

# The ammonium content in the Malayer igneous and metamorphic rocks (Sanandaj-Sirjan Zone, Western Iran)

VAHID AHADNEJAD<sup>1\*</sup>, ANN MARIE HIRT<sup>2</sup>, MOHAMMAD-VALI VALIZADEH<sup>3</sup> and SAEED JABBARI BOKANI<sup>4</sup>

<sup>1</sup>Geology Department, Payame Noor University (PNU), 19395-4697 Tehran, Iran; \*ahadnejad@khayam.ut.ac.ir

<sup>2</sup>Institute of Geophysics, ETH-Zürich, Sonneggstrasse 5, CH-8092 Zürich, Switzerland

<sup>3</sup>School of Geology, University College of Science, University of Tehran, Tehran

<sup>4</sup>Geological Survey of Iran (GSI), Azadi sq. Meraj St. P.O. Box 13185-1494, Tehran

(Manuscript received April 7, 2010; accepted in revised form October 11, 2010)

**Abstract:** The ammonium ( $\text{NH}_4^+$ ) contents of the Malayer area (Western Iran) have been determined by using the colorimetric method on 26 samples from igneous and metamorphic rocks. This is the first analysis of the ammonium contents of Iranian metamorphic and igneous rocks. The average ammonium content of metamorphic rocks decreases from low-grade to high-grade metamorphic rocks (in ppm): slate 580, phyllite 515, andalusite schist 242. In the case of igneous rocks, it decreases from felsic to mafic igneous types (in ppm): granites 39, monzonite 20, diorite 17, gabbro 10. Altered granitic rocks show enrichment in  $\text{NH}_4^+$  (mean 61 ppm). The high concentration of ammonium in Malayer granites may indicate metasedimentary rocks as protoliths rather than meta-igneous rocks. These granitic rocks (S-types) have high K-bearing rock-forming minerals such as biotite, muscovite and K-feldspar which their potassium could substitute with ammonium. In addition, the high ammonium content of metasediments is probably due to inheritance of nitrogen from organic matter in the original sediments. The hydrothermally altered samples of granitic rocks show highly enrichment of ammonium suggesting external sources which intruded additional content by either interaction with metasedimentary country rocks or meteoritic solutions.

**Key words:** Iran, Sanandaj-Sirjan Zone, Malayer, igneous rocks, metasedimentary rocks, ammonium.

## Introduction

Recent research has revealed that geological nitrogen has an important role in geological problems such as lithogeochemical explorations (Ridgway et al. 1990; Glasmacher et al. 2003), biogeochemical implications (Boyd 2001; Holloway & Dahlgren 2002), environmental studies (Crews et al. 2001), and petrological investigations (Honma & Itihara 1981; Hall 1999).

Nitrogen is a rare element in igneous rocks which is significant for nutrition of soils and has an important role in petrology. It includes an inorganic component as fixed ammonium, incorporated into potassium sites of minerals and, generally, concentrated in micas, feldspars, and clay minerals. Nitrogen in low-grade metamorphic and igneous rocks occurs as  $\text{NH}_4^+$ , and in sediments and sedimentary rocks as  $\text{NH}_3$  (Wedepohl 1978; Halama et al. 2010). The concentration of  $\text{NH}_4^+$  in igneous rocks is generally related to the kind and amount of the silicate minerals and the ammonium contents that are available for fixation during the existence of the minerals (Stevenson 1962). The  $\text{NH}_4^+$  ion has a similar estimated ionic radius to that of  $\text{K}^+$  ( $\text{NH}_4^+$  — 1.66 Å,  $\text{K}^+$  — 1.59 Å), which tends to explain the presence of ammonium in K-bearing minerals. Because of the stability of ( $\text{NH}_4^+$ ) in high temperature conditions and its survival in metamorphism, the concentration of geological nitrogen as a geochemical tracer in the rocks would be important to crustal processes. In the igneous rocks it is linked to their protolith; if they originate from melting of metasedimentary rocks or

assimilated by crustal component, their  $\text{NH}_4^+$  concentrations could be high. The hydrothermal activity and hydrothermal fluids could readily transport  $\text{NH}_4^+$  from other systems into rocks and cause the enrichment of altered samples in  $\text{NH}_4^+$ .

Several researchers have reported different mean concentration of N for igneous (e.g. Wedepohl 1978; Hall 1999) and low-grade metamorphic rocks (e.g. Juster et al. 1987). Wedepohl (1978) reported an average N concentration of around 20 ppm for granitoids and half of that amount for the gabbroic and dioritic rocks, whereas Hall (1999) suggested 35 ppm for the granitic, 6 and 2 ppm for the gabbroic and dioritic rocks respectively. Juster et al. (1987) pointed out that the low-grade metamorphic rocks routinely contain 200–400 ppm  $\text{NH}_4^+$ .

Hall (1993a) believed that the differences and uncertainties on ammonium contents of rocks may have three reasons: (1) Because analytical determination of ammonium and nitrogen in igneous rocks was developed recently and was not easy in the past, few workers tend to measure this element in their studies and there is not enough data from worldwide rock types to gain a precise average content; (2) Determination of ammonium in igneous rocks and especially volcanic types is difficult because of their very low ammonium content; (3) Geological processes such as alteration and country rocks can affect enrichment of ammonium.

In this study, we performed the first ammonium measurements on Iranian rocks which consist of the Malayer plutonic and metasedimentary country rocks in the Sanandaj-Sirjan Zone of Western Iran, for assessing its importance in the petrological processes.

## Geological setting

### Sanandaj-Sirjan Zone

The investigated area is located within the Sanandaj-Sirjan Zone (SSZ) which is a part of the Zagros orogeny. The SSZ has 1500 km length from northwest (Sanandaj) to southeast (Sirjan) in the western part of Iran and a width of 150–200 km (Mohajjel & Fergusson 2000) (Fig. 1). It separated from the Arabian platform during the Late Triassic to the Early Jurassic. Mesozoic rocks are dominant in this zone and Paleozoic rocks generally are common in the southeastern part (Berberian 1995). The SSZ is characterized by metamorphosed and complexly deformed rocks associated with abundant deformed and undeformed plutons, as well as widespread Mesozoic volcanics. These magmatic rocks, including the Malayer intrusive complex, generally have calc-alkaline affinities (e.g. Ahmadi-Khalaji et al. 2007; Azizi & Jahangiri 2008; Ahadnejad et al. 2008a; Ghalamghash et al. 2009).

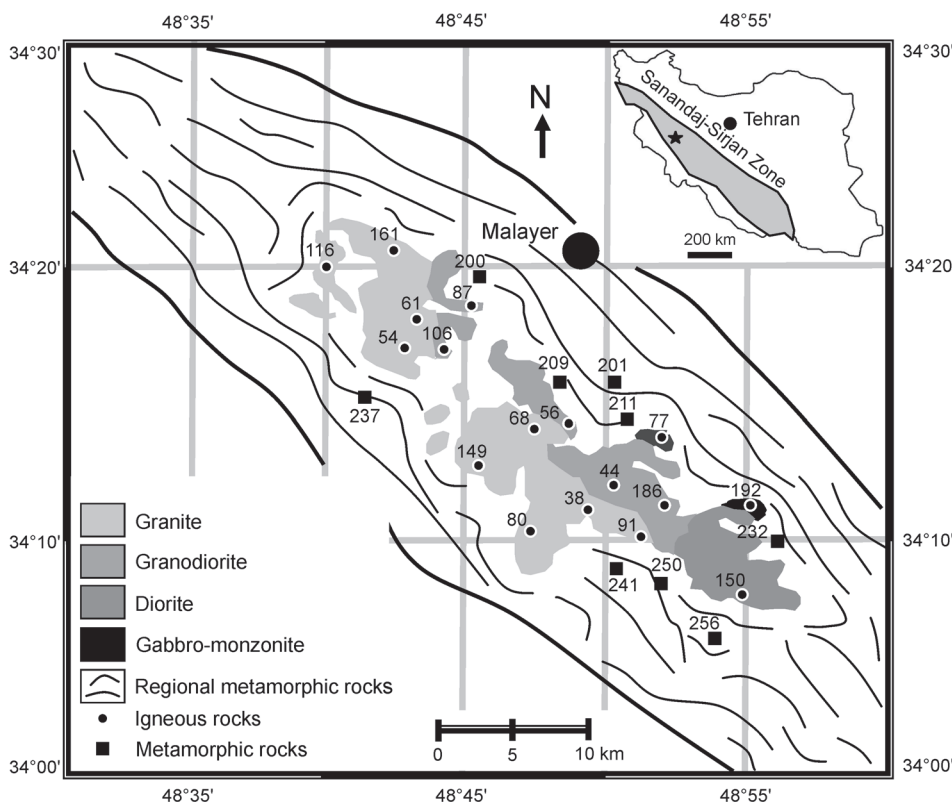
### Malayer intrusive complex

The Middle-Jurassic Malayer intrusive complex is an elongated batholith in the northern part of the SSZ. It is composed of granite, granodiorite, diorite and some small monzonitic and gabbroic bodies (Fig. 1). It is 35 km in length and 10 km in width and located in the southwest part of Malayer city, Western Iran. The Malayer complex underwent deformation

