.526	0.494
Al _{IV}	2.611	2.550	2.828	2.688	2.709	2.597	2.589	2.517	2.586	2.328	2.333	2.302	2.355	2.368
Al _{VI}	0.000	0.144	0.527	0.346	0.523	0.433	0.347	0.381	0.421	0.000	0.000	0.000	0.000	0.047
Cr	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.006	bdl	bdl	0.006	bdl
Fe _{total}	1.593	1.529	1.578	1.534	1.446	1.488	1.476	1.412	1.505	1.099	0.968	1.048	1.528	1.254
Mn	0.013	0.016	0.020	0.014	0.019	0.020	0.013	0.019	0.019	0.338	0.273	0.278	0.087	0.239
Mg	3.807	4.004	3.991	4.276	3.959	4.076	4.055	4.037	4.099	4.435	4.566	4.425	3.969	4.085
Ca	0.707	0.087	0.124	0.129	0.035	0.085	0.098	0.071	0.080	bdl	bdl	bdl	0.117	0.025
Na	0.143	0.143	0.124	0.087	0.223	0.132	0.165	0.144	0.107	0.383	0.310	0.303	0.267	0.205
K	1.435	1.452	1.462	1.342	1.709	1.483	1.528	1.563	1.266	0.845	0.890	0.915	0.893	0.838
F	0.341	0.421	0.088	0.283	0.273	0.717	0.275	0.257	0.224	1.263	1.017	1.039	0.325	0.891
Cl	0.026	0.023	0.029	0.013	0.017	0.016	0.023	0.026	0.028	0.200	0.169	0.158	0.113	0.143
Fe/Fe+Mg	0.295	0.276	0.283	0.264	0.268	0.267	0.267	0.259	0.269	0.199	0.175	0.191	0.278	0.235
Location	core	core	core	core	core	core	core	core	core	core	core	rim	core	rim

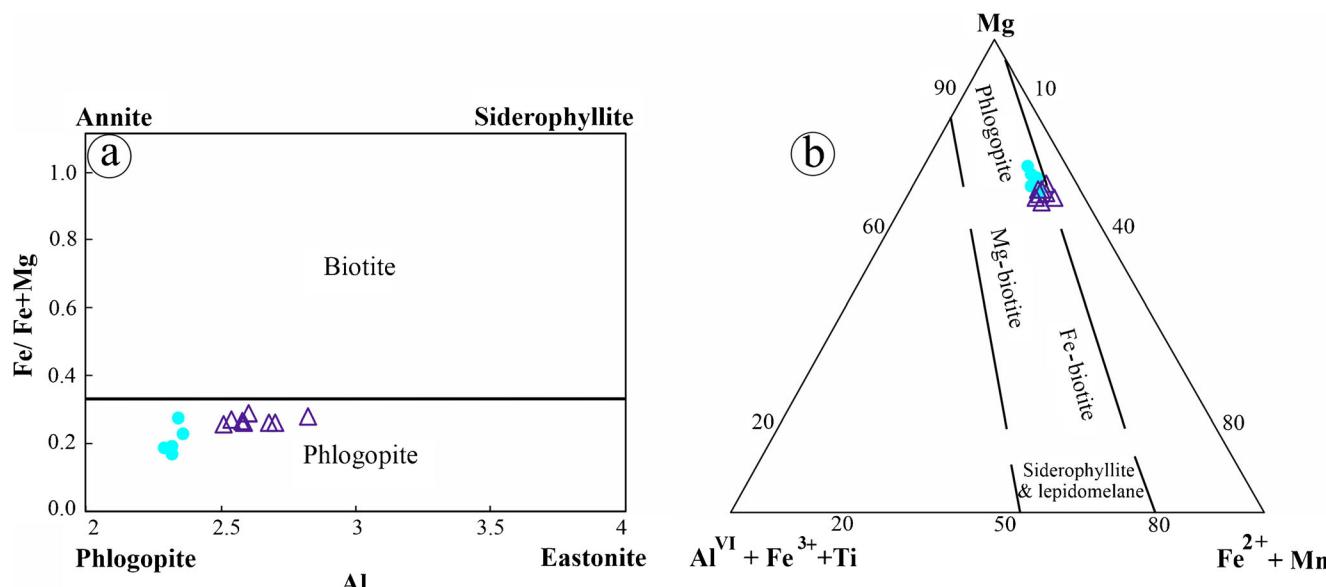


Fig. 7 Mineral chemistry of biotite in the Andarian volcanic rocks. **a** Al vs. $\text{Fe}/(\text{Fe}+\text{Mg})$ diagram showing the composition of biotite (Foster 1960). **b** Ternary diagram for biotite classification (Foster 1960). Symbols as in Fig. 4

move during hydrothermal alteration, making REE-related interpretation difficult. Therefore, we used only fresh samples for interpretation of chondrite-normalized REE and primitive mantle-normalized multi-element diagrams. For this reason, the rhyodacitic samples were not included. Chondrite-normalized REE patterns (McDonough and Sun 1995) of the Andarian volcanic rocks show general similar distribution patterns (Fig. 12a). In primitive mantle-normalized diagram (McDonough and Sun 1995), all of the Andarian volcanic samples display the enrichment in large ion lithophile elements (LILEs; e.g., Cs, Rb, Ba, and Sr), and depletion in high field strength elements (HFSE, e.g., Nb, Ta, and Ti) (Fig. 12b).

