

**GEOCHEMICAL AND FLUID INCLUSIONS STUDIES ON FLUORITE  
MINERALIZATION AT HOMR AKAREM AND HOMRET MIKPID  
GRANITES, SOUTH EASTERN DESERT, EGYPT**

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**ABSTRACT**

Homr Akarem and Homret Mikpid rare metal bearing granites are small granite masses dissected by numerous fluorite veins of variable thicknesses. These veins are structurally controlled trending NE-SW and NW-SE. Intensive alteration zones are recorded associated with these fluorite veins. These fluorites contain relatively high Y, Pb and low Sr contents with very low contents of Rb, Ba, Zr and Nb.

The chondrite normalized patterns of the studied fluorites show relative enrichment in the HREEs compared with the LREEs. The  $(La/Lu)_N$  ratio varied from 0.36 to 0.43, with distinct negative Eu-anomaly where  $Eu/Eu^*$  range from 0.12 to 0.13. Fluorites display REE patterns similar to those of the hosting granites, indicating a genetic relationship between the fluorite veins and granites. The exhibited patterns show a noticeable fractionation during ore deposition where La/Yb ratio measured 0.49 in Homr Akarem and 0.39 in Homret Mikpid fluorites.

Microthermometric investigation indicates that the studied fluorites of Homr Akarem and Homret Mikpid were probably deposited from low salinity (5-7 wt. % NaCl eq.) aqueous fluids due to boiling processes. The trapping conditions of Homr Akarem estimated at temperatures between 100°C and 230°C, and pressures between 120 and 300 bars; whereas for Homret Mikpid at temperatures between 100°C and 190°C, and pressures between 240 and 360 bars.

**INTRODUCTION**

Generally, fluorite is formed during a late magmatic crystallization of alkaline and per-alkaline granites as disseminations or as late-crystallizing hydrothermal mineralization [Sabet *et al.*, (1976); Strong *et al.*, (1984); Hussein (1990) and Deer *et al.*, (1992)]. Fluorite is restricted to the younger granites of Eastern Desert and some related veins and pegmatite bodies. It occurs as disseminations, as cavity and fracture fillings. Sometimes it forms gangue mineral associated with rare-metal mineralization such as Sn and W that are closely related to GIII granite of [Hussein *et al.*, (1982)].

Homr Akarem and Homret Mikpid rare metal granites have high contents of F, Rb, Nb, Ga, Zr, Y, Zn and REE [Hassanen & Harraz (1996) and Mohamed & El-Sayed (2007)]. The studied areas are located in the south Eastern Desert at 24°11' N, 34°2' E and 24°8'38" N, 34°22'13" E, respectively Fig. (1). Both granites host fluorite veins. The contacts between fluorite veins and granite are characterized by presence of intensive alteration zones.

The aim of the present work is to apply fluid inclusions data integrated with the available geological and geochemical data to elucidate the genesis of mineralization and formation conditions.

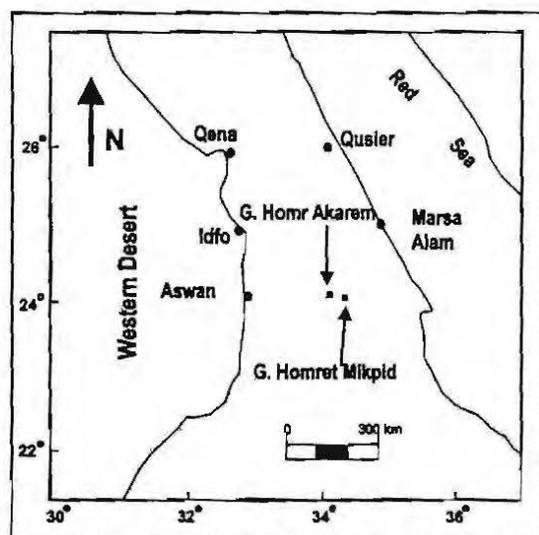


Fig. (1): Location map of the studied areas.

### GEOLOGICAL OUTLINE

Homr Akarem fluorite occurs as disseminated crystals within the granite and in numerous veins. The latter are structurally controlled, trending NE-SW and NW-SE and cut the granite. Fluorite is usually associated with mineralized quartz veins hosted by the country rocks at the northern part of Homr Akarem granite. The thickness of these veins ranges from 30 to 50 cm and their length varies from 30 to 80 m.

Homret Mikpid fluorite vein ranges from 30 to 50 m in length and from 10 to 50 cm in thickness. It is also structurally controlled trending NW-SE. Fluorite occurs also as disseminated grains within the granite.

