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THE LANTHANIDE TETRAD EFFECTS AND ITS CORRELATION WITH NA_2O, K_2O, ALKLIS, AND ZR/HF INVOLVING GRANITOID ROCKS OF WADI KHARM EL BELAWI AREA, NORTHERN EASTERN DESERT, EGYPT

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ABSTRACT

The basement rocks in Wadi Kharm El Belawi area are represented by Dokhan volcanics, granodiorites and younger granites. They were produced from calc alkali magma, under a compress regional regime. The lanthanide tetrad effects are observed in the REE pattern of older granites and younger granites of Wadi Kharm El Belaw. The values, of t_l. t_3. t_4, $TE_{1,3}$ were calculated and plotted vs. Na_2O. K_2O, total alkalis and Zr/Hf. The diagrams reveal that the tetrad effect developed conformable with the evolution of the alkali feldspar granites, and significant tetrad effects are confined to highly differentiated samples. The strong decrease in the Eu concentration in the highly evolved rocks is related to Eu fractionation between the residual melt and a coexisting high temperature aqueous fluid. The results point to significant changes in element fractionation behavior in highly evolved granitic melts indicating that ionic radii and charge (which commonly control the element distribution between minerals and melt), are no longer the exclusive control.

Keywords: Lanthanide titrate, Dokhan volcanics, granodiorites and younger granites

INTRODUCTION

The behavior of the rare earth elements (REEs) has been intensively studied in the past decades, and it has been found that the behavior of the REEs in most geological environments can be accounted by differences in their ionic radii as well as variation in valence states. However, an additional feature in the distribution pattern of the REEs is the tetrad effects. This effect can cause a split of chondrite normalized REE patterns into four curved segments called tetrads (first tetrad La, Ce, Pr. Nd; second tetrad “Pm”, Sm. Eu, Gd; third tetrad Gd, Tb, Dy, Ho; fourth tetrad. Er, Tm, Yb, Lu). The curved segments are either convex (M-shaped) or concave (W-shaped) lanthanide distribution patterns respectively (Masuda et al., 1987). The tetrad effects are noticed in the granitoid rocks of Wadi Kharm El Belawi area. Central Eastern Desert (CED) of Egypt

GENERAL GEOLOGY AND PETROGRAPHY

Wadi Kharm El Belawi area is located between longitude 33° 45' -33° 50'E and latitude 26° 45' -26° 55'N. It is covers by Precambrian rocks including Dokhan volcanics, and granitoid rocks. A geological map of Wadi Kharm El Belawi area was prepared from the field studies with the aid of previous maps (Fig. l). The exposed Precambrian rocks in the study area are classified according to Takla (2002):

VI- Intra- Plate Magmatism and Sediments (within plate granites) Youngest

Younger granites

Dokhan Volcanics

IV- Subduction- Related Granitoids (Arc granites) Oldest

The Subduction-related older granitoid (Arc granites), in the studied area are represented granodiorites (Fig.1). It occurs in the southern part of the study area. They form moderate hills cut by quartz veins, basic dykes and acidic dykes. They are medium grained reddish grey in color, hard and massive rocks. They weather to exfoliated boulders. Petrographically, the granodiorites consist of plagioclase (An_{20-25}), showing carlsbad twining. Alkali feldspar (orthoclase and perthite), and quartz as essential minerals. Biotite, hornblende, muscovite, tetanize, zircon, apatite and opaque's are accessory minerals. Chlorite, epidotic and clay minerals are secondary minerals.

