

## Geochemical Evolution of Rare Metal-Bearing A-Type Granites from the Aja Batholith, Hail Terrain, Saudi Arabia

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**Abstract:** The Aja Batholith, northeastern Arabian Shield, consists of five granite varieties namely: hornblende alkali feldspar granite, granophyre, arfvedsonite-aegirine alkali feldspar granite, porphyritic alkali granite and albite granite. Zircon, sphene, thorite, Samraskite, Ta-selenide, pyrochlore, fluorite, magnetite and hematite are magmatic rare-metal-bearing accessory minerals. In some rock varieties, hematite is post-magmatic where local metasomatic effects are visible in varying degrees and played a significant role in the genesis of silica-hematite-rich rocks (hematosilconite). The granite varieties in the batholith are highly siliceous ( $\text{SiO}_2=68\text{-}75\%$ ) with high  $\text{K}_2\text{O}$  (3.72-5.52%) and  $\text{Na}_2\text{O}$  (2.52-6.25%) and low  $\text{Al}_2\text{O}_3$  (8.35-13.5%),  $\text{MgO}$  (0.07-0.4%),  $\text{CaO}$  (0.17-1.5%), Ba (20-409 ppm) and Sr (6-134 ppm). The alumina saturation index (A/CNK) for most samples is  $< 1$  while the albitic index is  $> 1$  confirming their alkaline to peralkaline character. The granites have high and variable contents of Rb (81-495 ppm), Ga (20-52 ppm), Nb (10-414 ppm), Zr (290-31915 ppm), Y (22-552 ppm), Sn (3-101 ppm), and total rare earth elements (362-3518 ppm). These data indicate that the Aja batholith represents post-orogenic A-type granites. The generation of their parental magma probably involved partial melting of lower crustal rocks as a result of the decomposition of F-rich biotite. Comparison of the geochemical data with many specialized rare metal-bearing granites show that the Aja granites are enriched in Nb, Ta, Sn, Zr and REE, especially the arfvedsonite-aegirine alkali granite, the albite granite and the hematosilconite. Although the geochemical effects of metasomatism is locally visible; nonetheless, most of the chemical variations in the content of these elements appear to be the result of *in situ* fractional crystallization (feldspars, ferromagnesian minerals and rare metal bearing accessory phases) and fluorine complexing. The strong positive correlation of alkalis (Rb and K) that was mobile during metasomatism with elements that were not (Nb and Ta), argues strongly against metasomatic alteration in the granites. However, the hematosilconite is consistently rich in Fe, Si, Ca, Pb, Zn, Sn and poor in Na, K, Rb relative to the granites suggesting the local effect of metasomatism.

**Keywords:** Geochemistry, Petrogenesis, A-type granites, Rare-metals, Saudi Arabia.

### INTRODUCTION

Proterozoic granite complexes commonly exhibit an evolution from hornblende granite, to biotite granite to alkali feldspar and albite granite through magmatic differentiation processes that result in the formation of geochemically and mineralogically specialized end phases (Haapala, 1988; Rámó, 1991; Rámó and Haapala, 1995). Greisen-, pegmatite- and vein-type rare metal mineralizations are commonly associated with such late-stage highly fractionated granites (Haapala, 1988; Lehmann, 1990). The rare metal-bearing granites are thus specialized granites emplaced at relatively shallow crustal levels and associated with rare elements including Ta, Nb, Li, Rb, Cs, Sn, Zr, REE and W. In the Arabian Shield, granitoid rocks are formed during three main stages of the Neoproterozoic

crustal evolution, which are: (1) formation and accretion of island arcs in the period ~870–620 Ma, (2) continental orogenesis resulting from the collision with the northwestern margin of East Gondwanaland ~660–620 Ma, and (3) post-collision extension ~620–540 Ma (Greenwood et al. 1976; Schmidt et al. 1979; Stoeser and Camp, 1985; Króner, 1985; Johnson and Woldehaimanot 2003). The granites of the third stage (~620–540 Ma) attracted a great deal of interest (e.g. Stuckless et al. 1983; Drysdall et al. 1984; Du Bray, 1986; Ramsay, 1986; Ramsay et al. 1986; Sherbini and Qhadi, 2004; Qadhi, 2006) because some plutons are typically associated with high concentrations of rare metals such as Sn, U, Nb, Ta, Y, Zr and REE. Following these studies that have identified a group of metallogenetically specialized rocks in the Arabian Shield, the granites of the post-collision

stage should be extensively studied not only because of their geological implications, but also due to their huge economic significance.

At the Aja batholith, which is situated in the northeastern part of the Arabian Shield in Saudi Arabia (Fig.1, inset), high content of Sn and other rare metals (Zr, Nb, Ta, Y, REE) occur within highly evolved alkali feldspar and albite granite phases and also in pegmatite bodies that are spatially related to these granites. This study presents new petrological, major and trace elements for different types of granites located in the area, aiming to formulate a model for the origin and evolution of these granites and also determine the genetic relationship between the rare-metals and the granites.

**GEOLOGICAL SETTING**

The Aja complex, first named by Stoesser and Elliott (1980), comprises a group of granite varieties including

hypersolvus alkali feldspar granite, granophyre and albite granite. The complex covers the northern two-thirds of the Aja massif (Fig.1) with an area of about 4000 km<sup>2</sup> and it has been dated at 570±19 Ma (Stuckless et al. 1984). The granitic rocks of the Aja complex are divided into a peripheral zone and a core zone. The peripheral zone consists of porphyritic alkali feldspar granite and arfvedsonite-aegirine alkali feldspar granite that coincide with a prominent high radioactive anomalies and anomalous enrichment in REE and Nb, Ta, Y, and Zr. The core zone comprises granophyre and hornblende alkali feldspar granite. The porphyritic alkali feldspar granite forms the inner part of the peripheral zone of the batholith along its western side, while the arfvedsonite-aegirine alkali feldspar granite forms 1-7 km wide peripheral zone around two-thirds of the batholith to south, east and north (Fig.1). Alkali amphibole crystals in the arfvedsonite-aegirine granite show marked variation in abundance and size from place to place and locally form pegmatitic patches (appinite) of amphibole

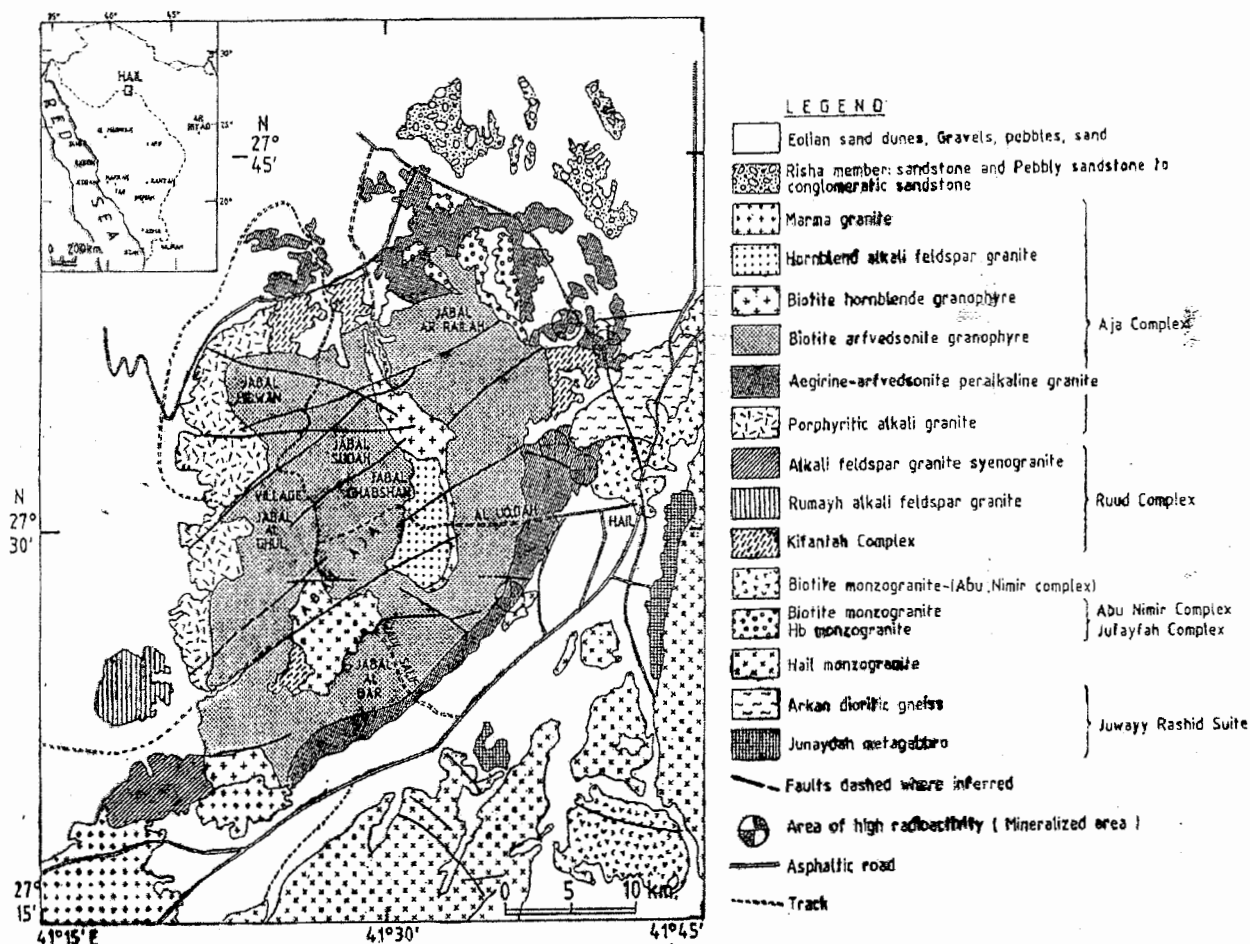


Fig.1. Geological map of the Aja batholith (modified from Ekren et al. 1987). Inset map shows the location of the study area near Hail city.

megacrysts (up to 10 cm long). The granophyre is considered by Ekren et al. (1987) as the chief unit within the core of the Aja batholith. However, detailed field survey shows a marked lithological variation from reddish to buff alkali-feldspar granite to medium-grained biotite granophyre. The contact between the two varieties is gradational and irregular.