Discussion

Tectonic setting and magmatic series of the volcanic rocks

There is evidence that the formation of ore deposits in the AAMZ is related to a back-arc (e.g., Richards and Sholeh 2016) or a continental-arc setting (Calagari 2004; Hassanpour 2010; Alirezai et al. 2015). However, a post-collisional setting is reported for plutonic and volcanic rocks in the AAMZ by previous studies (e.g., Dilek et al. 2010; Jamali et al. 2010; Maghsoudi et al. 2014; Moritz et al. 2016).

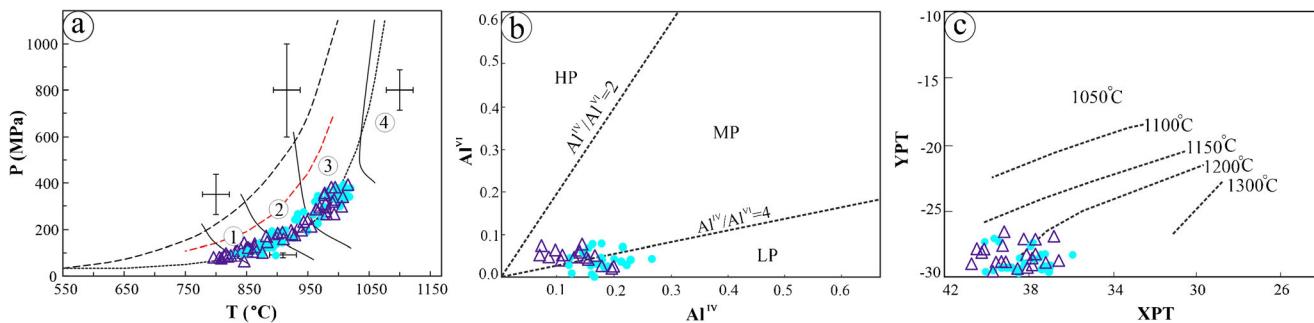


Fig. 8 **a** Distribution of the amphibole samples in T-P diagram (Ridolfi et al. 2010); (1) (Mg-Hbl + Pl ± Opx ± Mgn ± Ilm ± Bt), (2) (Tsc-Prg + Pl ± Cpx ± Opx ± Mgn ± Ilm), (3) (Tsc-Prg ± Pl ± Ol ± Cpx ± Opx ± Mgn ± Ilm), and (4) (Cpx ± Mgn ± Ol ± Pl). **b** Al^{IV} vs. Al^{VI} diagram of clinopyroxene samples (Aoki and Shiba 1973). **c** XPT vs. YPT diagram

(Soesoo 1997) of clinopyroxene samples for the estimation of temperature. ($\text{XPT} = 0.446 \text{ SiO}_2 + 0.187 \text{ TiO}_2 - 0.404 \text{ Al}_2\text{O}_3 + 0.346 \text{ FeO} - 0.052 \text{ MnO} + 0.309 \text{ MgO} + 0.431 \text{ CaO} - 0.466 \text{ Na}_2\text{O}$ and $\text{YPT} = -0.369 \text{ SiO}_2 + 0.535 \text{ TiO}_2 - 0.317 \text{ Al}_2\text{O}_3 + 0.323 \text{ FeO} + 0.235 \text{ MnO} - 0.516 \text{ MgO} - 0.167 \text{ CaO} - 0.153 \text{ Na}_2\text{O}$). Symbols as in Fig. 4

Table 6 Representative thermobarometry results of the Andarian volcanic rocks. (a) Amphibole-plagioclase thermometry (Holland and Blundy 1994), (b) Al-in-hornblende barometry (Anderson and Smith 1995), (c) Ti-in-hornblende thermometry (Ottens 1984), (d) Al [VI]-in-hornblende barometry (Laroque and Canil 2010)

Sample number	Hornblende andesite						Hornblende andesite					
	AN-40-1-2	AN-40-1-2	AN-40-8	AN-40-8	AN-40-10	AN-40-10	AN-43-10-1	AN-43-11	AN-50-22-3	AN-50-22-3	AN-72-21-1	AN-72-23-2
(^a T °C)	844	850	837	811	846	860	855	892	865	780	809	744
(^b P (kb))	1.02	0.82	1.66	2.21	1.35	2.11	2.06	1.04	1.98	1.01	1.59	2.08
Sample number	AN-42-2-1	AN-42-11-1	AN-44-1-3	AN-44-3-1	AN-40-8	AN-44-10-1	AN-44-22-1	AN-46-1-1	AN-48-7-1	AN-48-7-1	AN-48-18-2	AN-48-25-2
(^c T °C)	843	764	884	892	837	880	864	739	799	774	827	784
(^d P (kb))	2.47	2.73	0.80	1.02	1.66	1.00	1.16	2.84	2.30	1.66	0.93	1.63
Sample number	An-40-10	AN-41-2	AN-41-6	AN-41-3	AN-41-2-2	AN-41-3	AN-43-11	AN-50	AN-50-13	AN-50-22-2	AN-50-22-3	AN-50-23-2
(^e T °C)	897	830	924	906	854	921	943	911	906	837	816	799
(^f P (kb))	1.11	2.48	1.83	0.90	1.09	3.43	1.17	2.19	1.51	1.03	1.67	1.26
Sample number	AN-42-2-2	AN-42	AN-42-7	AN-44-1	AN-44-1-2	AN-4	AN-46	AN-46-13-3	AN-42-11	AN-42-19	AN-46-14-2	AN-48
(^g T °C)	-6	948	954	942	860	927	810	781	792	943	924	881
(^h P (kb))	0.98	2.41	1.43	0.65	0.43	1.93	2.72	1.47	2.27	2.94	3.51	1.06