Post orogenic magmatism is represented by Dokhan volcanics and younger granites. The Dokhan volcanics occur in the northern western part (Fig. 1). It constitutes a thick sequence of stratified lava flows of basalt, andesite, dacite and rhyodacite. Dokhan volcanics are reddish into deep purple in color. It is cut by basic and acidic dykes. Petrographically, The Dokhan volcanics show porphyritic texture in which the phenocrysts represented by white plagioclase surrounded by fine-grained groundmass of plagioclase, alkali feldspar and quartz. The younger granites of Wadi Kharm El Belawi occur in the central and northern eastern part (Fig. 1). It forms relatively high hills of yellowish buff color, it is cut by thin quartz veins and acidic dykes. The granitic rocks are hard, massive and medium to coarse-grained and slightly weathered. They are hypediomorphic granular, and composed of quartz, potash feldspars (orthoclase. microcline and perthite), and plagioclase (An_{5-12}) as essential minerals, showing albitiazation. Biotite, fluorite, muscovite, apatite, zircon, and opaques are accessory minerals. Secondary minerals include sericites and chlorites.

GEOCHEMICAl CHARACTERISTICS OF THE GRANITOID ROCKS

The fresh rock-samples were chemically analyzed for major oxides according to Shapiro and Branook (1962). The trace elements were determined using X-ray fluorescence spectrometer (Table 1). The rare earth elements (REEs) were determined by using Inductive Coupled Plasma spectrometer (ICP). The major oxides, trace elements, REEs and data of tetrads' of granitoids of Wadi Kharm El Belawi (Table 1) and (Table 2).

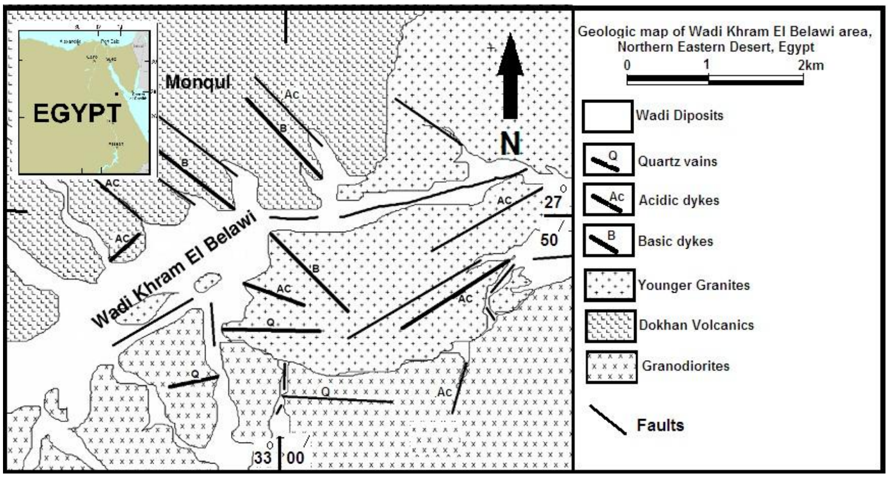

Fig. 1 Geological map for Wadi Kharm El Belawi area and it location in Egypt

The studied granitoid rocks are chemically classified using the following relationships:

On the CaO - Na_2O - K_2O triangular diagram (Fig. 2), (Condi and Hunter 1976), the older granite fall in the tonalite field while the younger granite samples fall in the granite monzonite field, except one sample plots in granodiorite field.

On the relation between TiO_2 vs Zr (Fig. 3) according to Chapple and White, (1974), the granodiorite samples fall in the granodiorite field while the granite samples plot in granite field.

On the relation between (K_2O+Na_2O) vs SiO_2 (Fig. 4) according to Irvine & Baragar (1971), all the samples fall in the subalkaline field.

The AFM diagram (Fig. 5) is used to distinguish between the iron-enrichment differentiation trend of the tholeiitic suites (Skaergaard trend, Wager and Deer, 1939) and the iron non-enrichment trend characteristic of the calc-alkaline suites (Kuno, 1968). The data of all rock types plot in the calc-alkaline field, according to Irvine and Baragar (1971). On the (Na_2O+K_2O) - Al_2O_3 - CaO diagram (Fig. 6) according to Shand (1951), all data of the granodiorite rocks fall in the peraluminous field.