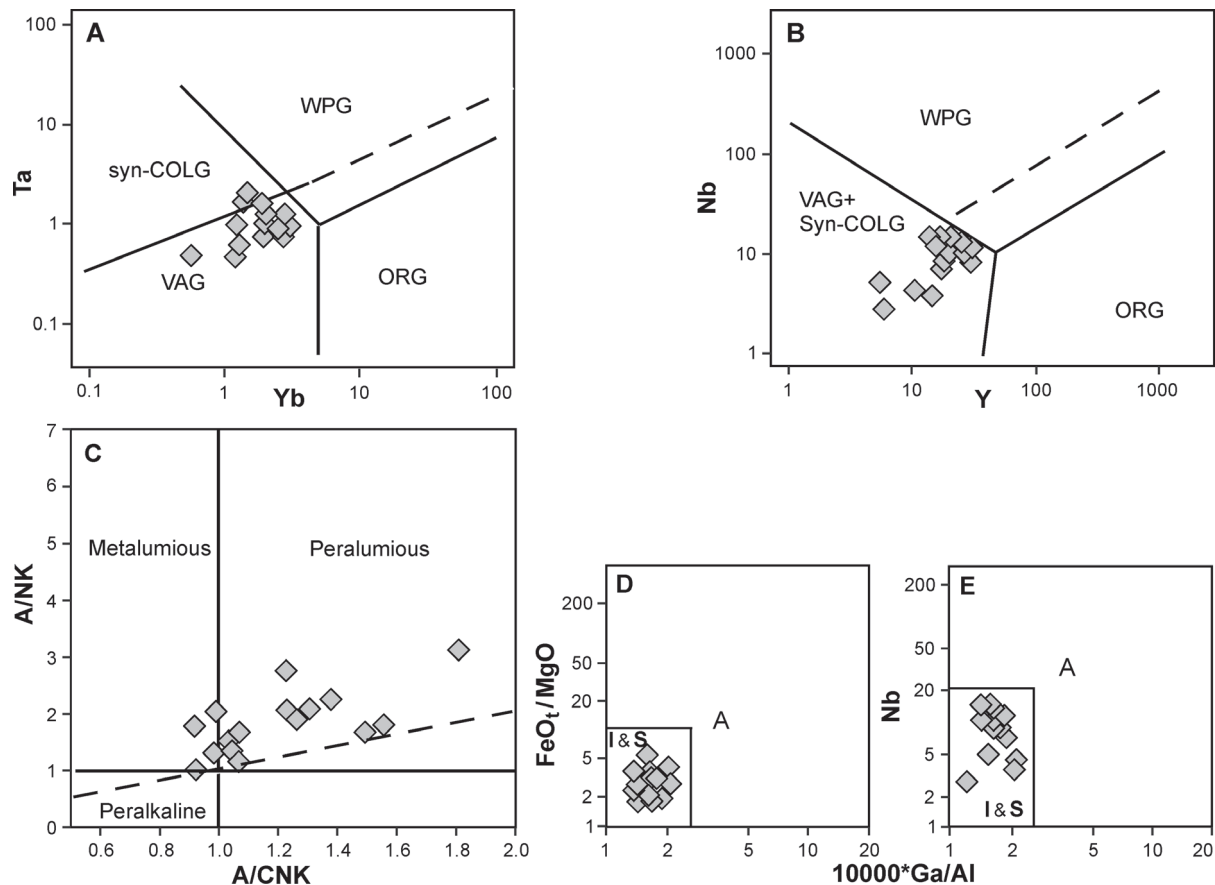
in the high-strain shear zone and gained a NW–SE direction parallel to the SSZ. Major structural features include thrust faults, strike-slip faults, and a variety of cleavages and foliations. Variable composition of rocks indicated different source rocks and hybridization of mafic and felsic magmas. Analysis of selected samples using ICP showed that they have  $\text{SiO}_2$  (wt. %) content from 46.82 (gabbro) to 77.35 (alkali-granite). They are highly peraluminous to metaluminous with high-K calc-alkaline affinity (Ahadnejad et al. 2008a).

The field, petrography, geochemistry, geochronology and isotopic data imply that the granitoids are the hybrid products of partial mixing between basic and granitic melts, generating hybrid phases, such as the tonalitic rocks. During ascent and emplacement of magma, mixing was followed by assimilation of metasedimentary country rocks. The assimilation and contamination are shown by metasedimentary enclaves and andalusite xenocrysts occurrences in the granitoids especially next to the contacts. This feature has been detected in the Malayer pluton, where initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios increase from an average of 0.7085 in the marginal Q-diorites and the 0.7087 in granodiorites, to ca. 0.7011 in the syenogranites from the central part of pluton (Ahadnejad et al. 2011). Furthermore, co-existence of antagonistic mineral assemblages (e.g. allanite + titanite + monazite + hornblende + muscovite + ...) indicate that primary magma originating from the mid to lower crust contaminated by supracrustal materials and the overall composition is significantly affected by this process. The scattered pattern of elements may have been caused by this process.

U-Pb zircon ages (Middle-Jurassic) has been obtained from all rock types of complex (Ahadnejad et al. 2011) indicate that emplacement of this pluton was performed during the subduction of Neotethys under Central Iran in an active continental margin tectonic setting. In the Pearce et al. (1984) discrimination diagrams the studied rocks plot mostly within the field of volcanic arc granites (VAG) (Fig. 2a and b). Most of the data are plotted in the peraluminous field in the  $A/\text{NK}-A/\text{CNK}$  diagram (Shand 1943). Despite relatively high  $A/\text{CNK}$  values, the granitic suite displays some affinities with I-type granitoids, and some samples contain hornblende and allanite. The distribution of samples in the diagrams  $\text{FeO}_t/\text{MgO}$  versus  $10000 \text{ Ga}/\text{Al}$  (Fig. 2d) and  $\text{Nb}$  versus  $10000 \text{ Ga}/\text{Al}$  (Fig. 2e) proposed by Whalen et al. (1987) do not suggest A-type character for Malayer granitoids.



**Fig. 1.** Schematic map of Malayer area and its location (star) in the Sanandaj-Sirjan Zone, Western Iran. The sample number and positions are shown as well.



**Fig. 2.** a — Ta versus Yb diagram and b — Nb versus Y (after Pearce et al. 1984) for studied rocks showing a volcanic arc setting. c — Most of the data are plotted in the peraluminous field in A/NK-A/CNK diagram (Shand 1943). d —  $\text{FeO}_t/\text{MgO}$  versus  $10000\text{Ga}/\text{Al}$  and e — Nb versus  $10000\text{Ga}/\text{Al}$  (Whalen et al. 1987) do not show A-type feature for Malayer granitoids.