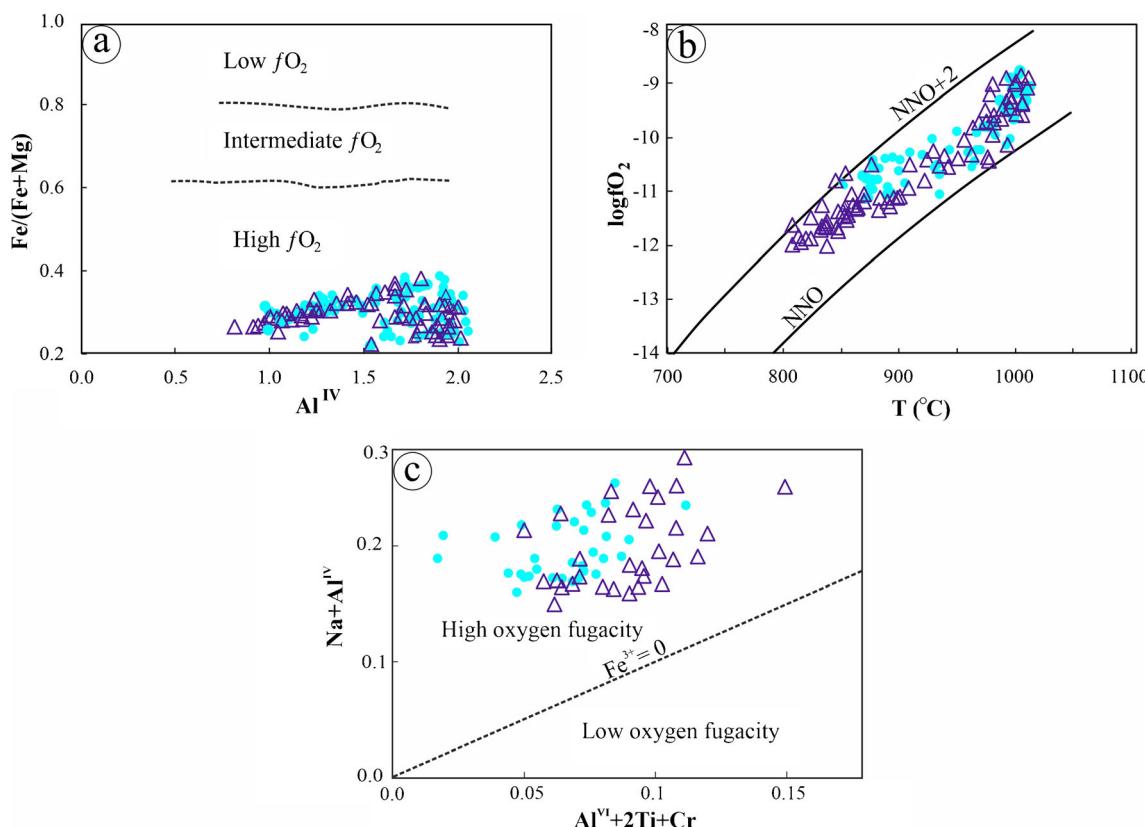


Fig. 9 Oxygen fugacity estimation of the Andorian volcanic rocks. **a** Binary Al^{IV} vs. $(\text{Fe}/\text{Fe} + \text{Mg})$ plot for amphibole (Anderson and Smith 1995). **b** $T (\text{°C})$ vs. $\log f\text{O}_2$ diagram for amphibole (Ridolfi et al. 2010). **c**

$\text{Na}+\text{Al}^{\text{IV}}$ vs. $\text{Al}^{\text{VI}}+2\text{Ti}+\text{Cr}$ diagram for Clinopyroxene (Schweitzer et al. 1979). Symbols as in Fig. 4

In order to discrimination different tectonic settings, various diagrams are used based on the whole rock chemistry of the volcanic rocks. In the $\text{TiO}_2/100-\text{La}-\text{Ce}/\text{P}_2\text{O}_5$ ternary diagram, the Andorian volcanic samples plot in the overlapping continental and post-collisional arc fields (Fig. 13a). Moreover, two other diagrams, including Zr–Y and $\text{Al}_2\text{O}_3-\text{TiO}_2$ diagrams (Fig. 13b, c), confirm an arc-related setting for the studied samples. Additionally, the $\text{Zr}^{\text{3+}}-\text{Nb}^{\text{5+}}-\text{Ce}/\text{P}_2\text{O}_5$ plot (Müller and Groves 1997) which allows to distinguish continental and post-collisional arcs, suggests the post-collisional arc setting (Fig. 13d). More evidences for such

setting are connected to the trace element and REE patterns of the Andorian volcanic rocks (e.g., the LILE enrichments and Nb, Ta, and Ti depletions). In fact, these results are consistent with the patterns of magmas generated in other post-collisional settings specifically with the Miocene–Quaternary volcanic sequences in the Lesser Caucasus (Dilek et al. 2010). The evaluation of post-collisional setting for the studied volcanic rocks is also compatible with a possible timing of continental collision events in the region. The age of initial collision between the Arabia-Eurasian plates is possibly related to Eocene (Allen and Armstrong 2008; Kheirkhah et al. 2009;

Fig. 10 Discrimination diagrams to distinguish magma source for the Andorian volcanic rocks. **a** Al_2O_3 vs. TiO_2 diagram for amphibole (Changyi and Sanyuan 1984). **b** MgO vs. $\text{FeO}^*/(\text{FeO}^* + \text{MgO})$ diagram for biotite (Zhou 1986). Symbols as in Fig. 4