The albite granite (Naysiyah apogranite) is a 0.7 km circular stock, approximately lies at about 10 km north of Hail city and NE of Aja batholith. The stock intrudes quartz diorite at sharp contact. It comprises fine-grained albite granite that was affected locally by silica-hematite alteration. The silica-hematite alteration also occurs as 500 × 200 m N-trending ridge in the eastern margin of Jabal Aja in contact with the arfvedsonite-aegirine alkali feldspar granite and has characteristic blackish brown, blackish gray, brown to deep reddish brown colours. They are inequigranular and their contacts with the adjacent granite is gradational and irregular. The intensity of alteration is not uniform within the ridge, which is manifested by the variation in colour, grain size, and degree of silicification.

#### PETROGRAPHY

**Alkali feldspar granite** is the most abundant granite type in the Aja batholith. Based on texture and composition of the ferromagnesian minerals, it can be divided into hornblende alkali feldspar granite, arfvedsonite-aegirine alkali feldspar granite, porphyritic alkali feldspar granite. All varieties are coarse-grained, hypersolvus and consist mainly of perthites and quartz. Aegirine (Fig. 2a), arfvedsonite, hornblende and biotite together with accessory zircon (Fig. 2b), iron oxides, sphene, apatite and allanite occur variably in these rocks. Fluorite occur as anhedral grains filling the interstices between the rock constituents. Evidence of secondary reactions on the alkali feldspar granite include: (1) the varying degrees of sericitization of feldspars and the presence of thin albite rims along the outer periphery of the perthite grains, (2) the presence of swapped rims between adjacent feldspar grains, and (3) the replacement of arfvedsonite and biotite partially by a mixture of ilmenite and chlorite. However, these secondary features are very minor in distribution.

**Granophyre** is equigranular, fine-to medium-grained, and consists of alkali-feldspar, quartz and minor biotite and plagioclase. Alkali feldspar and quartz show intergrowth and well developed granophyric and graphic textures (Fig. 2c). Accessory minerals include fluorite (Fig. 2d), zircon and deep brown opaque minerals. The biotite flakes commonly occur in cluster aggregates with fluorite and iron oxides.

**Albite granite** is inequigranular, fine-grained and

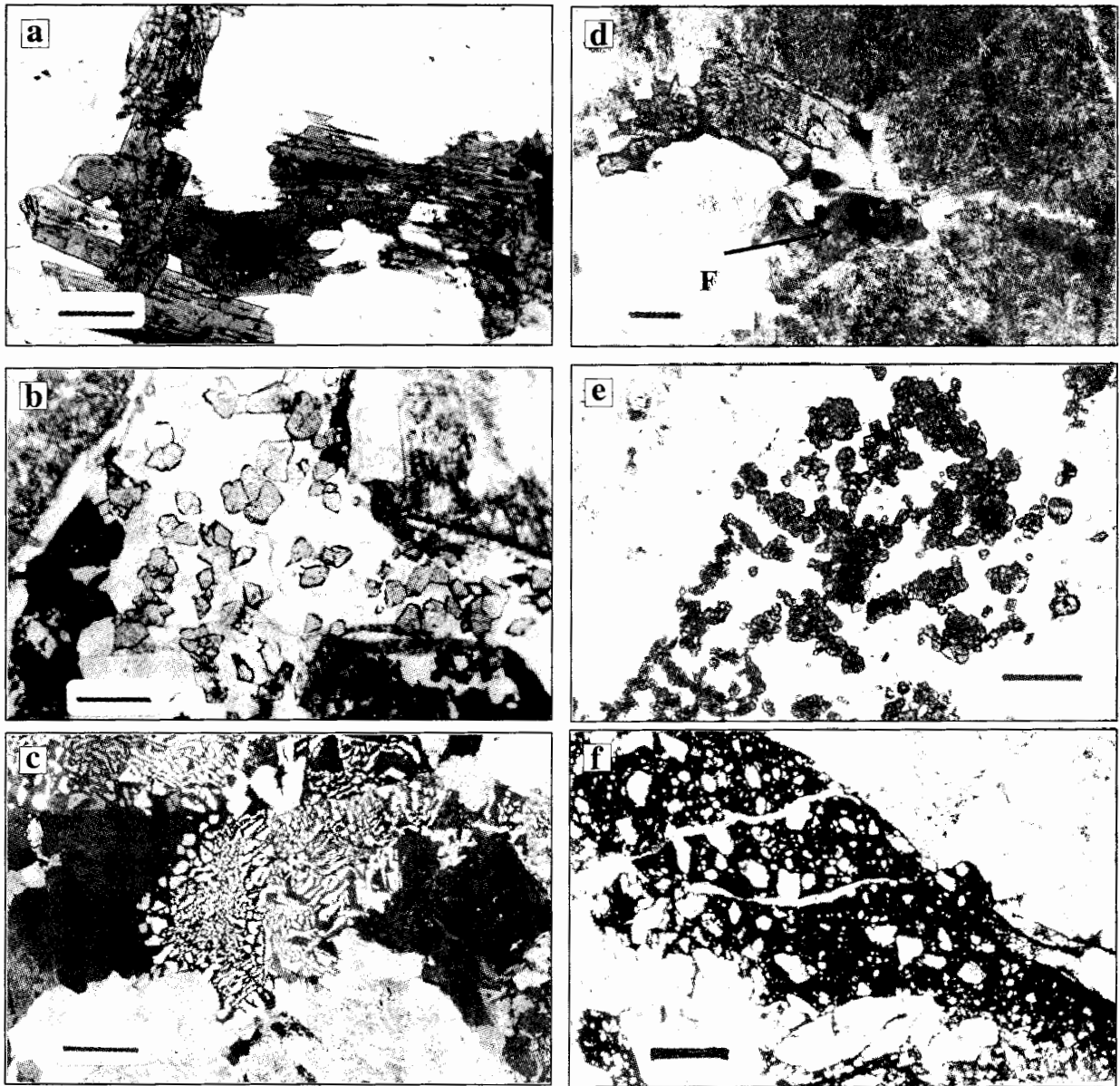
porphyritic with pale pink to pinkish white colour. The rocks are locally affected by silica-hematite alteration and become of reddish brown colour. In the least altered samples, the rocks consist of quartz, alkali-feldspar, albite, aegirine and riebeckite. Accessory minerals are relatively abundant including zircon, thorite (Fig. 2e), fluorite and deep brown opaque minerals.

**Silica-hematite rocks** consist of quartz and hematite that form more than 90% of the rock (Fig. 2f). Quartz is an essential component and occurs in three types. The first type is coarse- to medium-grained, anhedral and highly resorbed crystals, which impart to the rock a porphyrosomatic texture. It is highly deformed with development of undulose extinction. This type represents a magmatic mineral phase from the original granitic rock. The second type is the most abundant, frequently occurs as micro- to cryptocrystalline aggregates forming the rock matrix. It is often recrystallized as patches in the rock. The third type is subhedral to euhedral formed due to crystal growth. Iron oxides are represented by hematite and rare magnetite which occur as very fine-grained crystals with anhedral form. The amount of iron oxides varies even in the same sample and results in colour variation.

On the basis of petrographic study, two samples (A34 = albite granite and A18 = aegirine-arfvedsonite alkali feldspar granite) were selected and adopted for heavy mineral separation and subsequent XRD analysis. The diffractograms are shown in Fig. 3. Minerals of economic importance in the investigated rocks are subdivided into three groups: (1) the REE-bearing minerals (i.e. minerals which have high REE content) include allanite, xenotime, apatite, zircon, titanite and fluorite, (2) Nb-Ta-bearing minerals including Tasekenite, samarskite, and pyrochlore, (3) Th-U-bearing mineral such as thorite. It is worthy to mention that atomic substitution of REE, Y, Ta, Nb, Th, U and Zr elements are common and characteristic features among the above-mentioned minerals.