Table 1: Major oxides and Trace elements of the granitoid rocks of Wadi Kharm El Belawi area

Sample	1	2	3	4	5	6	7	8	9	10
Major oxides (wt %)										
	Granodiorites (X)					Granites (+)				
SiO_2	65.04	69.77	68.14	69.75	67.97	74.8	75.87	74.29	74.38	75.39
TiO_2	0.83	0.25	0.46	0.34	0.14	0.18	0.15	0.13	0.48	0.17
Al_2O_3	15.56	15.08	15.4	15.09	15.92	12.23	12.61	10.2	11.1	11.73
Fe_2O_3	4.49	3.69	2.85	2.38	2.52	1.75	2.04	2.43	2.83	1.97
FeO	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MnO	0.07	0.17	0.1	0.05	0.02	0.02	0.02	0.06	0.05	0.05
MgO	0.22	0.04	1.94	0.43	0.18	0.06	0.08	0.22	0.12	0.98
CaO	2.69	2.29	2.19	3.19	3.98	0.81	0.55	0.9	0.34	0.92
Na_2O	5.56	3.56	5.29	4.31	4.98	4.31	4.32	4.04	4.04	4.07
K_2O	1.66	0.97	0.74	1.1	0.59	3.29	3.41	4.53	4.13	3.61
P_2O_5	0.16	0.13	0.07	0.07	0.02	0.02	0.02	0.02	0.1	0.03
LOI	0.2	0.4	0.4	0.4	2.2	1.1	0.7	0.99	0.2	0.7
Total	100.6	99.69	100.2	99.27	100.81	100.2	101.63	100	101.2	101.41
Trace Elements (ppm)										
Ba	370	544	455	638	687	758	519	1382	1189	1519
Rb	46.9	33	50	13.5	79	179	179	87.3	50	20
Sr	256.5	356	286	258	332	52	40	25	15	12
Y	53.4	58	25	20	27	112	95	55	68	80
Zr	580	187	423	294	600	622	455	578	277	554
Nb	20	20	15	13	40	24	70	72	82	33
Hf	14.5	4	11	5.5	17.8	16	8.4	14	6.4	16

Table 2: REEs of the granitoid rocks of Wadi Kharm El Belawi area

Sample	1	2	3	4	5	6	7	8	9	10
Rock type	Granodiorite					Granites				
La	47.5	53	35	49	75.8	25	23	47	55	48
Ce	107	121	67	100	182	68	62.1	95	131	103
Pr	13.5	15	7.7	11	16.9	9.1	7	12	16	12
Nd	55	58	29.7	41.2	58.5	31	29	45	62	45
Sm	10.2	13	5.5	7	11.2	5.6	6	10	13	9.1
Eu	1.05	1.5	0.5	1.3	0.23	0.3	0.38	0.5	2.1	0.5
Gd	9.44	9.7	4.3	3.3	8.2	4.3	9.3	9.7	10.5	9
Tb	1.8	1.6	0.8	0.5	1.8	0.7	2.2	2	1.6	1.5
Dy	9.34	9.7	3.9	3	12.1	3.9	15.4	11	11	10
Ho	1.77	2	0.9	0.6	2.8	0.4	1.5	2.1	2.1	1.2
Er	5.35	5.8	2.6	1.9	9.3	2.5	11.8	7.6	6.6	6.7
Tm	0.9	0.9	0.4	0.3	1.6	0.4	1.9	1.3	1.1	1
Yb	5	5.5	2.6	2.2	10	2.6	11.4	7.4	6.3	6.9

In the MORB normalized trace element plots, both granodiorites and granites are enriched in most ion lithophile elements (LILE) (e.g. Rb, Ba) and depleted in Sr, P and Ti, with Nb anomalies. This pattern is typical for calc-alkaline subduction-related magmas (Fig. 7A &7B).