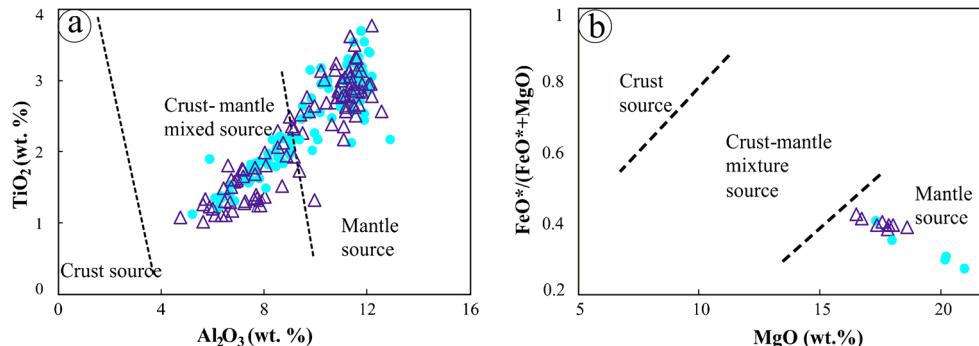


Table 7 Major oxides (wt%), trace elements, and rare earth elements (ppm) analysis of the Andarian volcanic rocks (*A* andesite, *R* rhyodacite)

Sample number	AN-38	AN-39	AN-43	AN-48	AN-49	MAN-55	AN-101	AN-U-93
	A	A	A	A	A	A	R	R
SiO ₂	63.81	62.76	60.88	62.96	62.59	65.05	70.75	65.55
TiO ₂	0.73	0.80	0.84	0.75	0.77	0.66	0.43	0.61
Al ₂ O ₃	16.58	15.12	15.43	15.64	15.55	16.17	15.71	15.73
Fe ₂ O ₃ *	3.50	4.81	5.06	4.66	4.82	4.43	2.13	3.91
MnO	0.10	0.06	0.08	0.07	0.08	0.03	0.01	0.07
MgO	1.67	3.60	3.86	3.58	3.59	2.92	1.56	1.75
CaO	6.86	5.01	5.76	4.77	4.95	3.24	1.19	3.26
Na ₂ O	4.67	5.00	5.17	4.91	4.92	5.20	5.19	4.50
K ₂ O	1.77	2.41	2.45	2.19	2.27	1.87	2.88	4.35
P ₂ O ₅	0.29	0.44	0.48	0.40	0.40	0.34	0.12	0.28
Total	99.97	100.02	100.01	99.94	99.94	99.90	99.99	100.01
Ba	667	896	953	794	816	645	546	569
Rb	24.06	34.49	47.41	43.40	45.91	52	75	133
Sr	671	938	1022	836	819	639	338	570
Zr	125	174	174	150	157	135	88.25	199
Nb	10.05	23.10	23.96	18.73	18.96	16.02	7.62	40
Cd	1.97	bdl	4.61	1.14	bdl	1.35	15.97	bdl
Cs	0.405	0.907	2.203	0.955	1.251	1.983	5.1	2.239
La	26.53	39.57	41.37	34.97	35.67	26.14	12.38	59.31
Ce	43.05	66.63	70.26	58.85	60.18	46.62	21.10	94.54
Pr	5.23	7.41	7.95	6.53	6.85	5.19	2.890	9.96
Nd	20.07	27.75	29.10	24.55	25.53	18.48	9.32	33.04
Sm	3.39	4.27	4.22	3.85	4.16	3.42	2.06	5.43
Eu	1.00	1.34	1.36	1.19	1.19	0.906	1.01	1.11
Gd	3.29	3.36	3.36	2.93	3.48	2.24	1.86	4.33
Tb	0.418	0.369	0.411	0.326	0.330	0.291	0.475	0.522
Dy	1.99	2.07	2.05	1.97	1.69	1.77	1.28	3.06
Ho	0.373	0.372	0.386	0.335	0.350	0.303	0.420	0.528
Er	1.47	0.979	0.906	0.942	1.05	0.911	0.664	1.643
Tm	0.185	0.113	0.160	0.104	0.148	0.136	0.368	0.240
Yb	0.944	0.805	0.979	0.855	0.836	0.778	0.894	1.563
Lu	0.233	0.147	0.197	0.146	0.142	0.127	0.192	0.187
Y	12.20	10.37	11.07	9.42	10.07	8.43	5.36	15.15
Hf	2.93	3.76	3.92	3.22	3.74	2.70	2.65	6.01
Ta	0.514	1.16	1.27	0.95	1.00	1.50	0.715	2.90
Pb	6.02	9.9	10.7	8.30	10.6	4.48	21.9	12.0
Th	6.06	11.99	11.74	9.33	10.04	7.03	4.75	46
U	1.45	2.65	2.66	2.22	2.35	1.89	1.65	5.09
Sc	20.69	18.40	18.55	17.90	17.80	18.47	16.90	19.20
V	97.87	94.75	96.38	96.96	99.54	93.70	57.10	77.10
Cr	70.41	110	110	97	110	77.15	37.63	30.81
Co	10.9	14.6	15.8	13.9	13.7	192	5.79	8.63
Ni	42.53	53	69	55	76	61	21.66	26.69
Zn	36.89	54	58	53	61	29.33	42	36.42

Dilek et al. 2010; Jamali et al. 2010; Sokol et al. 2018; Rabiee et al. 2020). However, the time of collision is still controversial.