#### GEOCHEMISTRY

Based on the petrographic investigations, 34 representative samples covering the different granite varieties were selected for major and trace element analyses. Major element compositions and Sc, Ba, and Ni abundances were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The remainder of trace elements and the rare earth elements (REE) were determined by inductively coupled plasma-mass spectrometry (ICP-MS). All the analyses were carried out at the ACME analytical laboratories Ltd., Canada. Analytical precision,



**Fig.2.** Photomicrographs of the Aja granites: (a) Aegirine crystals with green colour partially altered to arfvedsonite, PPL, bar scale = 1.6 mm, (b) Cluster aggregate of subhedral to euhedral zircon crystals in the aegirine-arfvedsonite alkaline granite, PPL, bar scale = 1.6 mm, (c) Well developed granophyric texture in the granophyre, CN, bar scale = 1.6 mm, (d) Anhedronal fluorite crystal (F) with deep blue colour, PPL, bar scale = 1.6 mm, (e) Thorite crystals clustered in aggregates in the albite granite, PPL, bar scale = 0.8 mm, (f) Highly altered granitic rock with blackish brown iron oxides and micro-to cryptocrystalline quartz, PPL, bar scale = 3.2 mm.

as calculated from replicate analyses, is 0.5% for major elements and varies from 2-5% for trace elements of >80 ppm, 2-10% for trace elements of 10-80 ppm, and 5-20% for trace elements of <10 ppm.

#### Major and Trace Element Variations

Chemical analyses of the different granitic types encountered in the Aja batholith are presented in Table 1.

The rocks are classified using R1-R2 diagram (Fig.4a) of de la Roche et al. (1980) and Bachelor and Bowden (1985). All the investigated samples fall in the field of anorogenic and post-orogenic granite and follow the alkaline trend. Using the classification scheme of Shand (1927), most of the studied granite samples plot entirely in the peralkaline field (Fig. 4b). Some samples of the biotite granophyre and hornblende alkali feldspar granites are metaluminous to

Table 1. Chemical data (Major and trace elements) of the Aja granites

No.	Granophyre							Hb alkali feldspar granite				Albite granite					
	A-19	A-20	A-21	A-22	A-23	A-33	A-47	A-25	A-26	A-27	A-41	A-37	A-3	A-5	A-34	A-45	A-31
SiO <sub>2</sub>	74.95	71.85	73.10	74.32	75.03	74.75	75.04	72.66	74.60	64.52	71.09	70.51	72.77	68.64	72.61	73.03	73.66
TiO <sub>2</sub>	0.18	0.33	0.16	0.12	0.13	0.13	0.17	0.27	0.15	0.29	0.51	0.50	0.19	0.26	0.47	0.35	0.26
Al <sub>2</sub> O <sub>3</sub>	11.79	12.37	12.79	12.33	11.92	12.04	12.10	10.66	10.28	13.49	10.60	11.15	9.82	9.13	8.35	10.99	8.96
Fe <sub>2</sub> O <sub>3</sub>	1.82	2.86	2.02	1.59	2.02	1.80	1.79	5.24	3.92	7.20	6.01	6.16	5.81	9.63	5.62	4.31	8.55
MnO	0.04	0.06	0.03	0.04	0.05	0.05	0.03	0.03	0.02	0.06	0.19	0.14	0.09	0.14	0.12	0.08	0.03
MgO	0.19	0.29	0.18	0.14	0.12	0.16	0.14	0.18	0.13	0.32	0.22	0.18	0.38	0.16	0.18	0.08	0.31
CaO	0.90	0.90	0.58	0.45	0.57	0.51	0.46	0.56	0.50	1.46	0.83	1.29	0.28	1.78	0.17	0.42	0.18
Na <sub>2</sub> O	3.36	3.48	3.58	4.01	3.82	3.84	3.40	2.54	2.70	6.25	3.65	4.24	4.08	2.52	3.92	3.98	2.81
K <sub>2</sub> O	4.59	4.81	5.09	5.25	4.96	5.35	5.47	5.29	5.84	4.59	4.96	4.62	4.26	3.85	3.72	5.52	3.26
P <sub>2</sub> O <sub>5</sub>	0.01	0.04	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.04	0.03	0.06	0.01	0.01	0.02	0.01	0.01
LOI	1.50	1.30	1.40	0.60	0.60	0.60	1.10	1.30	1.50	0.60	1.50	0.70	1.00	2.30	0.50	0.80	1.10
Sum	99.33	98.29	98.94	98.86	99.23	99.24	99.72	98.75	99.65	98.82	99.59	99.55	98.69	98.42	95.68	99.57	99.13
Ni	9	1	5	6	6	5	2	7	3	3	5	3	2	3	2	7	1
Co	1	2	4	2	2	2	3	1	1	1	1	3	1	2	2	1	2
Sc	1	2	1	1	1	1	1	1	1	5	1	5	1	1	1	1	1
V	3	6	3	3	3	3	3	3	3	5	3	7	3	3	8	3	7
Cu	11	5	15	26	19	11	4	19	15	9	20	13	23	26	15	15	10
Pb	19	4	27	17	17	21	13	16	13	15	9	22	27	29	69	16	32
Zn	111	24	97	71	76	87	101	273	71	33	119	32	96	896	415	47	244
Sn	16	3	19	11	16	10	10	14	10	5	9	9	15	27	101	8	17
W	5	1	24	28	29	49	29	11	7	1	8	33	22	33	19	31	34
Rb	226	81	239	231	243	229	191	250	192	114	136	149	316	347	495	159	195
Cs	2.0	2.0	2.0	2.0	2.0	2.0	1.0	1.0	1.0	2.0	1.0	3.0	1.0	3.0	3.0	1.0	1.0
Ba	35	245	60	97	30	88	120	29	141	1408	66	409	20	86	37	74	25
Sr	17	87	17	20	11	20	21	11	24	134	19	55	8	22	25	20	15
Ga	30	20	33	29	31	31	27	44	29	22	33	30	42	47	52	33	37
Ta	11	1	9	6	10	8	5	8	5	1	7	5	6	11	39	6	9
Nb	11	17	95	70	99	76	56	90	63	10	90	63	60	130	414	67	126
Hf	23	12	14	13	13	15	15	36	11	13	28	26	35	61	953	23	19
Zr	501	570	342	305	294	379	432	1301	290	555	1088	1001	1287	2101	31915	914	720
Y	134	22	115	73	113	80	76	153	64	33	108	94	83	161	552	88	157
Th	62	13	35	35	39	30	25	33	23	12	21	18	16	40	90	18	38
U	15	2	11	11	15	11	9	11	8	3	7	8	9	14	62	6	11
La	100.4	128.7	88.7	75.2	86.9	80.9	76.1	190.4	58.5	126.0	138.7	104.4	89.7	205.0	689.4	109.5	198.0
Ce	224.2	252.9	176.9	157.7	188.5	171.3	149.6	412.1	126.7	217.9	294.2	218.9	195.7	438.5	1500.3	228.4	341.9
Pr	25.1	27.4	21.2	17.5	21.1	19.0	17.5	48.0	13.7	22.0	36.6	26.7	23.3	52.4	174.0	28.1	50.1
Nd	98.6	102.5	80.1	66.4	83.8	72.7	58.8	192.4	53.3	78.6	137.3	100.1	97.0	209.7	599.9	105.5	200.4
Sm	22.2	15.4	18.2	13.8	18.2	14.7	12.6	39.2	10.9	12.3	29.5	21.3	20.1	42.3	127.4	22.6	39.0
Eu	0.51	0.78	0.45	0.54	0.34	0.64	0.71	2.13	0.58	1.80	1.92	2.34	1.07	2.25	6.97	1.48	2.15
Gd	19.96	7.67	14.70	11.49	15.86	12.84	10.99	31.05	9.33	7.88	23.72	17.57	15.80	34.53	94.13	17.97	31.65
Tb	3.25	0.97	2.70	1.86	2.81	1.99	1.97	4.78	1.67	1.09	3.45	2.75	2.46	5.01	13.44	2.69	4.56
Dy	22.17	5.32	18.01	13.04	19.31	14.43	13.16	30.95	11.41	6.63	21.37	16.81	15.63	32.39	91.89	16.20	30.45
Ho	4.70	0.92	3.83	2.61	4.18	3.01	2.82	5.91	2.38	1.25	4.37	3.67	3.28	6.46	21.77	3.55	6.07
Er	14.10	2.74	12.11	8.07	12.27	8.97	7.92	16.92	7.14	3.48	11.94	10.37	9.86	19.32	74.05	9.63	17.82
Tm	1.83	0.28	1.52	1.05	1.63	1.17	1.05	2.03	0.90	0.35	1.58	1.39	1.21	2.42	11.86	1.24	2.22
Yb	12.49	2.42	10.30	7.51	10.46	7.98	7.37	14.03	6.08	2.59	10.96	9.72	8.53	17.97	95.87	8.51	15.56
Lu	1.84	0.39	1.47	0.99	1.48	1.13	1.06	2.00	0.88	0.41	1.63	1.52	1.36	2.67	16.62	1.31	2.19

Table 1. Contd..