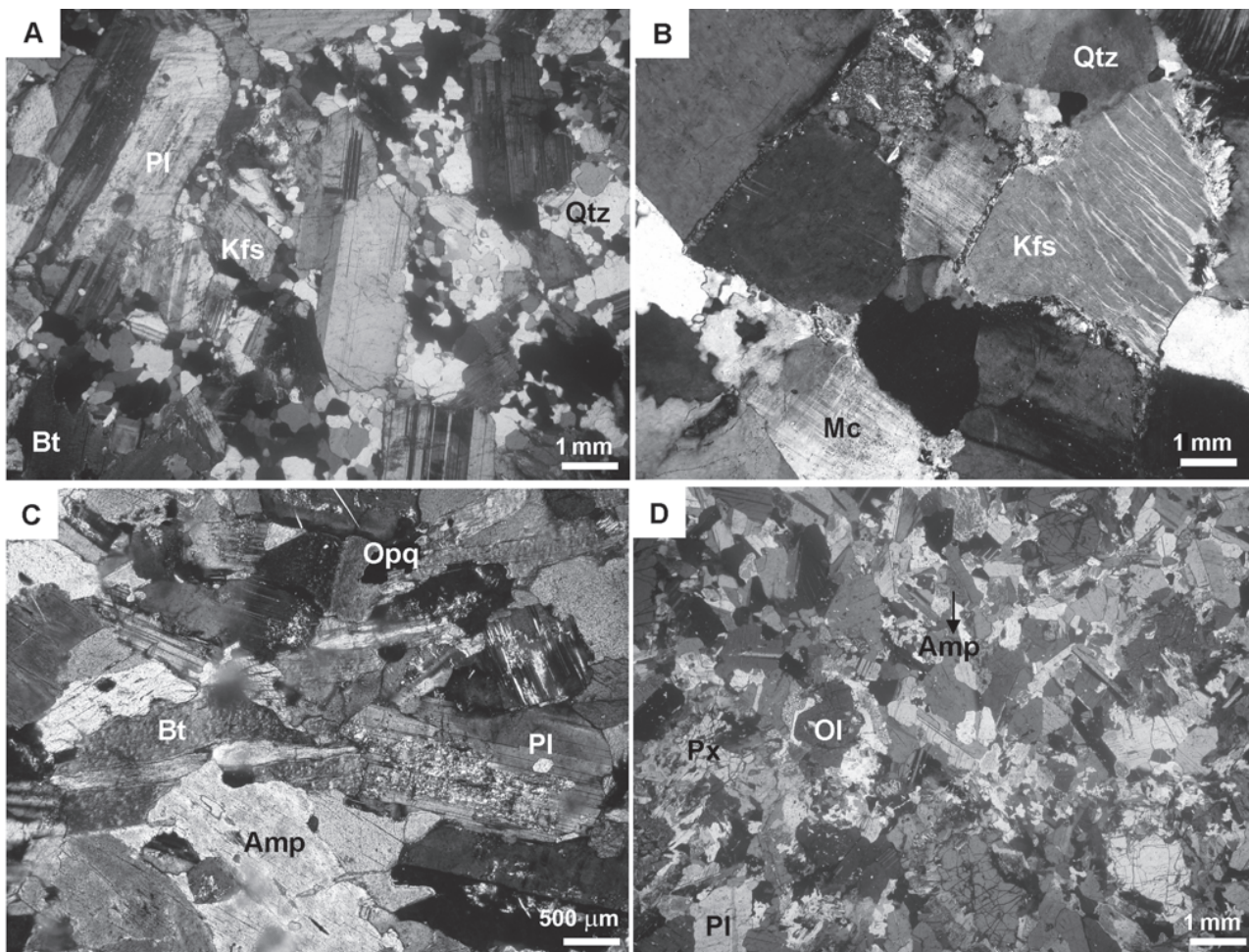
Petrographic studies show that the texture of the granitoids is mainly granular to porphyroid (Fig. 3a). They have mafic microgranular and metasedimentary enclaves which occur as angular to ellipsoidal shapes ranging from several cm to 0.6 meter in size. The mafic microgranular enclaves are dioritic in composition. The rock-forming minerals are mainly composed of K-feldspar (orthose and microcline), plagioclase, quartz, biotite and minor hornblende and muscovite. The accessory minerals are garnet, tourmaline, andalusite, cordierite, allanite, titanite, zircon and apatite. The andalusite is mostly observed in the contact of granitoids and metasedimentary country rocks. It has reaction rims containing aggregates of quartz, andalusite, muscovite, and biotite with symplectitic relationships which imply its disequilibrium with the melt. Clarke et al. (2005) indicate that these disequibrated andalusites in the granitoid rocks cannot have a magmatic origin and are considered to be xenocrystic derived from local peraluminous country rocks. They may be released from disaggregating, contact-metamorphosed metapelites into a silicate melt and, in general, such xenocrystic grains would be out of chemical equilibrium with that melt. Feldspars are euhedral to subhedral and frequently show exsolution lamellas of albite (microperthite) (Fig. 3b). Plagioclase minerals show polysynthetic twinning and zoning. They experienced mechanical crush and their crush zones are

filled by quartz and alkali feldspar. Quartz shows undulatory extinction. Myrmekites can frequently be observed around feldspars. The secondary minerals formed by alteration are muscovite, clinozoisite, sericite, clay minerals, chlorite, calcite and Fe-oxides.

The dioritic unit is located in the southeastern part of the complex and is accompanied by subordinate gabbroic and quartz monzodioritic rocks. It is lenticular in shape, medium- to coarse-grained, dark-coloured and mainly consists of plagioclase, amphibole, biotite, K-feldspar, and minor quartz (Fig. 3c). Accessory minerals are apatite, zircon, epidote and opaque minerals. Andalusite minerals are occasionally seen as xenocrysts. Apatite occurs as euhedral prismatic and acicular shapes resulting from rapid cooling of minor mafic components added to intermediate or felsic magma chambers.

A subordinate gabbroic unit is located in the corner of the diorite. It is dark-coloured, medium- to coarse-grained and its main constituents are plagioclase, amphibole, olivine, augite, and minor biotite and alkali feldspar (Fig. 3d). The apatite, epidote, and opaque minerals are accessory minerals.

Hydrothermal alterations in the Malayer granitic rocks are moderate and mainly occur on the corners of bodies, local shear zones and fractures. The major observed types of alterations are: sericitization, silicification, chloritization, oxidation and tourmalinization. Sericitization is the most



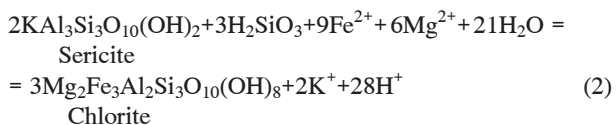
**Fig. 3.** Photomicrographs of Malayer igneous rocks. **a** — The porphyroid texture of granodiorite (XPL). **b** — Exsolution lamellas of albite (microperthite) in the alkali-feldspar. **c** — Diorite minerals (XPL). **d** — The olivine has been largely replaced by symplectic intergrowths in the gabbroic rocks (XPL). (Mineral abbreviations from Kretz 1983).

widespread alteration in the rocks. It is common in feldspars (plagioclase and alkali-feldspar) and sericitized grains reflect the zoning. This alteration implies low pH (acidic) conditions of the mineralized fluid (Faulkner 1992). Chloritization is generally observed along with sericitization due to alteration of mainly mafic minerals (biotite and amphibole). Amphibole and plagioclase minerals have also been altered into calcite. The replacement of the feldspar by epidote and sericite and the hornblende and biotite by chlorite is common and characteristic of the hydrothermal alteration associated with contact metamorphism.

Some small veins and veinlets of quartz and also small quartz crystals are formed due to silicification and rocks are normally silicified along faults and fractures. Tourmalinization in the magmatic rocks occurs as small patches and veinlets and is mainly found in contact with country rocks. Despite lack of mineral chemistry, the field observations demonstrate that tourmaline has probably originated from hydrothermal fluids. On the field scale, the brown surfaces of the granitic hills demonstrate chloritization and the iron oxide varnish of rocks. Locally, these rocks have been deeply weathered and intensely arenized to form soils which are

used as wheat farms and almond-tree gardens and have a sharp boundary with non-granitic country rocks.