Several discrimination diagrams have been used for tracing the magma affinity in the Andarian area. Zr/Y vs. Th-Yb graph (Ross and Bédard 2009) shows that all the volcanic rock

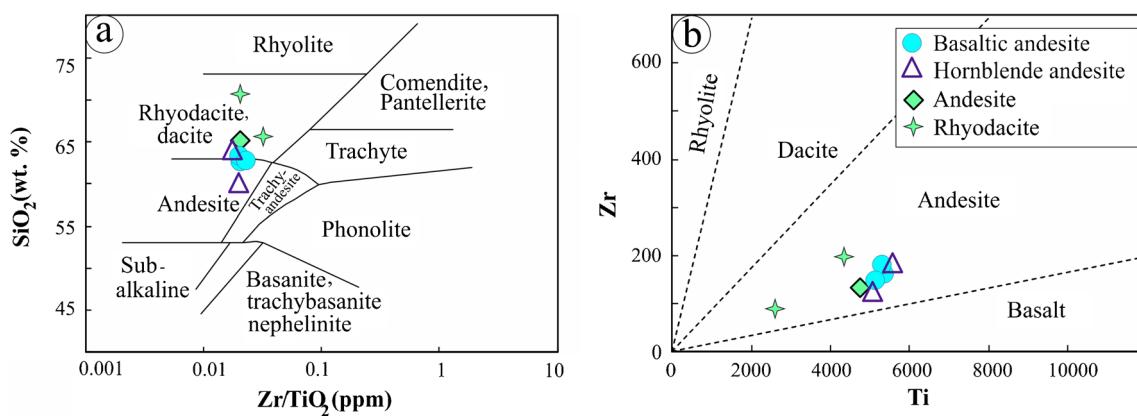


Fig. 11 Geochemical classification of the Andorian volcanic rocks. **a** Zr/TiO_2 vs. SiO_2 (Winchester and Floyd 1977). **b** Ti–Zr diagram (Hallberg 1984)

samples belong to the calc-alkaline domain (Fig. 14a). The AFM diagram of Fig. 14b (Irvine and Baragar 1971), which discriminate tholeiitic and calc-alkaline series, indicates a calc-alkaline affinity for the analyzed samples. The Zr vs. Y (Fig. 14c) binary diagram (Barrett and MacLean 1999) confirms the calc-alkaline nature of the studied samples. Furthermore, the calc-alkaline nature correlates with the mineral chemistry results such as biotite, amphibole, and clinopyroxene.

The chemical composition of biotite/phlogopite reflects the chemical composition of the rocks, providing that the mica is a primary magmatic mineral. Only in this case biotite/phlogopite provides reliable information. The Al^{VI} contents range from 0.0 to 0.52 apfu indicating a magmatic origin for the analyzed biotites/phlogopites (e.g., Nachit et al. 2005; Tavakoli et al. 2019, Table 5). Accordingly, the oxides of Al, Mg, and Fe content of the biotites from the Andorian volcanic rocks indicate calc-alkaline nature (Fig. 14d). Moreover, this result has been confirmed by the chemistry of clinopyroxenes and amphiboles. Clinopyroxenes of both rock types, with a wide range in Al_2O_3 content (0.60–5.99%), fall into the calc-alkaline field (after Le Bas 1962; Fig. 14e). According to Molina et al.'s (2009), amphiboles from sub-alkaline melts have typically lower Al_2O_3 and

TiO_2 content. As can be observed in Fig. 14 f, most of the studied points plot in the sub-alkaline domain. These findings have also been certified by the range of oxygen fugacity in the samples. Since ΔNNO values of the amphiboles in the studied volcanic rocks ($0.10 < \Delta\text{NNO} < 2.16$) correlate to normal calc-alkaline values ($-1 < \Delta\text{NNO} < +2.7$), it confirms that the samples were derived from calc-alkaline (arc-related) magma (Carmichael 1991; Behrens and Gaillard 2006; Ridolfi et al. 2010).

P–T conditions

The composition of magmatic plagioclase depends on different physical parameters such as temperature, total pressure, and the water content of the melt (e.g., Ustunisik et al. 2014; Bennett et al. 2019; Yang et al. 2019; Cao et al. 2019; Jamshidibadr et al. 2020). Zoning structures in plagioclases provide an opportunity to identify the dynamics and changes of the magma during its evolution. On the other hand, different zoning patterns in plagioclase phenocrysts can record the chemical relationships between melt composition and crystal growth.

As mentioned in the previous section, the studied phenocrysts show micro-scale oscillatory zoning with rather coarse

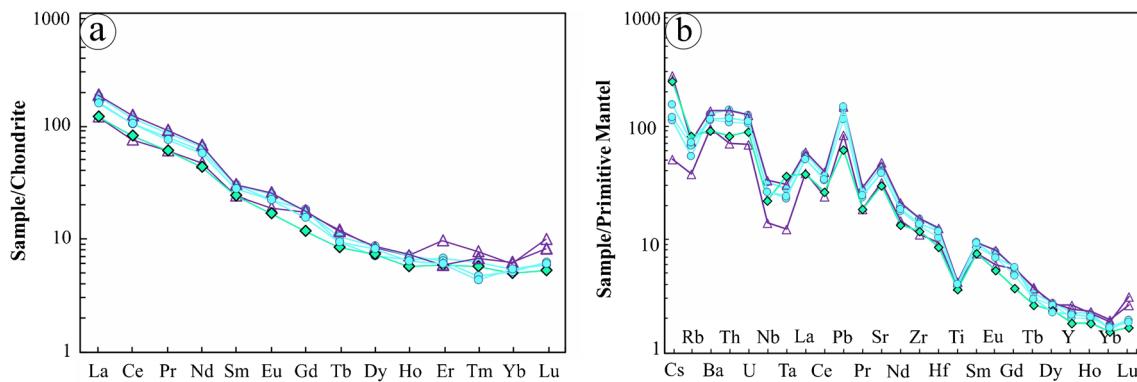


Fig. 12 **a** Chondrite-normalized rare earth element (REE) pattern of the Andorian volcanic rocks (McDonough and Sun 1995). **b** Primitive mantle-normalized multi-element diagrams (McDonough and Sun 1995)