No.	Aegirine-arfvedsonite alkali feldspar granite							Aegirine-arfvedsonite alkali feldspar granite					Hematisilconite				
	A-8	A-10	A-12	A-13	A-14	A-16	A-17	A-24	A-32	A-35	A-39	A-40	A-1	A-2	A-4	A-9	A-31E
SiO <sub>2</sub>	69.40	70.37	71.02	73.79	69.71	71.99	70.56	68.30	73.31	71.44	71.55	71.34	75.81	66.35	66.57	80.93	65.00
TiO <sub>2</sub>	0.54	0.38	0.46	0.41	0.26	0.24	0.40	0.50	0.18	0.37	0.43	0.47	0.13	0.32	0.24	0.30	0.37
Al <sub>2</sub> O <sub>3</sub>	10.45	10.24	10.30	10.45	12.53	10.49	9.83	11.74	9.62	10.80	11.17	11.05	12.50	10.85	11.54	6.12	2.46
Fe <sub>2</sub> O <sub>3</sub>	6.72	6.73	5.99	4.22	2.88	5.34	6.94	5.97	5.28	5.13	5.65	5.43	4.99	12.57	11.60	8.23	8.83
MnO	0.17	0.12	0.13	0.06	0.06	0.11	0.13	0.12	0.08	0.11	0.14	0.12	0.05	0.04	0.04	0.01	0.20
MgO	0.39	0.15	0.08	0.08	0.44	0.09	0.10	0.19	0.07	0.13	0.12	0.14	0.05	0.18	0.17	0.04	0.25
CaO	0.66	0.55	0.56	0.47	1.34	0.56	0.64	0.89	0.31	0.70	0.53	0.88	0.32	2.43	2.56	0.07	2.97
Na <sub>2</sub> O	5.03	5.24	5.17	3.85	5.49	5.01	5.25	5.48	4.62	5.01	3.99	4.01	0.09	0.09	0.07	0.09	1.30
K <sub>2</sub> O	4.30	4.13	4.25	4.56	4.60	4.53	4.14	4.88	5.25	5.23	5.05	5.11	0.04	0.04	0.04	0.15	0.41
P <sub>2</sub> O <sub>5</sub>	0.02	0.01	0.01	0.01	0.08	0.01	0.02	0.05	0.01	0.02	0.03	0.02	0.03	0.04	0.06	0.02	0.04
LOI	0.90	0.70	0.60	0.80	1.10	0.40	0.50	0.80	0.40	0.40	0.90	1.00	5.60	6.30	6.60	2.90	5.00
Sum	98.58	98.62	98.57	98.70	98.49	98.77	98.51	98.92	99.13	99.34	99.56	99.57	99.61	99.21	99.49	98.86	86.83
Ni	5	2	5	3	2	5	6	3	6	2	4	1	3	5	3	1	7
Co	1	1	1	1	3	1	1	2	2	3	2	1	1	2	2	1	1
Sc	2	1	1	1	3	1	1	4	1	1	3	3	1	1	1	1	21
V	3	3	3	3	12	3	3	3	3	3	6	5	13	17	17	3	3
Cu	15	19	17	4	15	13	12	12	14	13	15	3	12	16	12	20	73
Pb	65	36	42	20	35	28	27	15	28	18	22	22	17	26	24	47	2922
Zn	139	108	177	60	60	68	71	58	54	26	71	86	50	34	34	29	3492
Sn	14	13	15	9	12	7	10	9	10	9	8	9	8	31	28	53	275
W	7	1	1	28	2	8	6	16	100	21	12	1	9	2	2	15	24
Rb	149	160	171	149	357	170	164	156	210	153	134	136	3	5	5	10	83
Cs	2.0	1.0	1.0	1.0	7.0	1.0	1.0	1.0	1.0	2.0	1.0	2.0	-	1.0	1.0	1.0	-
Ba	53	35	21	23	342	21	21	237	23	57	322	237	27	51	56	20	156
Sr	13	10	11	9	124	11	8	35	6	14	37	28	17	44	43	8	141
Ga	35	36	37	35	36	35	34	37	38	38	31	30	43	41	43	29	1
Ta	16	8	10	6	12	6	6	5	9	6	5	6	5	14	12	30	370
Nb	212	109	126	72	140	71	79	71	102	73	64	70	52	160	135	338	9706
Hf	33	19	30	22	38	16	20	26	34	33	23	26	29	87	71	166	202
Zr	1189	653	1064	826	1093	596	781	956	1319	1309	924	974	1102	2850	2537	5622	8048
Y	254	137	136	91	196	78	122	93	147	96	86	96	86	203	189	402	3678
Th	41	31	30	18	44	19	22	19	27	17	18	18	18	43	43	77	1538
U	13	8	9	7	17	6	7	6	9	6	8	7	9	15	14	44	1686
La	246.4	163.6	197.6	124.0	57.1	139.8	145.8	215.9	130.3	123.1	104.9	129.4	127.2	76.7	66.6	401.9	10425.4
Ce	539.4	359.2	418.6	236.4	148.8	314.1	324.2	471.9	289.3	280.0	223.2	267.7	305.9	151.8	181.1	1131.1	21022.3
Pr	65.6	42.9	48.3	31.5	20.2	37.1	38.7	52.7	34.8	33.5	26.5	33.5	32.5	11.2	10.8	93.3	2250.5
Nd	264.6	177.6	194.4	134.0	94.6	152.2	161.9	204.5	142.8	139.2	100.3	124.9	134.0	46.5	43.5	327.9	8053.6
Sm	62.3	37.0	37.8	26.6	29.0	29.2	33.4	37.1	30.0	26.8	20.7	26.8	25.4	13.4	12.7	65.7	1557.2
Eu	3.69	2.06	2.21	1.47	1.82	1.54	1.73	2.51	1.78	1.74	2.09	2.49	1.29	1.09	1.05	3.90	90.89
Gd	53.17	31.20	29.75	20.14	32.06	21.62	26.69	25.51	26.10	21.12	16.98	21.66	20.05	21.41	18.88	52.79	1153.28
Tb	8.27	4.38	4.48	2.81	5.64	2.77	3.90	3.43	4.11	3.11	2.60	3.24	2.62	4.77	4.42	10.80	153.89
Dy	52.11	28.29	27.86	17.49	37.19	16.73	24.05	19.77	26.52	19.68	16.21	19.25	16.14	35.25	33.06	74.57	792.60
Ho	10.24	5.52	5.43	3.51	7.47	3.08	4.85	3.89	5.40	3.85	3.31	3.69	3.12	7.96	7.09	16.31	136.08
Er	26.93	15.95	15.46	10.02	20.98	8.79	13.78	11.19	15.71	10.98	9.66	10.47	9.11	23.54	21.12	46.59	287.81
Tm	3.12	1.90	1.93	1.22	2.35	1.14	1.65	1.41	1.95	1.39	1.33	1.37	1.10	2.99	2.69	5.83	31.95
Yb	19.99	13.09	13.62	8.20	15.54	8.72	11.58	9.57	12.58	9.75	9.22	10.13	7.93	21.10	19.50	39.62	172.23
Lu	2.80	1.92	2.08	1.22	2.07	1.34	1.60	1.48	1.89	1.45	1.28	1.41	1.19	3.29	2.95	5.76	19.90



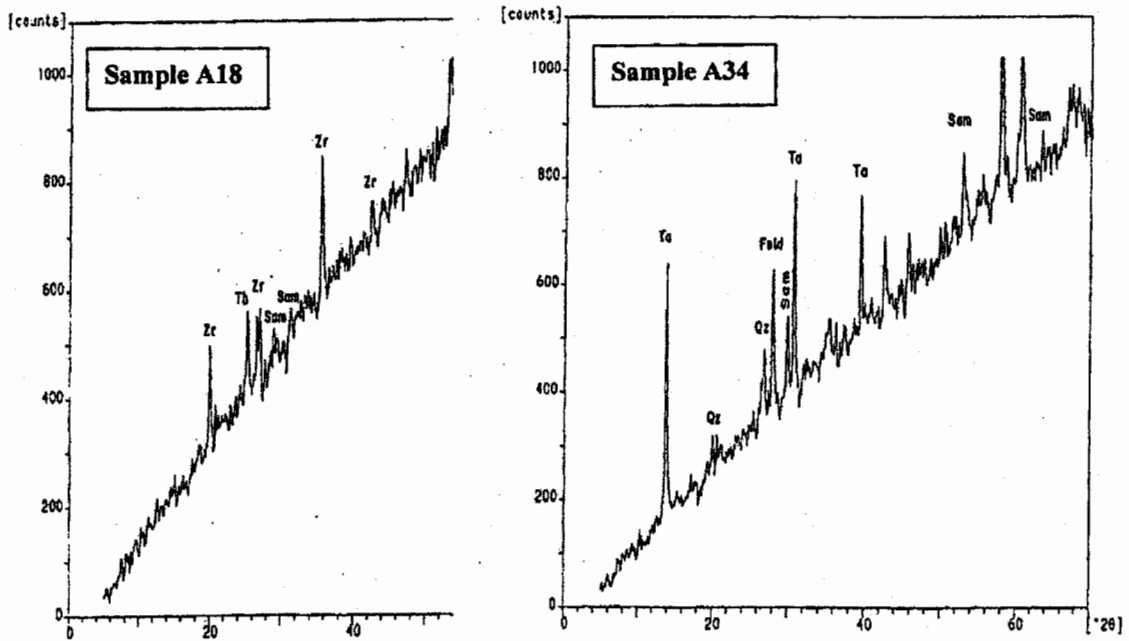


Fig.3. Diffraction patterns of heavy mineral separates in two samples (A-18 = aegirine-arfvedsonite alkali feldspar granite and A34 = albite granite) from the Aja granites. Mineral symbols are as follows: Zr=zircon, Th=thorite, Sam=samarskite, Ta=Ta-selenide, Qz=Quartz, Feld=feldspar.

mildly peraluminous in character ( $A/NK > 1$  and  $A/CNK = 0.9-1.12$ ). In the normative Q-Ab-Or diagram (Fig.4c), the biotite granophyre and the hornblende alkali feldspar granites are clustered close to the minimum melt composition at 0.5- 5 kbar and  $a_{H_2O} = 0.5-0.3$ . The composition of the aegirine arfvedsonite granite follow a trend toward the Ab corner and the Ab-Q side line of the diagram, reflecting the added Li and F in the melt (Manning, 1981; London, 1987).