To quantify alteration, the Ishikawa et al. (1976) alteration index (AI)=100\*(K<sub>2</sub>O+MgO)/(K<sub>2</sub>O+MgO+Na<sub>2</sub>O+CaO) was measured for all the granitic samples (Table 2). The key reactions measured by the index involve the breakdown of sodic plagioclase and replacement by sericite and chlorite:



Reaction (1) involves a loss of Na<sub>2</sub>O (and CaO) and a gain of K<sub>2</sub>O, whereas reaction (2) involves a loss of K<sub>2</sub>O and gains in FeO and MgO, on the basis of constant Al<sub>2</sub>O<sub>3</sub>. Samples Nos. 116 and 161 display expectedly high AI values (91 % and 92 %, respectively) and are located in the altered field of Wilt (1995) but sample No. 106 has a low value (ca. 41 %)

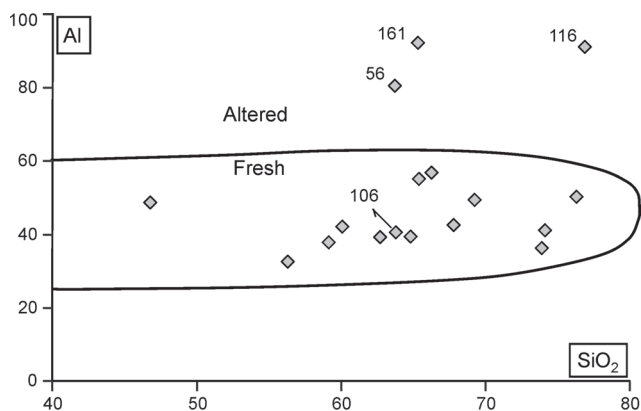


Fig. 4. Alteration diagram proposed by Wilt (1995) (weight percent of  $\text{SiO}_2$  versus Alteration Index =  $(\text{MgO} + \text{K}_2\text{O})/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO}) * 100$ ) shows the altered and fresh samples fields.

which plots in the fresh field (Fig. 4). The samples 116 and 161 are from syenogranite and monzogranite, respectively. The alteration of these samples consists of sericitization of plagioclase, chloritization of biotite and secondary muscovitization of the K-feldspar phenocrysts. The high K content of these samples, therefore, could be ascribed to sericitized plagioclase and secondary muscovite. The occurrence of andalusite caused the high Al-content in sample No. 161. Sample No. 106 is from granodiorite and shows alteration of K-feldspar and biotite to albite, muscovite, chlorite and epidote. This is consistent with sodic-calcic alteration which is supported by a chemical analysis that displays high contents of  $\text{Na}_2\text{O}$  and  $\text{CaO}$  (Table 2). Despite decreases of ammonium due to alteration of K-feldspar to sodic plagioclase (i.e. albite-oligoclase) (Honma & Itihara 1981) and/or epidote, muscovitization of K-feldspar and chloritization of biotite probably caused substantial enrichment of this sample from ammonium. This feature is in good agreement with Hall's (1993a) argument about the high ammonium content of chloritized biotite. Furthermore, Honma & Itihara (1981) showed that the muscovite contains an average of ~40 % of N concentration in a rock. With respect to high  $\text{Na}_2\text{O}$ ,  $\text{FeO}$ ,  $\text{MgO}$  and  $\text{CaO}$  and low  $\text{K}_2\text{O}$  content of 106 it is concluded that the reaction (2) is responsible for alteration in this sample which is supported by petrographic observations of chloritization. In addition, a characteristic feature of this sample is high Cl concentration which could provide a potential for ammonium concentration via ammonium-chlorite bearing inorganic compounds? (e.g.  $\text{NH}_4\text{ClO}$ ,  $\text{NH}_4\text{ClO}_2$ , etc.). However, minerals such as amphiboles, biotite and apatite could contain chlorine. On the other hand, sample No. 56 from fresh samples shows a high AI value (ca. 81 %). Concerning petrography it seems that it is in the incipient step of alteration via reaction (1) as shown by low  $\text{Na}_2\text{O}$  and fairly high  $\text{K}_2\text{O}$  and  $\text{H}_2\text{O}$ . The  $\text{MgO}$  content of this sample is high due to occurrence of augite (clinopyroxene).

The occurrences of tonalite, granodiorite and diorite as hybrid rocks, existing of disequilibrated andalusites, garnet, albanite, acicular apatite, titanite and cordierite in the rocks, and mafic microgranular and metasedimentary enclaves implied that they were probably produced by interaction of mafic and

felsic rocks accompanied by assimilation into metasedimentary rocks. This is supported by high values of  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.70797 to 0.7108) which are measured for all plutonic rock types at Isotope Geochemistry and Mineral Resources, ETH-Zurich, Switzerland, using the ID-TIMS technique. In addition, the high- and low-field anisotropy of magnetic susceptibility (AMS) and paleomagnetic analysis that were performed by the first author at the Paleomagnetic Laboratory of the Institute of Geophysics at ETH, show that the igneous rocks have low magnetic susceptibility (4–706  $\mu\text{SI}$ ) and belong to the ilmenite-series of Ishihara (1977). The value of  $3 \times 10^{-3}$  SI unit (equivalent to  $100 \times 10^{-6}$  emu/g unit of Ishihara 1979) is usually taken as the boundary dividing the magnetite- and ilmenite-series granitoids. The high field analyses (HFA) on the 39 among 90 drilled cores from throughout the pluton shows that all the samples are composed of dominant paramagnetic components except for 3 samples (8 %) which show a ferromagnetic character (Ahadnejad et al. unpubl. data). Finally, the biotite geochemistry of the rocks (Ahadnejad et al. 2008b) displays a reduced magma fugacity ( $10^{-15}$  to  $10^{-10}$  bar) for a crystallizing temperature of 700 °C at QFM buffer.

#### Metasedimentary rocks

The regional metamorphic rocks are slate, phyllite, and schist. Quartz, muscovite, biotite and K-feldspar are the main components of the rocks. The micas arranged into preferred orientations and caused slaty cleavages in slates (Fig. 5a). The slates and phyllites show granular and lepidoblastic to lepidogranoblastic textures, respectively. Andalusite and garnet are the major porphyroblasts in the schists (Fig. 5b). These rocks are composed of biotite, muscovite, quartz and feldspars. The schistosity of the rocks is oriented in the NW-SE direction. According to the diagram  $\text{FeO}_t/\text{K}_2\text{O}-\text{SiO}_2/\text{Al}_2\text{O}_3$  (Fig. 6) suggested by (Herron 1988), different metamorphic rock varieties of Malayer (slate, phyllite and schist) correspond to clays (Fig. 6), and have relatively uniform chemical compositions which may indicate differences from similar sedimentary rocks.

#### Sampling and analytical methods

Two groups of samples were analysed in this study. One group consists of 17 samples from various igneous rocks ranging from granite to gabbro including 3 altered samples. The modal analysis results indicate that they are syenogranitic to gabbro (Table 1 and Fig. 7). The other group consists of 9 samples from regional metamorphic rocks (slate, phyllite and schist). Samples are represented all rock types that occurred in the Mlayer area except for hornfels. The mean amount of material collected was about 4 kg per sample. We crushed the samples and analysed them in the AMDEL laboratories, Australia for major elements and in the Geological Survey of Iran (GSI) for ammonium.

The most popular technique for the determination of ammonium in geological samples is the colorimetric method based on the formation of indophenol blue and we used this method to measure the concentration of ammonium in the rocks at the Geological Survey of Iran (GSI). This method consists of sam-

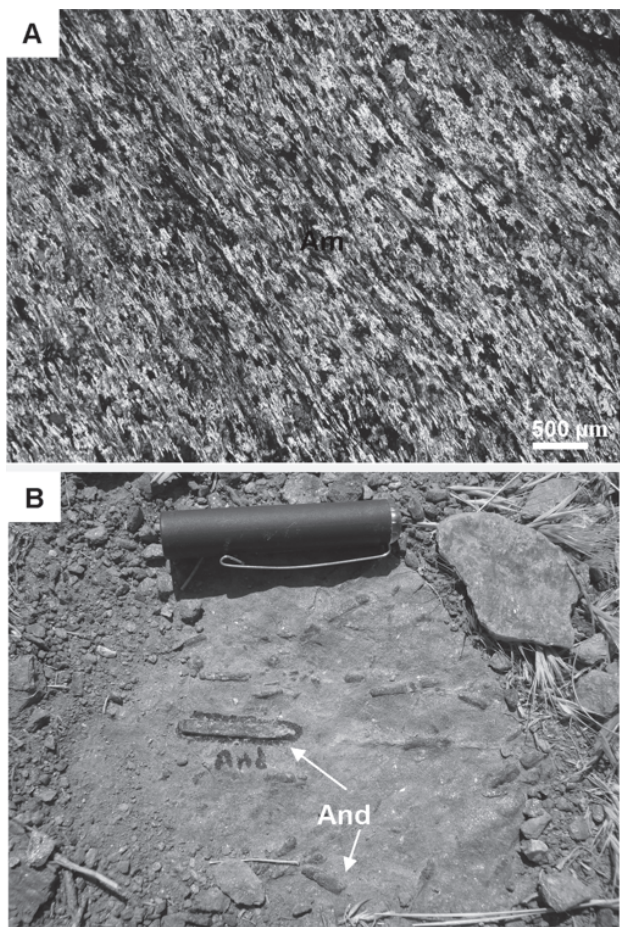


Fig. 5. a — Arrangement of platy minerals forms slaty cleavage in the direction NW-SE (XPL). b — Andalusite minerals in the metasedimentary rocks of Malayer.

ple digestion in cold HF for 7 days, followed by separation of ammonia by distillation from alkaline solution, and a colorimetric finish using the indophenol blue method. A detailed description of the method is given by (Hall 1993b).