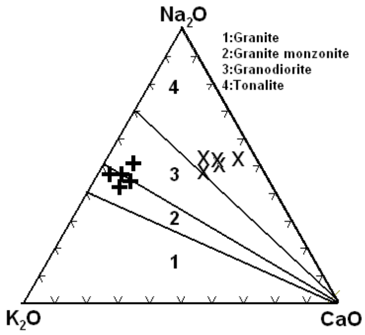

Fig. 2: Ca-Na_2O-K_2O diagram (Condi and Hunter 1979),

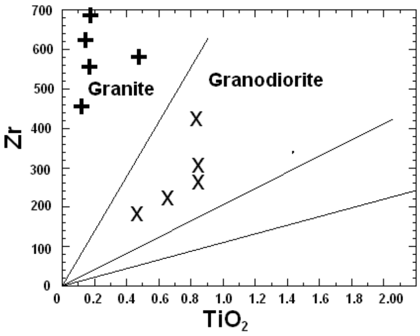

Fig. 3: Zr-TiO_2 diagram (Chapple and White, 1974)

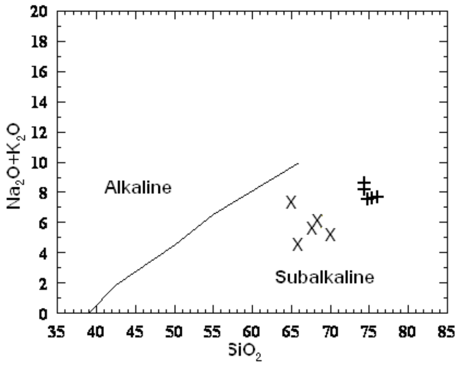

Fig. 4: AFM diagram (Irvine and Baragar, 1971).

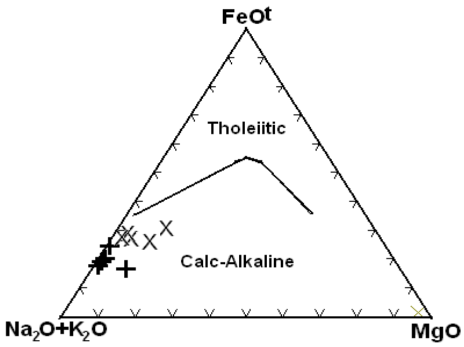

Fig. 5: (K_2O+Na_2O) vs SiO_2 (Irvine and Baragar, 1971)

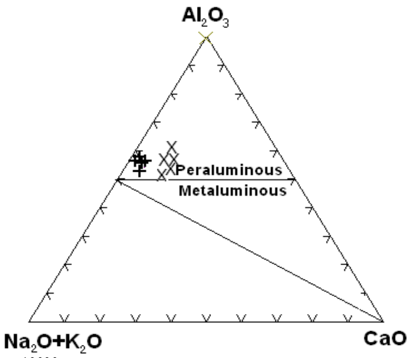

Fig. 6: (Na_2O+K_2O)–Al_2O_3–CaO diagram (Shand. 1951)

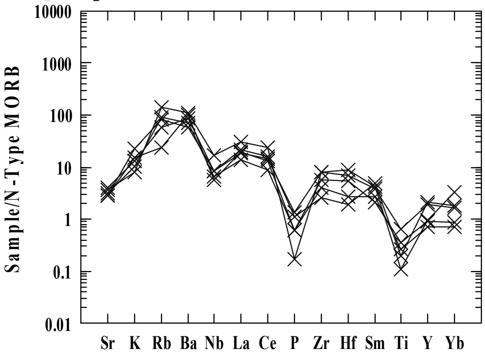

Fig. 7: A MORB-normalized trace element plots (Pearce, 1983) the studied rocks. Symbols as in Fig.2.