The chemical variations of some major elements are shown on Harker variation diagrams (Fig.5). The studied granites display regular variations of decreasing  $TiO_2$ ,  $Fe_2O_3$ , CaO, MgO, and  $Na_2O+K_2O$  with increasing  $SiO_2$ . In contrast, the  $Al_2O_3$  show scattered variation with increasing  $SiO_2$ . These variations reflect the important role of mineral fractionation (e.g. feldspar and ferromagnesian minerals) in the evolution of the Aja granites.

The element enrichment and depletion in the studied rocks are demonstrated on primordial mantle-normalized diagrams (Fig.6). The aegirine-arfvedsonite and the albite granites have similar patterns with lack of negative Nb anomalies. Both rock types show strong Ba, Sr and Ti anomalies that reflect the role of feldspar and iron oxides as major fractionating phases. The albite granite shows much higher Th, U, Hf, Zr and Sm enrichment (400-4000 time the mantle values) than the aegirine arfvedsonite granite (100-600 time higher than the mantle values). Comparing

with the aegirine-arfvedsonite and the albite granites, the trace element patterns of the granophyre and the hornblende alkali feldspar granites are characterized by similar trace element distribution patterns, but with small negative Nb anomalies. The hematossilconite rocks, which represent the altered part of the granite, have similar patterns with but with marked enrichment in Th, U, Nb, La, Ce, Nd, and stronger negative K, Rb, and Cs anomalies.

Rare earth element data are depicted in chondrite-normalized diagrams (Fig.7), using the normalizing values of Sun (1982). The granophyre and the hornblende alkali feldspar granite show regular and similar REE patterns, but the granophyre has less fractionated pattern and lower total REE ( $La/Yb_n = 5.01-6.72$ ;  $\Sigma REE = 452$  ppm, on average) than the hornblende alkali feldspar granite ( $La/Yb_n = 6.26-31.22$ ;  $\Sigma REE = 606$  ppm, on average). The aegirine arfvedsonite granite show moderately fractionated patterns ( $La/Yb_n = 2.4-14.7$ ;  $La/Sm_n = 1.2-3.49$ ) and display pronounced negative Eu anomalies ( $Eu/Eu^* = 0.18-0.34$ ). The albite granites have higher total REE and more fractionated HREE ( $\Sigma REE = 1407$  ppm, on average;  $Gd/Yb_n = 1.23 - 2.64$ , respectively) than the aegirine arfvedsonite granite ( $\Sigma REE = 606$  ppm, on average;  $Gd/Yb_n = 2.3 - 3.33$ , respectively). The hematossilconite shows fractionated REE patterns ( $La/Yb_n = 2.22-3.9$ ;  $Gd/Yb_n = 1.27-8.37$ ) and similar strong negative Eu anomalies ( $Eu/Eu^* = 0.19-0.21$ ) to those of the alkali

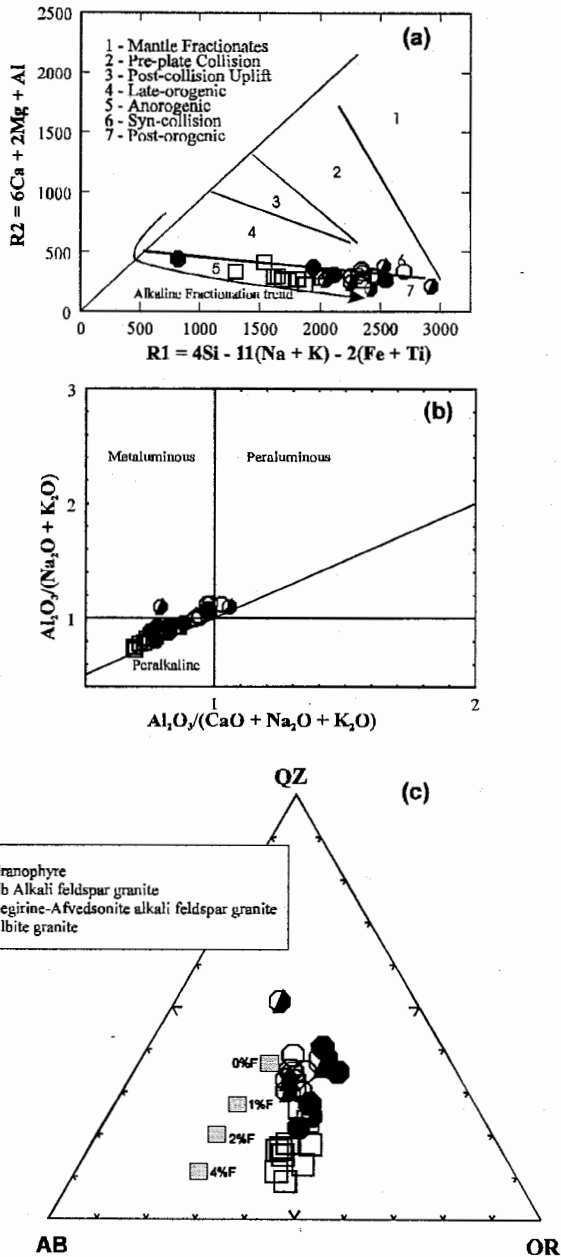


Fig.4. (a) R1-R2 diagram (Batchelor and Bowden, 1985), (b) a plot of Shand index (A/CNK vs. A/NK) for the studied granitoids; discrimination fields are from (Maniar and Piccoli, 1989), (c) Normative Q-Ab-Or plot of the investigated granites. Grey squares are minimum normative composition for the haplogranite system with 0, 1, 2 and 4% added fluorine at 1 kbar (Manning, 1981).

feldspar granite. They are characterized by marked enrichment in total REE ( $\Sigma\text{REE} = 10100$  ppm on average).

**Tectonic Setting**

The Aja granites correspond to “within-plate granite”

on the tectonic discrimination diagrams of Pearce et al. (1984) attesting to their derivation from sources consistent with an extensional tectonic environment (Fig.8a). The mineralogical features exhibited by the investigated granites that characterize A-type granites are: (1) hypersolvus feldspar assemblages, (2) presence of sodic-amphiboles and aegirine, (3) abundance of fluorite and (4) presence of REE bearing accessory minerals (Pitcher, 1993). Relative to I- and S-type granitoids, A-type granites typically have chemical compositions with high SiO<sub>2</sub>, F, Zr, Nb, Ta, Ga, Sn, Zn, Y, REE and Fe/Mg and low concentrations of CaO, Al<sub>2</sub>O<sub>3</sub>, Ba, and Sr (Whalen et al. 1987; Eby 1990). For the investigated granites, high FeO\*/MgO ratios and elevated concentrations of high-field strength (HFS) elements such as Zr, Nb, REE, and Y are especially characteristic for A-type granites (Fig.8b).

**DISCUSSION**

**Magma Source**

Many studies, based on isotopic research, have shown that the original magmas of some A-type granites are of mantle origin (Turner et al. 1992). On the other hand, the primitive isotopic signature of A-type granites has been interpreted as juvenile crust signature and they originated either by: (1) partial melting of F- and/or Cl- enriched dry, granulitic (or charnockitic) residue from which I-type granitoid melt was previously extracted (Collins et al. 1982) or (2) dehydration melting of calc-alkaline granitoids in the middle or lower crust (Skjerlie and Johnston, 1993; Patino Douce, 1997).

The hypothesis suggesting the derivation of post-orogenic A-type granites by fractional crystallization from a basic mantle-derived parental magma in the Arabian-Nubian Shield is suggested by many authors (Stern and Gottfried, 1986; Jarrar, et al. 1993; Beyth et al. 1994). The model involves the generation of a mafic magma by partial melting of a lithospheric mantle source in an extensional environment. This magma fractionated towards andesitic composition by separation of pyroxene, amphibole, plagioclase and Fe-Ti oxides. With further removal of plagioclase, hornblende, Fe-Ti oxides, the magma evolved towards A-type granite (Stern and Gottfried, 1986). In the Arabian Shield, mafic rocks of comparable age exist (e.g. 600 - 555 Ma Shammar Group; Hadley and Schmidt, 1980). However, the relatively small volume of these rocks and the lack of compositionally transitional series of the same age argue against these rocks representing parental magmas for the A-type granites.