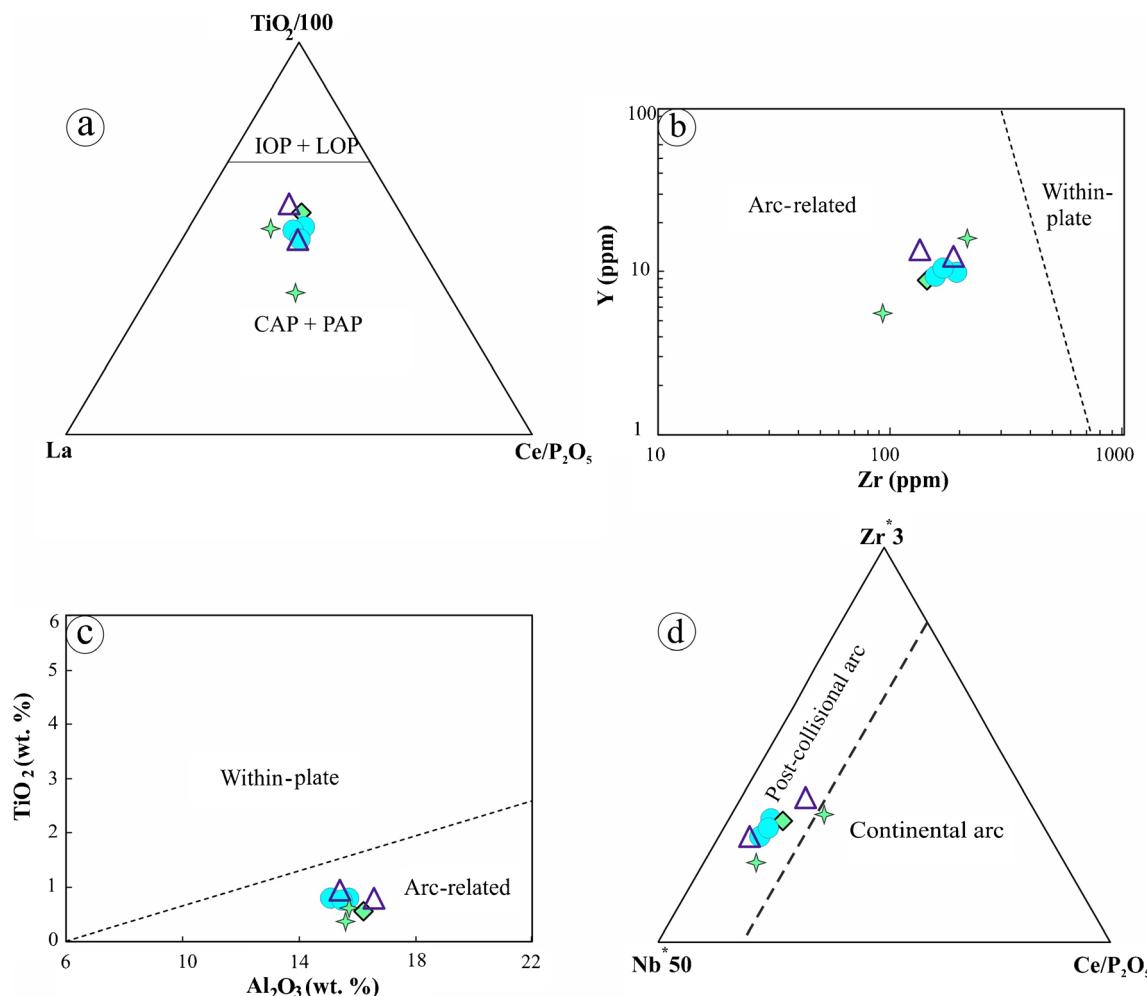


Fig. 13 Tectonic discrimination diagrams for the Andorian volcanic rocks. **a** $\text{TiO}_2/100$, La, and $\text{Ce}/\text{P}_2\text{O}_5$ diagram (Müller and Groves 1997). **b**, **c** Zr vs. Y diagram and Al_2O_3 – TiO_2 graph (Müller and Groves 1997). **d** Zr^*3 – Nb^*50 – $\text{Ce}/\text{P}_2\text{O}_5$ plot (Müller and Groves 1997).

CAP: continental arcs; PAP: post-collisional arc; IOP: initial oceanic rocks; LOP: late oceanic arcs; WIP: within-plate settings. Symbols as in Fig. 11

oscillations ($>10 \mu\text{m}$) and the ΔAn amplitude of 4 mol% (0.5 to 6.8 mol%) in both the core and rim. Supposing the same crystallization sequence for amphibole and plagioclase, estimation of the plagioclase formation state will be possible by using amphibole thermobarometry (Cao et al. 2019). Plagioclase in a large magma chamber can produce fluctuations of An contents at a rate of $\sim 3\%$ An per kbar (Ustunisik et al. 2014). Therefore, the wide range of ΔAn (0.5 to 6.8 mol%) in the oscillatory zoning of plagioclase suggests relatively unstable pressure conditions in the magma chamber during plagioclase crystallization. These results are consistent with the wide variations in the pressure values recorded by the amphibole geobarometer (0.5–2.9 kbar). Development of oscillatory zoning with coarse oscillations in plagioclase is interpreted either as magma mixing (e.g., Streck 2008; Neave et al. 2013; Velasco Tapia et al. 2013; Lai et al. 2016) or changes in the physicochemical parameters in a magma chamber (Yang et al. 2019). The wide range of variations

in the physicochemical parameters ($P = 0.5\text{--}2.9 \text{ kbar}$, $T = 707\text{--}899^\circ\text{C}$, water-rich, $f\text{O}_2 = 0.10 < \Delta\text{NNO} < 2.16$) is confirmed by amphibole chemistry. Considering the same crystallization conditions for amphibole and plagioclase, oscillatory zoning in plagioclase was probably controlled by changes in the physicochemical conditions rather than magma mixing.