**Results and discussion**

In this reaserch we reported average ammonium contents of 580 for slate, 515 for phyllite, 242 for andalusite schist,

Table 1: Modal analyses of Malayer igneous rocks.

Name	38	44	54	56	61	68	77	80	87	91	149	150	186	192	106*	116*	161*
Rock type	MG	Gd	MG	Gd	SG	MG	Mz	Gd	To	SG	SG	Di	Gd	Gb	Gd	SG	MG
Quartz	21	24	23	17	22	17	4	24	25	26	39	8	19	3	23	43	18
Alkali Feldspar	30	16	28	19	41	30	38	25	3	38	31	3	10	3	23	34	34
Plagioclase	25	43	26	43	18	29	44	30	57	19	16	51	56	50	40	12	27
Biotite	16	7	15	16	11	16	9	11	6	6	8	12	7	10	6	6	14
Muscovite	0	1	0	0	4	0	0	1	1	3	2	0	1	0	1	0	0
Amphibole	3	5	4	1	0	3	0	5	2	4	0	13	5	13	4	0	0
Pyroxene	0	0	0	0	0	0	0	0	2	0	0	8	0	12	0	0	0
Opaque	3	2	2	3	1	3	3	2	3	1	1	4	1	4	2	1	3
Accessory*	2	2	2	1	3	2	2	2	1	3	3	1	1	5	1	4	4
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

\*Accessory minerals include: Apatite, Zircon, Allanite, Monazite, Tourmaline, Spene, Andalusite, ...

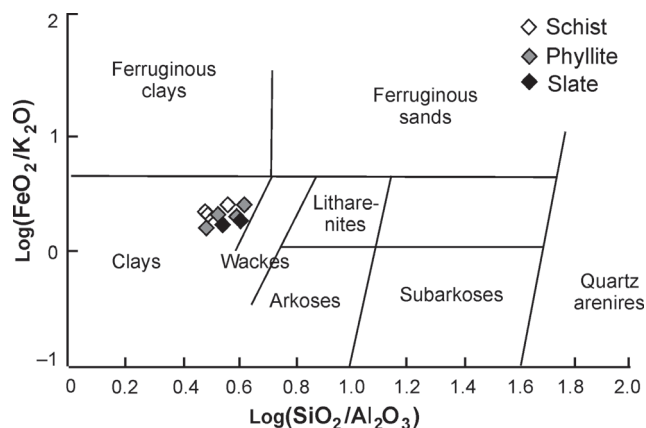


Fig. 6. Classification of metasedimentary rocks from the Malayer based on Herron's (1988) diagram.

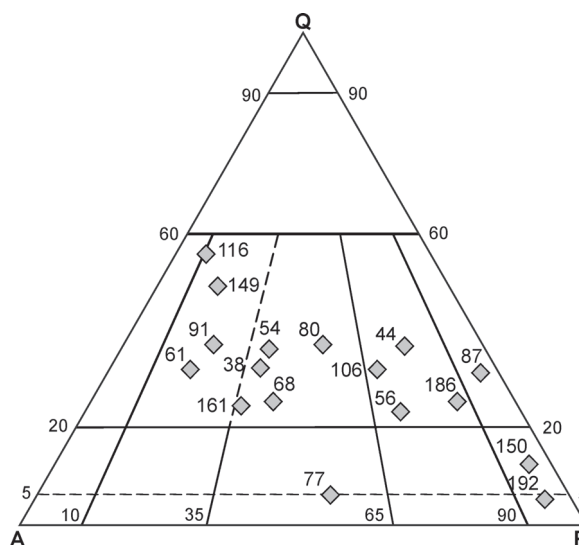


Fig. 7. Classification of granitic rocks in the QAP diagram, according to their actual (modal) mineral constituents (after Streckeisen 1976).

39 for granitoids, 20 for monzonite, 17 for diorite, 10 for gabbro in the Malayer rocks.

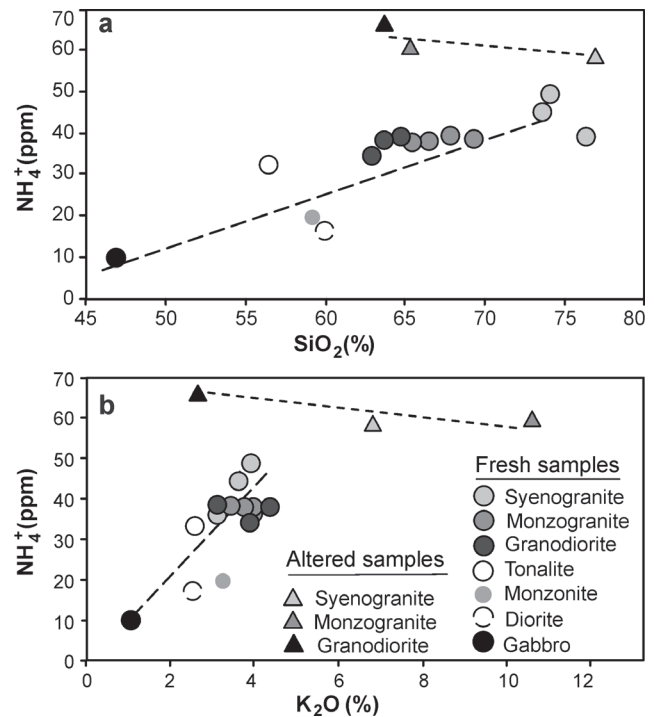
The ammonium content of the Malayer igneous rocks systematically increases from basic to more felsic rocks as follows: 10, 17, 20, and 39 as averages for gabbro, diorite, monzonite, and granitoids respectively (Table 2). Among gra-

**Table 2:** Whole rock geochemistry and ammonium content of Malayer igneous rocks (SG = Syenogranite; MG = Monzogranite; Gd = Granodiorite; Mz = Monzonite; To = Tonalite; Di = Diorite; Gb = Gabbro) (mineral abbreviations from Kretz 1983).