Previous investigations of post-orogenic granites in the



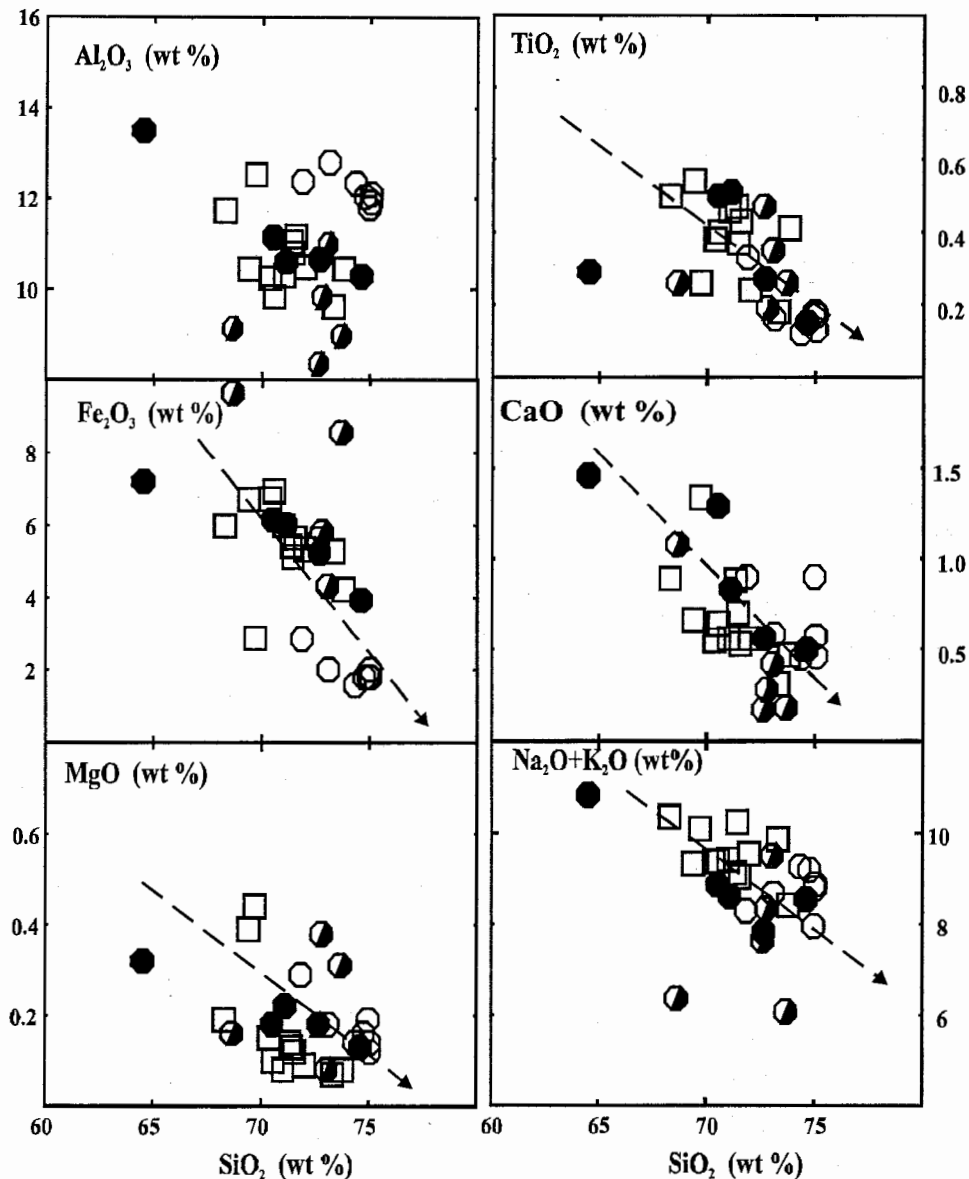


Fig.5. Harker variation diagrams of some major elements in the Aja granites. The plotted trends are visual estimate and show the evolution from the least evolved to the highly evolved granite samples. Symbols as in Fig.4.

Arabian Nubian Shield (e.g. Sylvester, 1989; Küster and Harms, 1998; Moufti et al. 2002) pointed towards crustal origin for these rocks by partial melting of lower crust followed by fractional crystallization (Landenberger and Collins, 1996; King et al., 1997). Although it has been proposed that A-type granites originated from the partial melting of F- and/or Cl-enriched dry granulitic (or charnockitic) residue from which a granitoid melt was previously extracted (Collins et al. 1982; Clemens et al. 1986; Landenberger and Collins, 1996; King et al. 1997), this residual model cannot explain the geochemical characteristics of subsequent A-type granites (Creaser et al.

1991). Geochemically, enriched or anomalous sources are not required for the generation of rare-metal A-type granites such as the Aja granites (Christiansen et al. 1986). Also, the generally alkaline to peralkaline nature of the Aja granites and their shallow level of emplacement suggest that they are not evolved S-type granites derived from partial melting of pelitic sedimentary rocks.

According to experimental studies (Skjerlie and Johnston, 1993; Patino Douce, 1997), dehydration melting of calc-alkaline granitoids in the shallow crust (at depths of 15 km or less) is a likely origin for A-type granites. The Neoproterozoic crust in the Arabian Shield is juvenile

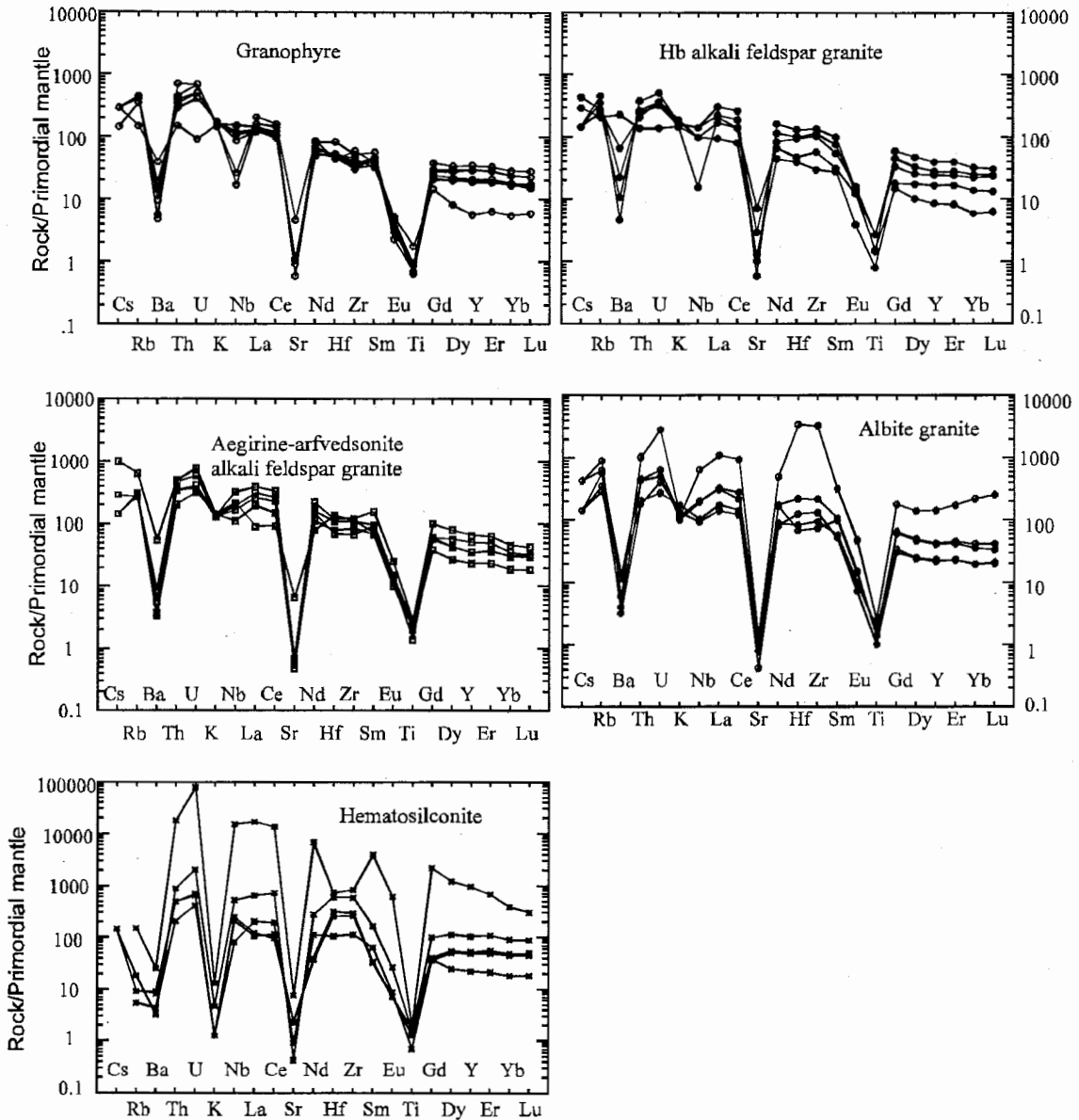


Fig.6. Primitive mantle-normalized multi-element diagrams for the Aja granites. Normalizing values are from Sun and McDonough (1989).