In both areas at the vein contacts, highly altered zone is represented by very friable kaolinitic rock. This zone fades away from the vein passing to the proper granite.

## PETROGRAPHY

In hand specimen fluorite shows cubic habit and vitreous luster. The color of Homr Akarem fluorite is usually white on the border of the vein changes gradually to green inwards. Homret Mikpid fluorite has pale to deep green color. Close to the boundaries, the fluorite tends to be banded with narrow rhythmic zoning owing to variation in color arranged inward the vein; violet and white changing to green. The zonal feature in colour of fluorite in both areas is possibly due to the formation from mineralizing solutions that had varied composition during deposition or due to its multi-phase mode of formation (Soliman, 1984 and Fawzy and Abdel Rahman, 2002).

Fluorites form massive and coarse-grained crystals. In thin section, they are transparent, fractured and the fractures filled with fine grained quartz crystals. Fluorites include small crystals of apatite, rhombic shaped crystals of calcite, euhedral six-sided crystals of quartz and some irregular grains of galena.

## ANALYTICAL METHODS

The analyses of trace elements were done by X-ray fluorescence. The contents of REEs were analysed by ICP-MS, while the fluorine content was analysed by SIE (Selective Ion Electrode), in Genalysis Laboratory Services, Australia.

Microthermometric studies were conducted on double polished wafers 0.2-0.3 mm thick using a Chaixmeca heating/freezing stage (Poty et al., 1976) at the Geology Department, Assiut University. The stage was calibrated for temperatures between -100°C and +400°C using Merck chemical standards.

## GEOCHEMISTRY OF FLUORITE

### Distribution of Trace Elements

Concentrations of trace elements of the studied fluorites are given in Table (1). Y and Pb contents are higher than other trace elements being 426 and 533 ppm, 99 and 63 ppm in Homr Akarem and Homret Mikpid fluorites, respectively. Y is quite similar to REEs, it accumulates selectively on account of its ionic radius being similar to that of Ca. The interaction between the fluid and the wall rocks in the exo-contact may have influenced the anomalous enrichment of Y in the fluids [Monecke *et al.*, (2002)]. The green color of fluorite may be due to the enrichment in Y relative to REEs [Awad (1995) and El Mansi (2000)]. The high content of Pb may be due to the presence of galena as inclusions in fluorite.

Sr content range from 25 ppm (in Homret Mikpid fluorite) to 35 ppm (in Homr Akarem fluorite), which is relatively lower than the average Sr content in the hydrothermal worldwide fluorites of 56 ppm [Barbieri *et al.*, (1984)]. The contribution of Sr from the mineralizing solutions and the geochemical relationship between Sr and Ca are responsible for their incorporation into the crystal lattice of fluorites. The Ca site in the fluorite will accept Sr substitution but will not accommodate significant amounts of Rb [Kesler *et al.*, (1983)]. They also mentioned that all of the fluorite samples

included in their study contained less than 10 ppm Rb which is consistent with the results obtained in this investigation which contain up to 8 ppm Table (1).

Table (1): Trace elements analyses of the studied fluorites

Element (ppm)	Mikpid	Akarem
F%	41.37%	45.75%
Y	533	426
Pb	63	99
Sr	25	35
Li	17	8
Nb	3	1
Rb	8	1
Ba	2	2
Zr	5	2
Mo	8	27

#### Distribution of REE

Total REEs of the studied fluorites measured up to 155 ppm. REE-analyses and chondrite-normalized REE patterns, using the chondrite values from [Anders & Grevesse (1989)] are given in Table (2). Generally, during crystallization of a silicate melt, the REE will be concentrated in the residual solutions generated from an alkaline magma. Distribution of the REEs in fluorites depends mostly on the solutions containing REE during crystallization as well as the charge of RE-cations and the temperature of formation. The alkalinity and volatile content mostly have a marked effect on REEs differentiation and accumulation in magmatic and post magmatic processes. High alkalinity in the fluids favours the accumulation of HREEs and Y. In alkaline fluids with halogens as complexing ligands, REE fractionation is mainly controlled by complexing reactions. Trivalent REE-complex stabilities generally increase with decreasing ionic radius and hence, HREE are enriched in solution and REE patterns show La/Lu ratios < 1 [Bau (1991); Bau & Möller (1992); Möller (1991) and Wood (1990 a & b)]. Thus, mostly the fluids were high in alkalinity and their HREEs accumulate in these fluorites.

Bellanca *et al.*, (1981) mentioned that fluorite with low levels of LREEs and high HREEs had rather crystallized from solutions with high amounts of complexing anions (like F and OH) than that with high amounts of LREEs. The depletion of LREEs can be attributed to the preferential complexation of HREEs during the migration of the mineralizing solutions [Sallet *et al.*, (2005)].