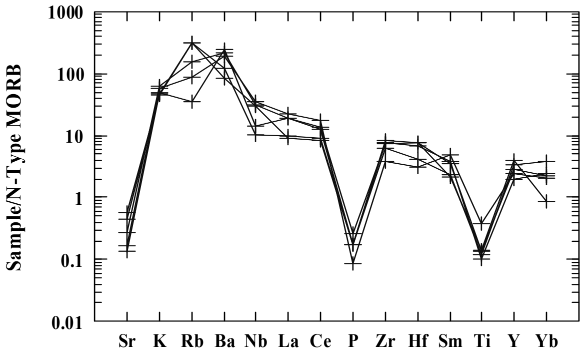

Fig. 7B: MORB-normalized trace element plots (Pearce, 1983).

It is noted that the pattern of granites displays non-pronounced Nb troughs and their samples plot in the within plate granite field (WPG) on Y + Nb vs. Rb diagram (Fig. 8) of Pearce et al. (1984). However, it is interpreted and documented that highly fractionated felsic calc-alkaline granites commonly refer to a change in the tectonic environment accompanied by a change to more alkaline composition.

The Rb-Sr ratio has been used to indicate of magma generation within the crust (Condi and Hunter, 1976), the Rb-Sr variation diagram (Fig. 9) shows that all the data of the granitoid rocks fall in the area under crustal thickness between 20 - 30 km.

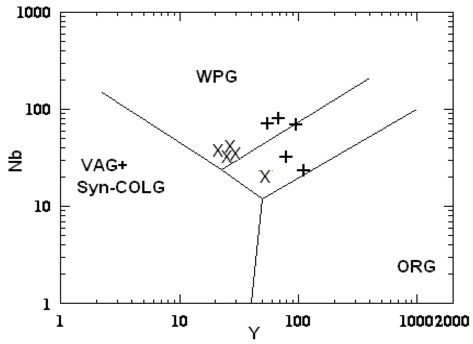

Fig. 8: Nb- Y (Pearce et al. 1984)

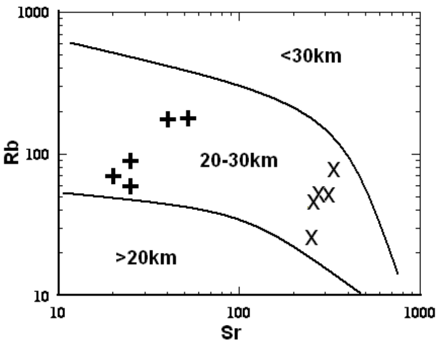

Fig.9: Rb-Sr diagram (Condi and Hunter,1976)

TETRAD EFFECT

The lanthanide elements lie in group III and period 6 in periodic table. They include 14 elements, starting with Lanthanum and ended by Lutetium (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu). They are characterized by 3+ valances except Ce which have 3+ and 4+ valance and Eu which have 2+ a 3+ valance. Fidelis and Siekierski (1966) and Peppard et al. (1969) initially observed the tetrad effect in patterns of liquid- liquid REE distribution coefficients. Nugent (1970), Sinha (1978), Dzhurinskii (1980), Bau (1996), and Bau and Dulsk (1995) and Mioduski (1997) The tetrad effect is due to variation in the exchange interaction of unpaired 41-eleclron, spin- orbit coupling or crystal field stabilization. Masouda el al. (1987) classified the tetrad effect into two different types, M- and W type (M-type in solid sample as residue and W-type in the interacting fluids as extract). The labels M- and W- refer to upward or downward curved REE patterns respectively. Mahdy, (2004) mentioned the tetrad effect is represented in Egypt in four localities, 1- Albitized granites of Nuweibi area, Central Eastern Desert (CED), (Helba et al., 1997). 2- Episyenitized granites of Kab Amii area (CED), (Mahdy and E Kammar, 2003), 3- Albitized granites of Gabal Igla El Ahmar area (CED) (Arbab, 2003), and lastly Samaan (2004), seed that the tetrad effect is represented in Gabel Hadaybarea, South Eastern Desert (SED), Egypt. The spider diagrams for the REEs for the granodiorites and granites of Wadi Kharm El Belawi area (Figs. 10 and 11) show that the granites are more strong tetrad effect than granodiorites.