(600 - 900 Ma) and composed of mafic layer of modified oceanic crust (Gettings et al. 1986; McGuire and Stern, 1993) overlain by an island arc association of calc-alkaline rocks dominated by tonalite and granodiorite (Jackson, 1986). These rocks are attractive sources to produce melts of granitic composition at shallow crustal levels (Skjerlie and Johnston, 1993; Patino Douce, 1997). Thus, it is possible that the studied A-type granites could have been derived by partial melting of the older (850-690 Ma) calc-alkaline granitoids in the Arabian Shield. The main heat source of partial melting of these rocks is via underplating of mafic magma, such as that of the temporally associated

post-orogenic volcanics and mafic dykes in the Arabian Shield (Johnson, 2003).

**Evolution Processes and Origin of Rare Metal Enrichments**

Reviews of the published work concerning the enrichment of ore elements in silicic rocks indicate three major models: (1) fractional crystallization (Lehmann, 1982; Christiansen et al. 1986; Pollard et al. 1987; Clarke et al. 1993; Dostal and Chatterjee, 1995), (2) fluorine complexing (Taylor et al. 1981; Webster and Holland, 1988), and (3) interaction of the melt with hydrothermal aqueous fluids (Higgins et al. 1985; Nurmi and Haapala, 1986).

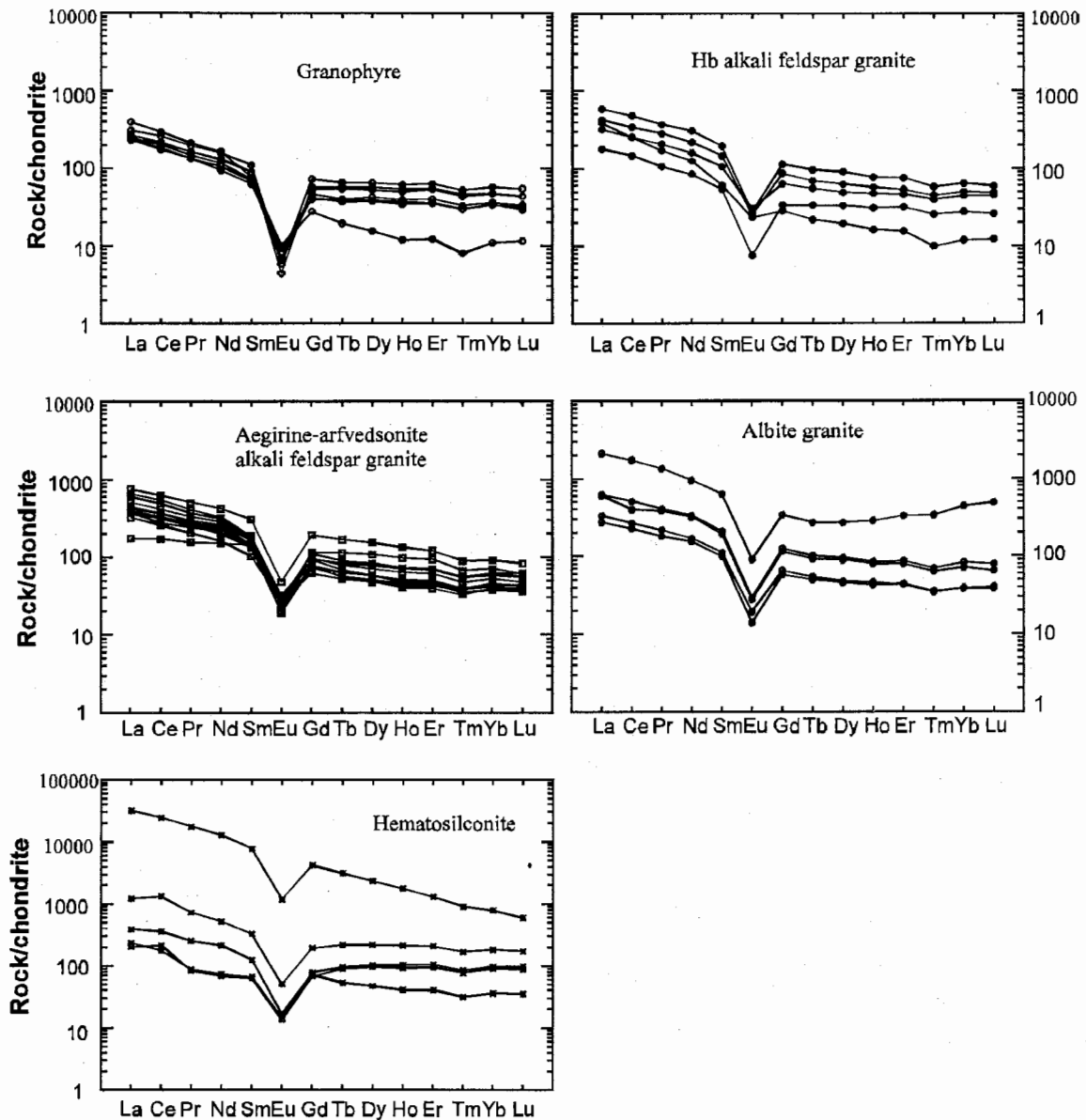


Fig.7. Chondrite-normalized REE patterns of the Aja granites. Normalizing values are from Sun (1982).

### Fractional Crystallization

The following field, petrographic and geochemical observations argue strongly for a comagmatic origin of the different granite varieties in the Aja granite batholith: (1) intrusive sharp contact with the country rocks with no alteration in the country rocks, (2) gradational contact between the different granite varieties that means comagmatic relationship, (3) the magmatic textures and mineralogy (euhedral aegirine laths aligned along growth planes of quartz and K-feldspar) indicate that aegirine was an early magmatic phase and (4) replacement textures of albite after K-feldspar (evidence of metasomatism) in the

alkali feldspar granite and albite granite are very minor and do not agree with the percolation of a large amount of fluid through the pluton required by a metasomatic process. Geochemically, some compositional variations observed in the Aja granite batholith (Fig.5) are compatible with partitioning of elements between a silicic melt and minerals crystallizing from that melt (e.g. plagioclase, alkali feldspar, and biotite). Moreover, the trends defined by the LILE (Rb, Ba, Sr, and K) in log-log diagrams can be interpreted in terms of main evolutionary processes through the successive steps of a magmatic suite (McCarthy and Hasty 1976; Tindle and Pearce, 1981; Brown et al. 1984; Charoy and Raimbault,

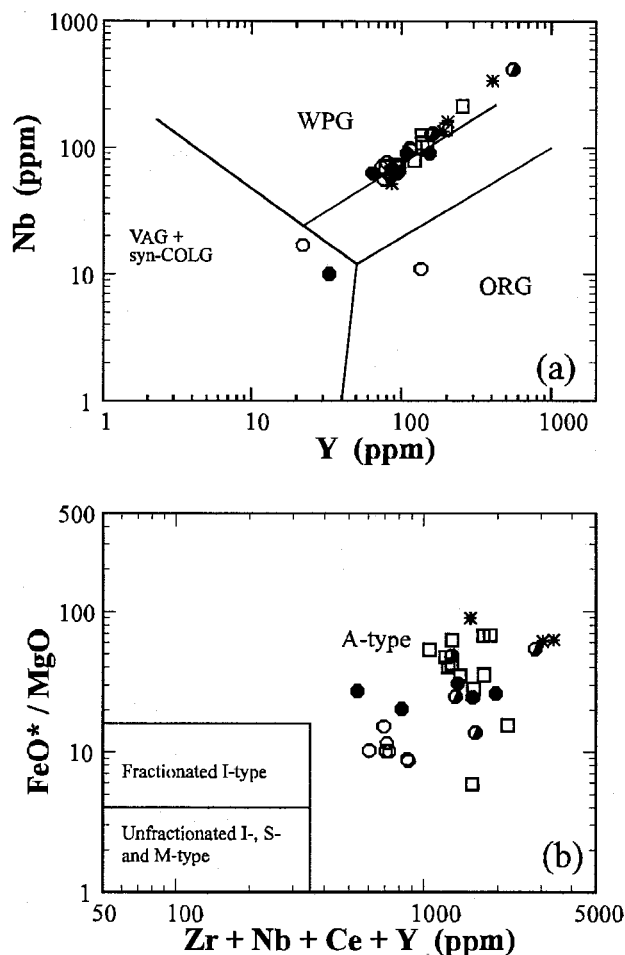


Fig. 8. Tectonic discrimination diagrams for the Aja granites. (a) Rb vs. Y+Nb diagram (Pearce et al. 1984), (b) FeO\*/MgO vs. Zr+Nb+Ce+Y diagram (Whalen et al. 1987). Symbols as in Fig. 4.