Additional support for variable physicochemical conditions (i.e., P , T , $f\text{O}_2$, and water activity) comes from the compositional diversity in the studied amphiboles that varies from edenite to tschermakite (Scaillet and Evans 1999; Grove et al. 2003; Rooney et al. 2011; Lisboa et al. 2020). The thermobarometric data reveal that the calculated values for the Andorian volcanic rocks are more variable than the expected values. The wide range of pressure (0.5–2.9 kbar for the amphiboles) demonstrates that the magma probably crystallized at a large depth range.

Furthermore, pressure conditions of a number of phenocrysts have been evaluated from crystal core to the rim

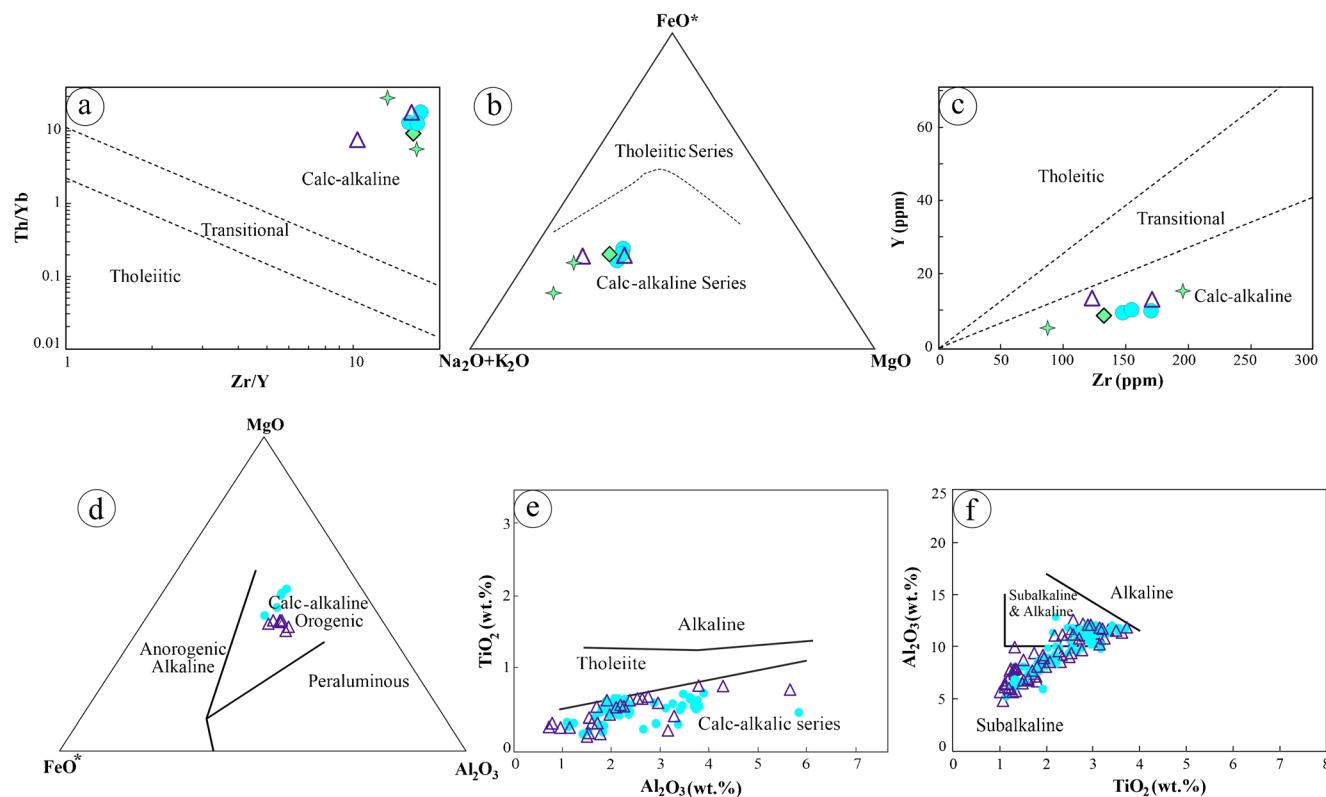


Fig. 14 The magmatic affinity of discriminant diagrams for the Andorian volcanic rocks. **a** Zr/Y vs. Th-Yb diagram (Ross and Bédard 2009). **b** AFM ($A=Na_2O+K_2O$, $F=FeO^*$, and $M=MgO$) diagram (Irvine and Baragar 1971). **c** Zr vs. Y diagram (Barrett and MacLean 1999). **d**

Discrimination diagram to distinguish magma series for the Andorian volcanic rocks for biotite (Abdel-Rahman 1994). **e** Al_2O_3 vs. TiO_2 diagram for clinopyroxene (after Le Bas 1962). **f** Amphiboles in the TiO_2 vs. Al_2O_3 diagram (Molina et al. 2009). Symbols as in Fig. 11