Quantification of the tetrad effect: Two methods are employed for quantification of the tetrad effect

a-Irber methods (1999): This method depends on the quantify of t1, t2, t3 and t4

$\mathbf{t_1= (Ce/Ce^1 x\ Pr/Pr^1)^{0.5} t_2= (Sm/Sm^1 xEu/Eu^1)^{0.5}}$

$Ce/Ce^1= Ce_{cn}/(La_{cn}^{2/3} xNd_{cn}^{1/3})$ $Sm/Sm_1=Sm_{cn}(Pr_{cn}^{2/3} xGd_{cn}^{1/3})$

$Pr/Pr^1= Pr_{cn}/(La_{cn}^{1/3} xNd_{cn}^{2/3})$ $Eu/Eu^1= Eu_{cn}/(Pm_{cn}^{1/3} xGd_{cn}^{2/3})$

$\mathbf{t3= (Tb/Tb_1 xDy/Dy_1)^{0.5}}$ $\mathbf{t4= (Tm/Tm_1 xYb/Yb_1)^{0.5}}$

$Tb/Tb_1= Tb_{cn}(Gd_{cn}^{2/3} xHo_{cn}^{1/3})$ $Tm/Tm_1= Tm_{cn}(Er_{cn}^{2/3} xLu_{cn}^{1/3})$

$Dy/Dy_1=Dy_{cn}(Gd_{cn}^{1/3} xHo_{cn}^{2/3})$ $Yb/Yb_1=Yb_{cn}(Er_{cn}^{1/3} xLu_{cn}2/3)$

*La_{cn}= chondorite - normalized lanthanide concentration

Degree of tetrad effect $=TE_{1.3.4}= (t1xt3xt4)^{0.5}$

If $TE_{1.3.4}$=1 then no tetrad effect is found e.g. Cl- condorite from Anders and Grevess (1989). But if $Te_{1,3,4}$> 1 then there Ia tetrad effect

b- Monccke et al., (2000) method

$$t1 = \frac{X_{B1}X_{C1}}{X_{A1}X_{D1}}$$

X_{A1} = chondrite- normalization concentration of the first elements in the tetrad (e.g. La, Pm, Gd and Er).
$X_{B1}$and X_{C1} = chondrite- normalization concentration of the central elements in the tetrad (e.g. Ce, Pr, Sm, Eu,Tb, Dy, Tm and Yb).

X_{D1}= chondrite-normalization concentration of the last elements in the tetrad (e.g. Nd, Gd. Ho.and Lu). In this research the method of Ibar (1999) was used for calculation of tetrad effect. Table 3 shows the REEs data and the $t_1$and t_3 for the granitoid rocks of Wadi Kharm El Belawi area.

Table 3: calculation of some geochemical data and calculation of t_1, t_3, t_4 and $T_{1,3}$

Sample	1	2	3	4	5	6	7	8	9	10
Alk	5.48	5.02	5	4.33	6.3	6.67	5.4	5	4.8	5.1
Zr/Hf	40	46.8	38	53.5	34	38.9	54	41	43	35
Sr/Eu	62.9	178	192	203	664	53.6	69	29	6.5	16
Data of T_1, T_3 and T_4										
t_1	1.04	0.97	1.01	0.76	1.28	1.1	1.01	1.1	0.77	1.1
t_3	1.31	0.99	0.96	0.77	1.39	1.7	1.15	1	0.77	1
t_4	1.05	1.01	1.04	1.12	1.08	1.2	1.15	1.1	1.19	1.1
Calculation of t_1*t_3										
$T_{1.3}$	1.17	0.98	0.99	0.77	1.31	1.4	1.08	1	0.77	1

Plot of the tetrad effect ($T_{1,3}$) vs Na_2O, K_2O, Total Alkali, and Zr/Hf

Na_2O (wt %): In the relation between Na_2O (wt %) and $T_{1.3}$ (Fig. 12) showing positive relation duo to albitization in granites and petrographically these rocks increase in sericite alteration of K-feldspars and plagioclase and chloritization of biotite.