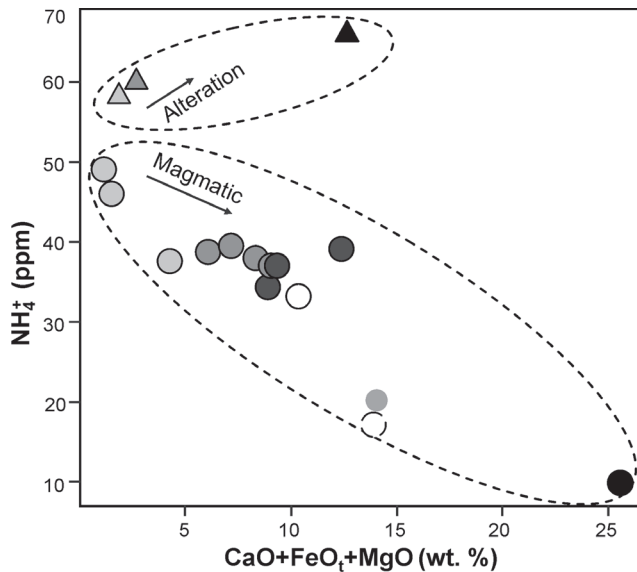
Sample	Rock	Mineralogy*	NH <sub>4</sub> <sup>+</sup>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	FeO <sub>t</sub>	MgO	CaO	Sample	Rock	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	Ba	Rb	Sr	LOI	ASI	DI	Al%	Total
38	MG	Qzr+Kfs+Pl+Mc+Bt+Amp+And	39	67.83	14.90	3.83	4.61	3.35	0.97	1.85	38	MG	0.30	0.13	0.06	639	229	182	2.17	0.99	80	42.63	100.0
44	Gd	Qzr+Pl+Kfs+Bt+Amp+Zn	39	64.77	16.60	3.21	3.94	4.78	1.36	3.04	44	Gd	0.54	0.16	0.07	935	180	285	0.91	1.07	70	39.57	99.4
54	MG	Qzr+Mc+Kfs+Pl+Tur	39	66.28	15.30	3.77	0.90	4.64	2.44	3.82	54	MG	0.59	0.13	0.08	406	40.2	568	1.97	1.22	62	56.80	99.9
56	Gd	Qzr+Pl+Amp+Kfs+Bt+Px (Aug)+And	39	63.72	15.90	4.37	0.24	5.37	5.01	2.01	56	Gd	0.60	0.14	0.07	70.4	8.6	247	2.66	1.81	58	80.64	100.1
61	SG	Qzr+Kfs+Mc+Pl+Bt+Tur	46	73.88	14.10	3.66	6.00	0.48	0.17	0.73	61	SG	0.05	0.46	0.00	83.3	268	66	0.29	0.93	96	36.27	99.8
68	MG	Qzr+Kfs+Pl+Bt+Amp	38	65.42	15.80	3.91	2.44	3.95	2.00	2.37	68	MG	0.50	0.20	0.07	401	123	215	3.23	1.26	70	55.13	99.9
77	Mz	Pl+Kfs+Bt+Qzr+Amp	20	59.18	18.30	3.25	3.38	6.83	1.95	5.15	77	Mz	0.81	0.19	0.09	900	129	408	0.58	0.99	56	37.87	99.7
80	MG	Qzr+Pl+Kfs+Mc+Bt+Amp	39	69.24	15.40	3.40	2.36	3.54	1.20	2.32	80	MG	0.37	0.16	0.06	433	119	317	1.66	1.31	64	49.57	99.7
87	To	Qzr+Pl+Bt+Kfs+Amp+Px+Ms+And	33	56.32	20.10	2.63	7.91	6.42	2.11	1.83	87	To	0.84	0.11	0.08	2330	320	322	1.00	1.05	75	32.73	99.3
91	SG	Qzr+Kfs+Pl+Bt+Amp+Ms+Tur	49	74.12	14.60	3.88	5.10	0.35	0.16	0.62	91	SG	0.07	0.32	0.00	57.7	222	28	0.65	1.06	95	41.39	99.9
149	SG	Qzr+Mc+Kfs+Pl+Bt+Ms	38	76.36	13.20	3.14	1.49	1.70	0.45	2.05	149	SG	0.17	0.09	0.03	308	64.7	322	1.03	1.38	82	50.35	99.7
150	Di	Pl+Amp+Bt+Qzr+Kfs+Px+Zn	17	60.04	17.20	2.47	3.45	8.24	2.26	3.08	150	Di	1.30	0.12	0.12	338	199	216	1.28	1.23	59	42.01	99.6
186	Gd	Qzr+Pl+Kfs+Bt+Amp+And+Aln	35	62.73	17.50	3.88	4.08	4.60	0.92	3.31	186	Gd	0.46	0.11	0.06	1410	134	380	1.92	1.03	70	39.38	99.6
192	Gb	Pl+Amp+Px+Bt+Ol	10	46.82	21.40	1.06	0.66	13.70	5.52	6.23	192	Gb	2.33	0.06	0.26	116	27	271	1.40	1.58	29	48.85	99.4
106?	Gd	Qzr+Pl+Kfs+Amp+Bi+Ms+Ep+Chl+And	66	63.76	15.40	2.64	3.66	5.42	2.85	4.32	106?	SG	0.60	0.14	0.10	537	161	103	0.86	0.92	62	40.76	99.8
116?	SG	Qzr+Kfs+Pl+Bt+Chl+Ser	58	76.90	13.40	6.80	0.19	0.89	0.46	0.52	116?	SG	0.06	0.02	0.01	36.2	78	125	0.49	1.55	89	91.07	99.7
161?	MG	Qzr+Kfs+Pl+Bt+And+Chl+Ser	60	65.29	19.70	10.60	0.13	0.90	1.01	0.82	161?	MG	0.17	0.27	1.01	13	102	156	0.82	1.49	85	92.41	100.7

nitic rocks, the muscovite- and biotite-bearing syenogranites have the highest values of ammonium (49 and 46 ppm). This is in accordance with this fact that ammonium is an isomorphous substitute for potassium in the rock-forming minerals (K-feldspar, muscovite and biotite) via diagenetic recrystallization, metamorphic reactions or crystal fractionation. The strongly peraluminous and potassic granitoids contain higher concentrations of ammonium than metaluminous granitoids and it decreases toward monzonite, diorite and gabbro. This is probably attributed to a general decrease in alkali earth metal concentrations from felsic to mafic rocks.

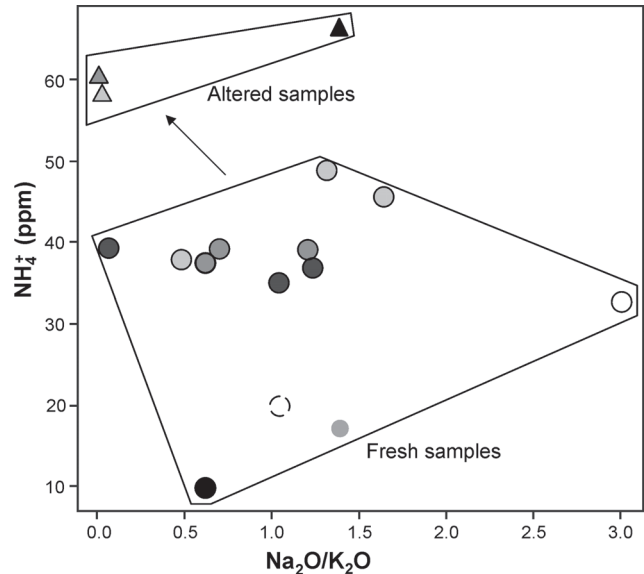
Although some scatters were observed in the diagram, there is nearly good correlation between SiO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> (Fig. 8a). Furthermore, the diagram of K<sub>2</sub>O vs. NH<sub>4</sub><sup>+</sup> exhibits a strong positive correlation, however, in the altered samples their correlation is weakly negative (Fig. 8b). Figure 8 approves a good correlation between NH<sub>4</sub><sup>+</sup> and some major elements (e.g. SiO<sub>2</sub> and K<sub>2</sub>O). At least in the fresh samples, positive correlation between NH<sub>4</sub><sup>+</sup> and SiO<sub>2</sub> implies that NH<sub>4</sub><sup>+</sup> could be a good petrological tool for evaluating differentiation of a rock suit. In other words, more evolved rocks have been enriched in ammonium which is consistent with high K-feldspar contents of these rocks. This feature is supported by positive correlation between NH<sub>4</sub><sup>+</sup> and K<sub>2</sub>O as well. These results document the role of ammonium for balancing potassium in the K-bearing minerals. The ammonium has negative correlation with FeO<sub>t</sub> and CaO (not shown), but this changes to positive in the altered samples. In general, the Malayer samples demonstrate a magmatic trend of increasing CaO+FeO<sub>t</sub>+MgO with decreasing NH<sub>4</sub><sup>+</sup> (Fig. 9). This feature may either indicate differentiation by fractional crys-



**Fig. 8.** The positive correlations of **a** — SiO<sub>2</sub> vs. NH<sub>4</sub><sup>+</sup>, and **b** — K<sub>2</sub>O vs. NH<sub>4</sub><sup>+</sup>.



**Fig. 9.** The relationship between  $\text{FeO}_t + \text{CaO} + \text{MgO}$  and  $\text{NH}_4^+$  contents in the fresh and altered igneous rocks. Note the magmatic and alteration trends (symbols are as Fig. 8).