(Table 3). The results show an irregular variation in the patterns of temperature but a decrease in the pressure from core to rim. An increasing SiO_2 , chemical compositional changes, and decreasing calculated temperature and pressure in the amphiboles from core to rim are attributed to a normal zoning (Walker et al. 2013; Erdmann et al. 2014). In spite of the changes in the crystallization pressures and temperatures, the chemical composition of most amphibole phenocrysts with the exception of a few phenocrysts (these phenocrysts have edenite cores with rims approaching hastingsite) remains unchanged from core to rim. Therefore, the rim-ward decreasing pressure cannot be explained by the likely presence of compositional zoning. Therefore, this suggests that the changes in crystallization pressure and temperature in the Andorian volcanic rocks are probably due to the role of relatively unstable pressure and temperature in the magma chamber recorded by the composition of plagioclase, amphibole, and clinopyroxene.

Magma nature

Chondrite-normalized REE patterns (McDonough and Sun 1995) of the Andorian volcanic rocks (Fig. 12a) are characterized by steep, LREE-enriched patterns ($La_N/Yb_N \sim 19-33$;

Rollinson 1993; Bea 2015) with no significant Eu anomalies ($Eu/Eu^*=0.91-1.10$; Taylor and McLennan 1985), implying the possible presence of residual garnet in the magma source (Gill 2010). In contrast, the concaved-shaped HREE pattern, as well as higher values of Lu_N (5.14–9.47) and Er_N (5.66–9.21) than Yb_N (4.84–6.07) and Tm_N (4.22–7.47) values in the studied samples, probably reflects amphibole crystallization (Davidson et al. 2007; Bea 2015). Moreover, the Sm/Yb ratio is an indicator for constraining the mantle source mineralogy (Shaw 1970; Aldanmaz et al. 2000; Li and Chen 2014). Sm/Yb ratios between 2–4 and greater than 4 are assumed as residual amphibole and garnet in magma source, respectively (e.g., Kay et al. 1999; Kay et al. 2010). The garnet presence in magma source as a residual phase is inconsistent with estimated pressures for the studied volcanic rocks. Instead, amphibole appears to be more likely as a residual mineral regarding the estimated pressure as calculated by amphiboles chemistry (0.5 to 2.9 kbar) for the Andorian volcanic rocks. Oxygen fugacity and water pressure are the factors that can influence Eu anomaly (Kay et al. 2010). The absence of Eu anomalies in the Andorian volcanic samples may be due to a high oxygen fugacity in the magma source (Wilson 1989; Rollinson 1993). This feature is compatible with a high fugacity of magma that result from the amphibole and clinopyroxene chemistry in the

previous section. In primitive mantle-normalized diagram (McDonough and Sun 1995), all of the Andarian volcanic samples display the LILE enrichments (e.g., Cs, Rb, Ba, and Sr) and HFSE depletions (e.g., Nb, Ta, and Ti) (Fig. 12b). The results obtained in this section correspond well to the result reported for the Mivehrood pluton (Fig. 2) adjacent to the Andarian volcanic rocks (Alirezaei et al. 2015) that suggest they may have co-magmatic origin. Furthermore, as described by Ghorbani (2021), all rock types associated with the second to fourth magmatic episodes in the AAMZ are co-magmatic (based on petrographic descriptions together with geochemical data). In terms of mineral chemistry and petrology, the petrogenetic relationship between the Andarian hornblende and basaltic andesite rocks is close that suggests co-magmatic nature for the volcanic rocks. In addition, the similar normalized trace element and REE patterns in both rock types support the co-magmatic origin for them.

Conclusion

The magmatism in AAMZ evolved in five main episodes from Upper Cretaceous to Quaternary. The studied volcanic rocks are representative of the fourth magmatic episode in the Andarian region, northwest Iran. Based on the petrology, mineral chemistry, and bulk rock geochemistry data from the Andarian volcanic rocks, the following conclusions were obtained:

1. The Andarian volcanic rocks include basaltic andesite, andesite, hornblende andesite, dacite, and rhyodacite showing a range from 60.88 to 70.75 wt% in SiO₂. The Neogene (possibly Pliocene, based on stratigraphic field relations) Andarian volcanic rocks mainly consist of hornblende and basaltic andesite. Despite their lithological differences, these rocks share broad similarities in mineral chemistry, thermobarometric data, and geochemistry, indicating co-magmatic origin.
2. The Andarian volcanic rocks display LILE enrichments, HFSE depletions, and strong LREE-enrichment with no Eu anomalies, similar to that of post-Miocene volcanic sequences in other parts of AAMZ and the Lesser Caucasus.
3. Considering mineral chemistry, amphibole, and plagioclase, the Andarian volcanic rocks were crystallized at high oxygen fugacity conditions ($\log f\text{O}_2 = -8.8$ to -12 bars) and at temperatures ranging from 707 to 899°C and pressures ranging from 0.5 to 2.9 kbar. Therefore, the wide range of pressure, temperature, and oxygen fugacity, as well as oscillatory zoning in plagioclase, demonstrates that physiochemical conditions are possibly unstable in the magma chamber.

4. The bulk rocks' geochemistry and mineral compositions (biotite, amphibole, and clinopyroxene) clarify that the Neogene Andarian volcanic rocks are derived from an arc-related calc-alkaline magma in a post-collisional setting. Therefore, the magma nature and tectonic setting perfectly correlate the published data in the AAMZ and occurrences in the Lesser Caucasus.

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Data availability Representative data are available in the manuscript.

Declarations

Competing interests The authors declare that they have no competing interests.

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