K_2O (wt %): The sericitization on the feldspars increasing K content in the granitoids so that the relation between $T_{1,3}$ vs K_2O (Fig. 13) show the K_2O content in granites more the content in granodiorites

Total Alkali: Alkali means that the summation of K_2O +Na_2O (wt %), the relation between Alk. vs T1, 3 (Fig. 14), show positive relation and the granitic rocks more in alkali.

Zr/Hf: The Zr/Hf ratio average is 39 (Erlank et al., 1978), and is close to the chondritic ratio of 38 (Anders and Grevesse, 1989). The average for pegmatites is about 25 (Erlank et al., 1978) and the Zr/Hf ratio shift toward smaller value with increasing evolution of the silicate melt Bau (1996). The plot of tetrad effect vs Zr/Hf shows negative (Fig. 15). The studied granitoid samples range in their Zr/Hf ratio from 34 to 53.5.

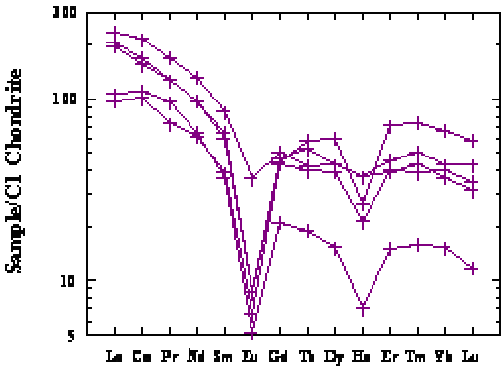

Fig. 10: Spider diagram for granodiorite

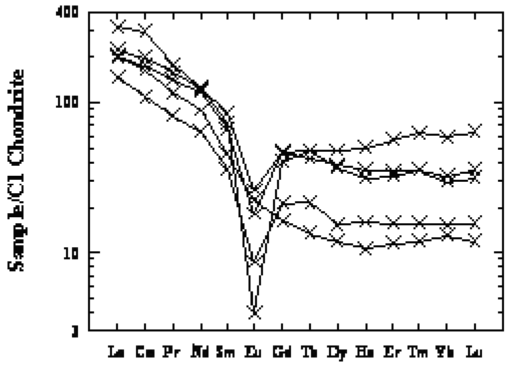

Fig. 11: Spider diagram for granite

The lanthanide tetrad effects and its correlation with Na_2O, k_2O, alk.

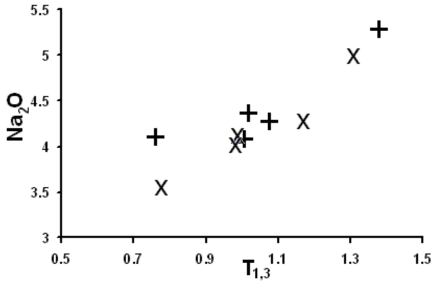

Fig. 12: T1,3 vs Na2O (wt%)

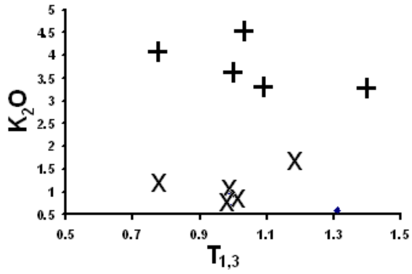

Fig. 13: T1,3 vs K2O (wt%)