1994) where linear trends are likely to result from Rayleigh fractionation (McCarthy and Hasty, 1976). Figures 9a-c represents logarithmic plots of Sr vs. Rb/Sr, Rb vs. K/Rb and Rb vs. Sn (elements whose concentrations are controlled by feldspar and biotite fractionation). The element variations define two linear trends. The first trend represents granitic rocks and is continuous (without compositional gap between all varieties) indicating that all the granitic varieties are comagmatic and their evolution is mainly controlled by fractionation of feldspars and mica. The second trend represents the altered rocks (hematosilconite), which are characterized by lower Rb, Rb/Sr and K/Rb relative to the granitic rocks. The importance of trace or accessory minerals in controlling the composition of the Aja granites is well-displayed by Zr-Hf, Ta-Nb, and Th-U variations (Figs. 9d-f). The variations in these elements show strong

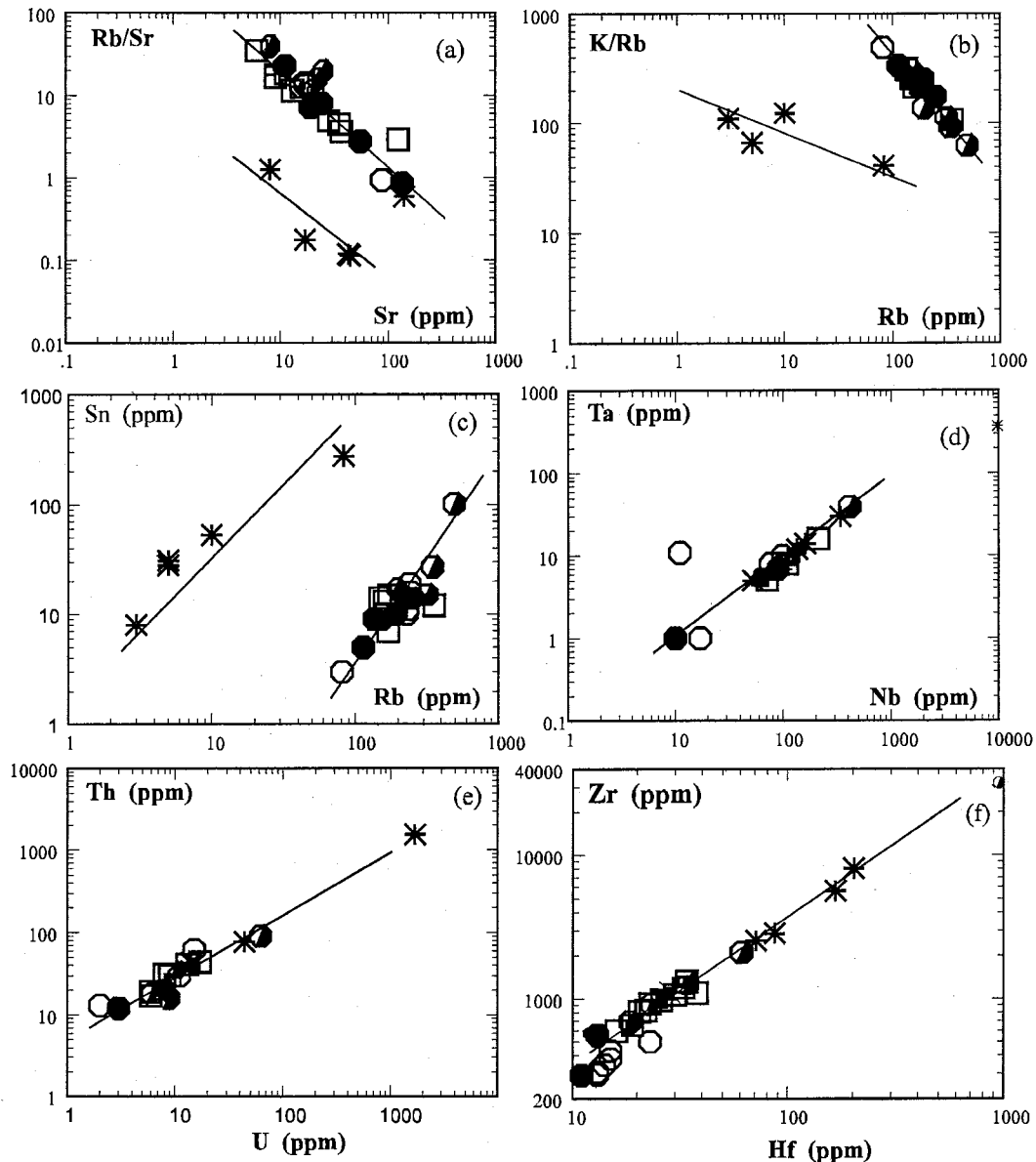
linear correlations that emphasize that they are strongly controlled by magmatic fractionation of accessory minerals (Lehmann, 1982; Lehmann and Mahawat, 1989; Charoy and Nornoha, 1996). The binary scatter diagram of Th vs. U shows strong positive correlation that indicates a magmatic behaviour of Th and U during magmatic differentiation. The Th/U ratios in the Aja granites are very close to 2.5–3.5 which is very close to the Th/U in igneous systems (Levinson, 1974).

#### Fluorine Complexing

Comparing the granitoid rocks of the Aja batholith with many A-type granites show that the Aja granites, especially the albite granite and the aegirine-arfvedsonite alkali feldspar granite, are highly enriched in Ta, Nb, Y, Zr and REE. This enrichment cannot be explained by normal fractionation and may suggest processes other than differentiation that may contribute to the abundance of these elements. The effects of fluorine in granites is well known and it is suggested that the F-rich fluid could produce HREE and HFSE enrichment in the late stages of evolution of granitic melt due to F complexing (Dingwell, 1988; Rogers and Satterfield, 1994). The addition of F into the melt promotes the formation of  $\text{SiO}_3\text{F}$  complexes of HREE and HFSE, resulting in depolymerization and reduction in the availability of  $\text{SiO}_4$  tetrahedra to form HREE- and HFSE-bearing phases (Dingwell, 1988). The development of F-bearing fluids and their interaction with the silicic melt at the late magmatic stage enhance element fractionation, since the addition of fluorine decreases silicate melt viscosity (Mysen and Virgo, 1985) and expands the primary phase field of quartz (Manning, 1981; Manning and Pichavant, 1983), thus extending the duration of crystallization. In the studied granites, there is much evidence for the role of F-complexing in their evolution. Field evidence includes the presence of magmatic albite granite and pegmatite veins associated with ore minerals and fluorite. Geochemical evidence include the very high contents of HFSE and REE (Table 1), which are difficult to interpret by fractional crystallization alone and the evolution of the granites in a trend following the addition of F to the melt (Fig. 4c).

#### Metasomatism

Metasomatic processes may be especially effective in altering the magmatic composition of a variety of igneous rocks including rare metal granites. In fact, field and textural evidence supplemented with chemical data leave no doubt that the hematosilconite is the result of hydrothermal alteration. Two principal genetic models have been invoked for the hydrothermally altered rocks: a magmatic model



**Fig.9.** Variation diagrams of some trace elements and ratios in the Aja granites. The plotted trends are visual estimate and show the evolution from the least evolved to the highly evolved granite samples. Symbols as in Fig. 4.

(Clarke et al. 1993) as a result of magmatic differentiation and a metasomatic model (Higgins et al. 1985; Nurmi and Haapala, 1986) that envisages transformation of magmatic granite into altered granites by post-magmatic hydrothermal alterations. In the Aja granite batholith, the contacts between the silica-hematite alteration rocks and adjacent granite is gradational and irregular. The intensity of alteration is not uniform within these rocks, which is manifested by the variation in colour, grain size, degree of silicification.

Bulk rock analyses and petrographic studies of the altered rocks show that metasomatism mobilized Na, K, Rb, Fe, Zn, Pb, W and Sn (Table 1). These elements show enrichment

and depletions in the altered rocks beyond those explicable by normal variations of the granites. The unaltered rocks as a whole shows strong correlation between element pairs that respond very differently to metasomatism. The strong positive correlations of alkalis (i.e. Rb) that was mobile during metasomatism with elements that were not (Fig.9), argues strongly against metasomatic alteration in the granites. However, altered rocks are consistently rich in Fe, Si, Ca, Pb, Zn, Sn and poor in Na, K, Rb relative to the unaltered granites (Table 1 and Fig.9), which support the role of post-magmatic hydrothermal alteration in the origin of hematossilconite.

## CONCLUSIONS

The Aja batholith represents one of the largest peralkaline-alkaline A-type granite intrusions in the Arabian Shield. It consists mainly of alkali feldspar granite, granophyre, albite granite, and silica-hematite altered rocks (hematosilconite). The occurrence of aegirine-arfvedsonite granite as rim to the Aja batholith, the abundant pegmatite dykes and pods, the presence of miarolitic cavities and appinitic patches with megacrysts of alkali pyroboles as well as petrographic criteria of abundant fluorite, and subsolidus re-equilibration all suggest that the aegirine-arfvedsonite granite was crystallized from magma enriched in H<sub>2</sub>O and fluorine. The rock varieties are highly evolved and they were

emplaced during a post-orogenic tectonic event. Their origin is thought to have involved partial melting of a tonalitic source rock followed by fractional crystallization. High radioactive anomalies and enrichment in Nb, Th, U, Zr and REE are associated with the batholith. According to field data and geochemical studies, the enrichment in these metals appears to be the result of fractional crystallization (feldspars, ferromagnesian minerals and rare metal bearing accessory phases) and fluorine complexing. Local geochemical effect of hydrothermal alteration is visible in varying degrees in the granitic rocks and played a significant role in the genesis of the silica-hematite-rich rocks and their enrichment in rare metals. The hydrothermal alteration took place after complete solidification of the Aja granites.

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