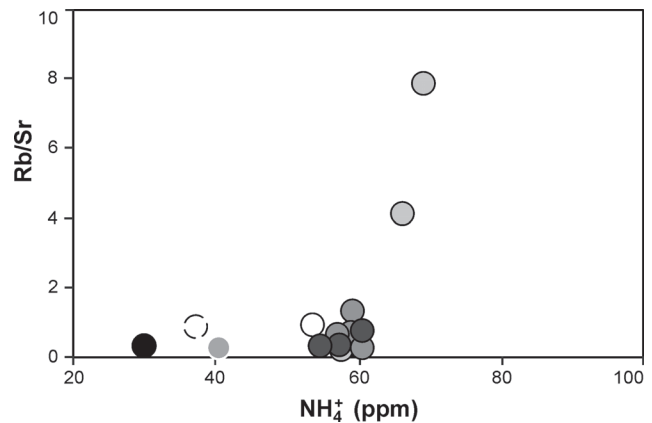
**Fig. 10.** The diagram of alkali ratios ( $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ) versus ammonium content of Malayer plutonic rocks show enrichment of altered samples (symbols are as Fig. 8).

tallization or production by partial melting of metasedimentary rocks. On the other hand, altered samples show an alteration trend of increasing  $\text{CaO} + \text{FeO}_t + \text{MgO}$  with increasing  $\text{NH}_4^+$  (Fig. 9).

The alkali ratios ( $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ) against ammonium contents diagram shows distinctive ammonium enrichment for altered samples (Fig. 10). As seen in the diagram, by decreasing value of  $\text{Na}_2\text{O}/\text{K}_2\text{O}$ , which implies increasing of alteration (Hall 1999), the ammonium contents are raised. The variability and scattering of data can be explained by assimilation processes that involved additional ammonium from country rocks. This is supported by abundant metasedimentary enclaves as assimilation traces in igneous rocks. However, no clear correlation between rock type and  $\text{NH}_4^+$  content is evident from this diagram.

Because Rb is incorporated in K minerals and Sr in Ca minerals, during fractional crystallization, Sr tends to become concentrated in plagioclase, leaving Rb in the liquid phase. Hence, the Rb/Sr ratio in residual magma may increase over time, resulting in rocks with increasing Rb/Sr ratios with increasing differentiation. Typically, Rb/Sr increases in the order plagioclase, hornblende, K-feldspar, biotite, muscovite. The Rb/Sr ratios of the studied igneous rocks increased from mafic to felsic rocks. The ammonium contents correlate positively with Rb/Sr ratios (Fig. 11) which indicate increasing ammonium concentration in more differentiated rocks.

Generally, the wide range of ammonium concentration in the granitoids prevent us classifying them into I- and S-type based on their ammonium content (e.g. Hall 1999; Kohút & Pieczka 2003). The S-type granitic rocks, which originate from molten sedimentary rocks, may have different values of the  $\text{NH}_4^+$  due to inhomogeneous sources and overlap with I-types. However, Tainosho & Itihara (1988) show that  $\text{NH}_4^+$  contents of biotites from S-type granitic rocks are higher than those for I-type granitic rocks. In the Malayer grani-



**Fig. 11.**  $\text{NH}_4^+$  vs. Rb/Sr diagram for Malayer igneous rocks. Note the high concentration of ammonium in the most evolved rocks (symbols are as Fig. 8).

toids, because most of the  $\text{NH}_4^+$  data overlap, it is difficult to distinguish I- and S-types granitoids.

The samples of 106, 116, and 161 were selected from altered ones for assessing alteration effects on the ammonium concentration in granitoids. The results show that the ammonium content is high in these rocks (Table 2).

Hall et al. (1991) assumed that in the altered granites, the hydrothermal solutions have introduced additional ammonium from an external source to the granitic plutons. This source could be decay of nitrogenous organic compounds of sediments or soil that converted to ammonia. Subsequently, the ammonia immediately converted to the ammonium ion by solution in groundwater and can then be incorporated into silicate minerals and preserved indefinitely. This is a significant petrological characteristic of ammonium that enables geologists to distinguish initial hydrothermal alteration in granites.



**Table 3:** Major elements and ammonium content of Malayer metamorphic rocks.

Sample	Rock	Mineralogy	NH <sub>4</sub> <sup>+</sup>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	FeO <sub>t</sub>	MgO	CaO	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	LOI	Total
200	Slate	Qtz+Kfs+Ms+Grt	584	68.31	17.46	4.12	0.14	7.08	1.08	0.46	1.03	0.11	0.09	0.25	100.13
201	Slate	Qtz+Kfs+Ms+Grt	577	65.74	19.23	4.35	0.17	6.74	0.97	0.39	0.87	0.06	0.13	0.91	99.56
209	Phyllite	Qtz+Ms+Bt+Kfs+Grt	518	67.12	16.38	3.15	0.10	7.09	0.97	0.23	0.94	0.14	0.14	3.41	99.67
211	Phyllite	Qtz+Ms+Bt+Grt	511	63.28	20.84	4.21	0.09	6.47	0.86	0.19	1.02	0.09	0.15	2.67	99.87
232	Phyllite	Qtz+Ms+Bt+Grt+Kfs	514	65.10	19.40	3.77	0.12	7.32	0.94	0.17	1.01	0.09	0.14	1.92	99.98
237	Phyllite	Qtz+Ms+Bt+Grt+Kfs++Ser	519	67.41	17.52	3.94	0.09	7.10	0.91	0.22	0.93	0.11	0.11	1.46	99.8
241	Schist	Qtz+Ms+Bt+And+Grt	258	64.74	21.23	3.31	0.11	6.81	0.93	0.19	1.01	0.12	0.14	1.07	99.66
250	Schist	Qtz+Ms+Bt+And+Sil+Grt	231	65.17	18.71	2.95	0.86	7.04	0.79	0.21	0.89	0.91	0.12	2.09	99.74
256	Schist	Qtz+Ms+Bt+And+Grt+Crld	239	63.82	21.19	3.11	0.93	6.75	0.92	0.24	1.03	0.86	0.16	0.84	99.85

The 2 samples from slates, 4 samples from phyllites and 3 samples from schists of the Malayer metasedimentary country rocks were analysed. As shown in Table 3, ammonium is progressively depleted from slate with 580 ppm, to the phyllite with 515 ppm and andalusite schist with 242 ppm. Bebout & Fogel (1992) suggested that during regional and contact metamorphism, the ammonium contents decrease with increasing temperature. This is fully confirmed by our research, where the ammonium contents decrease from low-grade metamorphic to schists. This feature may reflect a loss of nitrogen by breakdown of NH<sub>4</sub><sup>+</sup>-bearing minerals during thermal decomposition, devolatilization, or cation exchange (Hallam & Eugster 1976).

### Conclusions

(i) The current paper presents the first ammonium analysis for Iranian rocks in the Malayer area. The results show that ammonium contents increase from mafic (gabbro) to felsic (granite) igneous rocks. This is probably caused by increasing of potassic minerals in felsic types. Due to good correlation between K and ammonium, it is concluded that at least in granitoids the main carrier of NH<sub>4</sub><sup>+</sup> is biotite and muscovite. In the case of mafic types, feldspars could be suitable hosts for ammonium.

(ii) The altered granitoids are highly enriched in ammonium (with an average of 61 ppm) compared with those fresh samples (39 ppm) which suggests that the solutions feed rocks for ammonium from external sources.

(iii) There is a significant negative correlation between NH<sub>4</sub><sup>+</sup> and mafic elements (CaO+FeO<sub>t</sub>+MgO). This implies a magmatic trend for ammonium concentration in igneous rocks and documents that ammonium concentration increases during differentiation of a rock suit.

(iv) It is difficult to ascribe the Malayer granitic rocks to I- or S-type granitoids, on the basis of ammonium contents.

(v) The altered samples show the opposite trend of increasing NH<sub>4</sub><sup>+</sup> with increasing mafic elements.

(vi) The metasedimentary rocks have high concentration of ammonium which may imply nitrogen rich source materials (clays). The micas are the NH<sub>4</sub><sup>+</sup> carrier in metamorphic rocks.

(vii) Progress in metamorphism caused a decreasing of ammonium contents in metamorphic rocks by thermal decomposition and devolatilization.

**Acknowledgments:** The authors would like to thank Dr. Milan Kohút and Igor Petrik for their constructive comments.

This research was financially supported by the Iran National Science Foundation, Grant No. 86103/32.