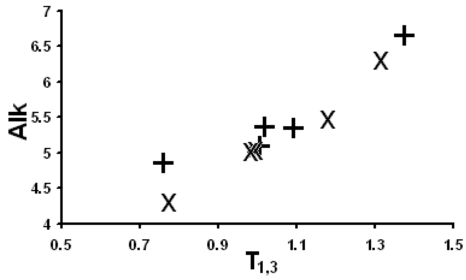

Fig. 14: T1,3 vs Alk

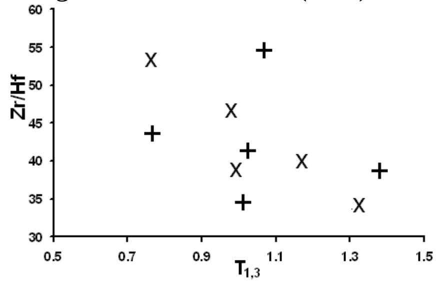

Fig. 15: T1,3 vs Zr/Hf

CONCLUSION

In Wadi Kharm El Belaw area the Precambrian rocks are represented by older granites, Dokhan volcanics and younger granites. The Subduction- related granitoids (Arc Granites) represented by granodiorites and Intra-plate Magmatism and Sediments represented by Dokhan volcanics and younger granites. The granitoid rocks of Wadi Kharm El Belawi area originated from a calc-alkaline magma, and under compressional regime, i.e. collision related. The tetrad effect strongly appears in alkali feldspar granites. The quantified tetrad effect in the alkali feldspar granites ($T_{1.3}$,), is plotted it vs. geochemical parameters (Na_2O, K_2O, Alkali and Zr/Hf,), known to be sensitive to granitic melt differentiation and magmatic-hydrothermal transitional environments. The strong correlation of the tetrad effect with Na2O, and Alkali, reveals the gradual development of the tetrad effects conformable with granite evolution. Significant tetrad effects are only seen in highly evolved granitic rocks (there peraluminous), the fractionation trends of Alkali and Zr/Hf are only partly explained by mineral fractionation (e.g. feldspar). The strong decrease of Eu concentration in highly evolved granitic rocks is more likely to indicate Eu fractionation between a residual melt and a coexisting aqueous high-temperature fluid. The results point to significant changes in the behavior of elements in highly evolved granitic melts, where classic mineral/melt element fractionation, based on ionic radii and charge, is no longer the exclusive control.

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التأثير الرباعي للانثانيدات و علاقتها مع أكاسيد الصوديوم و أكاسيد البوتاسيوم والقلويات الكلية مع الزركونيوم والهافنيوم وتشمل الصخور الجرانيتية لمنطقة وادي خرم البلاوي ، الصحراء الشمالية الشرقية ، مصر

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الخلاصة

تتكون صخور القاعدة في منطقة وادي خرم البلاوي من دخان االبراكين والجرانيوليت و الجرانيت الأحدث. وهي تتكون من المجما الكالسي قلوي تحت نظام إقليمي مضغوط .

وقد لوحظ تأثير اللانثانيد الرباعي في نمط العناصر الأرضية النادرة في الجرانيت القديم و الجرانيت الحديث في وادي خرم البلاوي $TE_{1,3}$, t_4, t_3. وقد تم رسمها مقابل أكاسيد الصوديوم و البوتاسيوم والقلويات الكلية مع الزركونيوم والهافنيوم .

وقد كشفت الرسوم البيانية عن أن تأثير الرباعي مطابقا لتطور الجرانيت الفلسباري القلوي و تعتبر التأثيرات الرباعية علي عينات شديدة التميز .

يرتبط الإنخفاض الشديد في تركيز الأوروبيوم في الصخور المتطورة بدرجة عالية بتجزء الأوروبيوم بين المنصهر المتبقي و سوائل مائية شديدة الحرارة .

تشير النتائج إلي تغيرات كبيرة في سلوك تجزءة العناصر في إنصهار الجرانيت عالي التطور مما يشير إلي أن النصف أقطار الأيونية والشحنة (التي تتحكم في توزيع العناصر بين المعادن و الإنصهار) لم تعد لها السيطرة الأساسية .