In general, the REEs spectral configuration in fluorites shows relative depletion in LREEs relative to the heavier ones. The configuration represents a natural complement to that in F-rich granites and distinctively with within plate granite [Taylor (1964)]. This relation reflects a continuous REEs fractionation sequence within the melt and its residual hydrothermal fluids. The investigated fluorites display REE patterns similar to those of the hosting granites. This is interpreted as reflecting similar patterns between the fluids and granitic melts from which they were derived and which was preserved because of the rapid precipitation which did not allow differential separation of the different REEs [Strong *et al.*, (1984)]. These contents are comparably higher than those given by [Vinogradov & Vinogradov (1973) and Ganzeyev & Sotskov (1976)] for the hydrothermal fluorites (100 ppm). In general, the total REEs in hydrothermal fluorite are much lower than in the parent granite and this is more pronounced for the light RE members. Similarly, the granites hosting fluorites show high contents of total REEs up to 103 ppm. But the fluorites have higher total REEs contents than their hosting granites; this is probably due to the mineral inclusions in fluorite. Tb and La are strongly fractionated by fluorite; variation diagram using Tb/La versus Tb/Ca ratios can be used to determine the environment of formation and degree of fractionation of fluorite [Möller *et al.*, (1976)]. Plots of the studied fluorites on Tb/Ca versus Tb/La diagram supports that they represent the hydrothermal phase of the latest magmatic differentiation Fig. (2).

According to [Ganzeyev *et al.*, (1983)], the fluorite /liquid partition coefficient exceeds 100 for all the RE members. The excess REEs displaced from the granitic rock forming mineral phases are taken in the crystalline fluorite in the ratio in which they are present in the mineralizing solution [Fleischer (1969)].

The chondrite normalized patterns of the studied fluorites show a relative enrichment in the HREEs compared with the LREEs, where  $(La/Lu)_N$  varied from 0.36 to 0.43, with distinct negative Eu-anomaly Fig. (3), where  $Eu/Eu^* = 0.12-0.13$ . The patterns also show a noticeable fractionation during ore deposition where  $(La/Yb)_N$  ratio measured 0.49 in Homr Akarem and 0.39 in Homret Mikpid fluorites; this ratio is also consistent with [Möller *et al.*, (1976)] who stated that the later formed fluorite incorporates more of the heavier REE, yielding low  $(La/Yb)_N$ .

Eu was taken by the feldspars in the early stages of crystallization, for that it is depleted in the late residual fluids, from which fluorite crystallized. The Eu deficiency in F-rich hydrothermal solutions depends mainly upon its selective fractionation in feldspars [Fernando (1995)], whatever the alkalinity of the parent granite. High alkalinity affects mainly the distribution of Eu in a given mineral species and not in the rock, [Ganzeyev & Sotskov (1976)]. According to [Haskin *et al.*, (1968)], the feldspars contribution to the Eu concentration is above fifteen times greater than its chondrite content. Actually, the negative Eu anomaly in the fluorite is a general feature that reflects its initial concentration in the granites-related fluorite mineralization, [Khalil *et al.*, (1978); Geringer *et al.*, (1988) and Hassaneen (1996)]. The negative Eu-anomaly in the fluorite indicates its depletion in the medium in which fluorite was formed. The late magmatic melt is diagnostically deficient in Eu [Gill (1996)].

According to [Möller & Mücke (1984) and Jarrar (1992)] the pronounced negative Eu-anomaly in fluorine-rich granitic melt might have been caused by two interrelated factors: the culmination of the fluorine activity reduces  $Eu^{2+}$  stability in the melt and enhances its retention in the refractory Ca-plagioclase.

The size of the Eu-anomaly is influenced by the interaction of the fluid with the magma as well as Eh and T conditions during fluid migration and fluorite precipitation [Goldstein *et al.*, (1995); Kempe & Goldstein (1997) and Monecke *et al.*, (2002)].

The tetrad effect appears to be developed more or less independently from the size of the Eu anomaly and the  $Y_N/Dy_N$  ratio in the hydrothermal fluids. The interaction between the fluid and the wall rocks in the exo-contact possibly affected the size of the tetrad effect of individual tetrads [Monecke *et al.*, (2002)]. The tetrad effect in lanthanide patterns of fluorites was quantified by equations 2 and 3 proposed by [Monecke *et al.*, (2002)]. Homr Akarem fluorite is characterized by  $T_1 = 0.03$ ,  $T_3 = 0.07$ ,  $T_4 = 0.06$  and  $T = 0.06$ . Homret Mikpid fluorite is characterized by  $T_1 = 0.02$ ,  $T_3 = 0.05$ ,  $T_4 = 0.03$  and  $T = 0.04$ . All these tetrads are very weak and below the level of significance (0.2).  $T_2$  cannot be calculated because Pm doesn't occur in nature.