### References

- Ahadnejad V., Valizadeh M.V. & Esmaily D. 2008a: The role of shear zone on the emplacement of Malayer Granitoid Complex, NW Iran. *J. Appl. Sci.* 8, 4238-4250.
- Ahadnejad V., Valizadeh M.V., Esmaily D. & Bokani S.J. 2008b: Setting In-House XRF reference material for minerals; a case study- biotite minerals of Malayer Granitoid rocks (Western Iran). *J. Appl. Sci.* 8, 4369-4375.
- Ahadnejad V., Valizadeh M.V., Deevsalar R. & Rezaei-Kahkhaei M. 2011: Age and geotectonic position of the Malayer granitoids: Implication for plutonism in the Sanandaj-Sirjan Zone, W Iran. *Neu. Jb. Geol. Palaont. Abh.* doi: 10.1127/0077-7749/2011/0149.
- Ahmadi-Khalaji A., Esmaily D., Valizadeh M.D. & Rahimpour-Bonab H. 2007: Petrology and geochemistry of the granitoid complex of Boroujerd, Sanandaj-Sirjan zone, western Iran. *J. Asian Earth Sci.* 29, 859-877.
- Azizi H. & Jahangiri A. 2008: Cretaceous subduction related volcanism in the northern Sanandaj-Sirjan Zone, Iran. *J. Geodyn.* 45, 178-190.
- Bebout G.E. & Fogel M.L. 1992: Nitrogen-isotope compositions of metasedimentary rocks in the Catalina schists, California: Implications for metamorphic devolatilization history. *Geochim. Cosmochim. Acta* 56, 2839-2849.
- Berberian M. 1995: Master blind thrust faults hidden under the Zagros folds: active basement tectonics and surface morphotectonics. *Tectonophysics* 241, 193-224.
- Boyd S.R. 2001: Ammonium as a biomarker in Precambrian metasediments. *Precambrian Res.* 108, 159-173.
- Clarke D.B., Dorais M., Barbarin B., Barker D., Cesare B., Clarke G., El Baghdadi M., Erdmann S., Foerster H.J., Gaeta M., Gottesmann B., Jamieson R.A., Kontak D.J., Koller F., Gomes C.L., London D., Morgan G.B. (VI.), Neves L.J.P.F., Pattison D.R.M., Pereira A.J.S.C., Pichavant M., Rapela C.W., Renno A.D., Richards S., Roberts M., Rottura A., Saavedra J., Toselli A.J., Ugidos J.M., Uher P., Vilaseca C., Visona D., Whitney D.L., Williamson B. & Woodard H. 2005: Occurrence and origin of andalusite in peraluminous felsic igneous rocks. *J. Petrology* 46, 441-472.
- Crews T.E., Kurina L.M. & Vitousek P.M. 2001: Organic matter and nitrogen accumulation and nitrogen fixation during early ecosystem development in Hawaii. *Biogeochem.* 52, 259-279.
- Faulkner E.L. 1992: Introduction to Prospecting. *Geological Survey Branch, Canada, Mineral Resources Division, Paper*, 1986-4.
- Ghalmghash J., Nédélec A., Bellon H., Vousoughi Abedini M. & Bouchez J.L. 2009: The Urumieh plutonic complex (NW Iran):

- A record of the geodynamic evolution of the Sanandaj-Sirjan zone during Cretaceous times. Part I. Petrogenesis and K/Ar dating. *J. Asian Earth Sci.* 35, 401–415.
- Glasmacher U.A., Zentilli M. & Ryan R. 2003: Nitrogen distribution in Lower Palaeozoic slates/phyllites of the Meguma Supergroup, Nova Scotia, Canada: implications for Au and Zn-Pb mineralisation and exploration. *Chem. Geol.* 194, 297–329.
- Halama R., Bebout G.E., John T. & Schenk V. 2010: Nitrogen recycling in subducted oceanic lithosphere: The record in high- and ultrahigh-pressure metabasaltic rocks *Geochim. Cosmochim. Acta* 74, 1636–1652.
- Hall A. 1993a: The influence of secondary alteration on the ammonium content of granites, exemplified by the Rosses complex of Donegal. *Mineral. Mag.* 57, 591–598.
- Hall A. 1993b: Application of the indophenol blue method to the determination of ammonium in silicate rocks and minerals. *Appl. Geochem.* 8, 101–105.
- Hall A. 1999: Ammonium in granites and its petrogenetic significance. *Earth Sci. Rev.* 45, 145–165.
- Hall A., Bencini A. & Poli G. 1991: Magmatic and hydrothermal ammonium in granites of the Tuscan magmatic province, Italy. *Geochim. Cosmochim. Acta* 55, 3657–3664.
- Hallam M. & Eugster H.P. 1976: Ammonium silicate stability relations. *Contr. Mineral. Petrology* 57, 227–244.
- Herron M.M. 1988: Geochemical classification of terrigenous sands and shales from core or log data. *J. Sed. Res.* 58, 820–829.
- Holloway J.M. & Dahlgren R.A. 2002: Nitrogen in rock: Occurrences and biogeochemical implications. *Global Biogeochem. Cy.* 16, 1118–1134.
- Honma H. & Itihara Y. 1981: Distribution of ammonium in minerals of metamorphic and granitic rocks. *Geochim. Cosmochim. Acta* 45, 983–988.
- Ishihara S. 1977: The magnetite-series and ilmenite-series granitic rocks. *Min. Geol.* 27, 293–305.
- Ishihara S. 1979: Lateral variation of magnetic susceptibility of the Japanese granitoids. *J. Geol. Soc., Japan* 85, 509–523.
- Ishikawa Y., Sawaguchi T., Iwaya S. & Horiuchi M. 1976: Delineation of prospecting targets for Kuroko deposits based on modes of volcanism of underlying dacite and alteration haloes. *Min. Geol.* 26, 105–117 (in Japanese with English abstract).
- Juster T.C., Brown P.E. & Bailey S.W. 1987:  $\text{NH}_4^+$ -bearing illite in very low grade metamorphic rocks associated with coal, north-eastern Pennsylvania. *Amer. Mineralogist* 72, 555–565.
- Kretz R. 1983: Symbols for rock-forming minerals. *Amer. Mineralogist* 68, 277–279.
- Kohút M. & Pieczka A. 2003: Ammonium content in the Hercynian Granites of the Western Carpathians and its petrogenetic significance. *GeoLines* 16, 53–54.
- Mohajjel M. & Fergusson C.L. 2000: Dextral transpression in Late Cretaceous continental collision, Sanandaj-Sirjan Zone, western Iran. *J. Struct. Geol.* 22, 1125–1139.
- Pearce J.A., Harris N.B.W. & Tindle A.G. 1984: Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. *J. Petrology* 25, 956–983.
- Ridgway J., Appleton J.D. & Levinson A.A. 1990: Ammonium geochemistry in mineral exploration — a comparison of results from the American cordilleras and the southwest Pacific. *Appl. Geochem.* 5, 475–489.
- Shand S.J. 1943: Eruptive rocks. Their genesis, composition, classification, and their relation to ore-deposits with a chapter on meteorite. 2nd edition. *John Wiley & Sons*, New York, 1–444.
- Stevenson F.J. 1962: Chemical state of the nitrogen in rocks. *Geochim. Cosmochim. Acta* 26, 797–809.
- Streckeisen A.L. 1976: To each plutonic rock, its proper name. *Earth Sci. Rev.* 12, 1–33.
- Tainosho Y. & Itihara Y. 1988: The difference in NH content of biotites between I-type and S-type granitic rocks in Australia. *J. Geol. Soc., Japan* 94, 749–756.
- Wedepohl K.H. 1978: Handbook of Geochemistry. V2. Heidelberg, New York.
- Whalen J.B., Currie K.L. & Chappell B.W. 1987: A type granites: Geochemical characteristics, discrimination, and petrogenesis. *Contr. Mineral. Petrology* 95, 407–419.
- Wilt J. 1995: Correspondence of alkalinity and ferric/ferrous ratios of igneous rocks associated with various types of porphyry copper deposits In: Pierce F.W., Bolm J. et al. (Eds.): Porphyry copper deposits of the American Cordillera Arizona. *Geol. Soc. Digest* 20, 180–200.