Table (2): Average content of REEs of the granites and content of REEs of the studied fluorites together with chondrite normalized values.

Element	Homret Mikpid granite	Homret Mikpid Flourite		Homr Akarem granite	Homr Akarem Flourite	
	Av. ppm	ppm	C.N	Av. ppm	ppm	C.N
La	10.14	10.06	22.25	6.4	12.46	27.93
Ce	27.1	27.01	23.77	17.1	31.93	28.11
Pr	4.1	4.43	26.54	3	5.05	30.26
Nd	15.87	22.76	27.49	12.1	24.29	29.34
Sm	4.7	10.23	39.62	5	9.68	37.49
Eu	0.25	0.58	5.96	0.06	0.5	5.14
Gd	5.5	17.09	51.78	5.73	15.1	45.76
Tb	1.2	2.97	49.25	1.3	2.59	42.95
Dy	8.5	19.75	50.1	9.5	17.13	43.45
Ho	2.1	4.74	53.32	2.32	4.2	47.24
Er	7.7	14.96	59.65	8.7	13.37	53.31
Tm	1.6	2.24	59.26	1.75	2.03	53.7
Yb	12.56	14.44	58.25	13.71	13.96	56.31
Lu	2.22	2.26	61.58	2.36	2.37	64.57
$\Sigma$ REE	103	153		89	155	
Eu/Eu*			0.13			0.12
La/Lu			0.36			0.43
La/Yb			0.39			0.49
Y/Dy			2.3			2.1

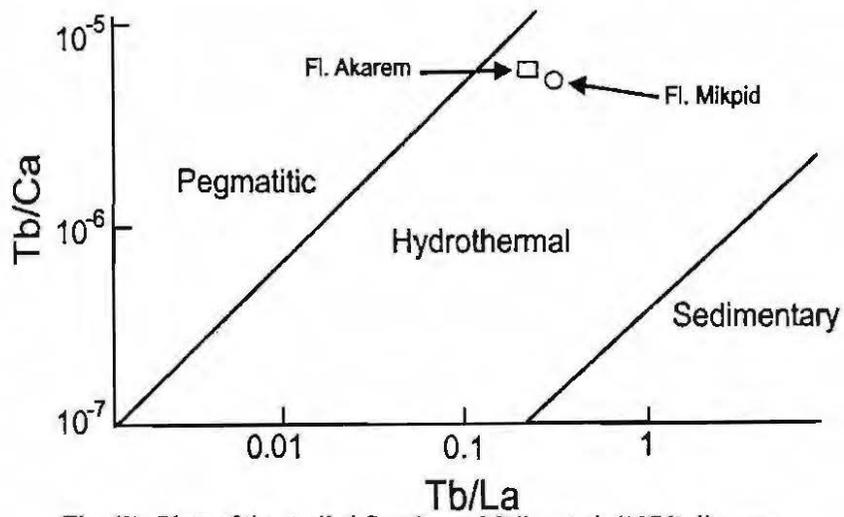


Fig. (2): Plots of the studied fluorite on Möller et al. (1976) diagram.

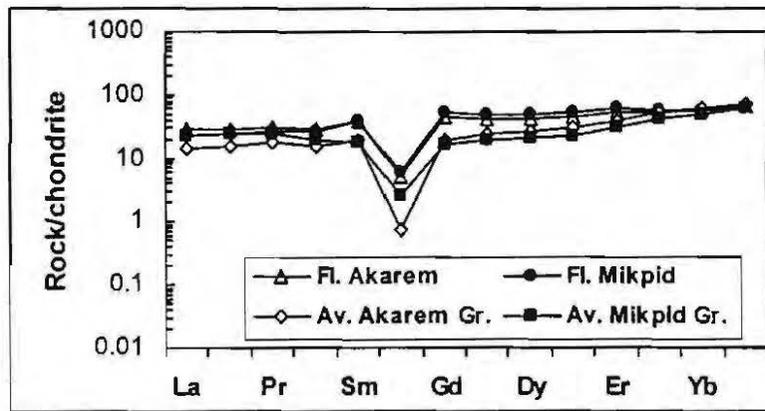


Fig. (3): The Chondrite normalized patterns of Homr Akarem and Homret Mikpid fluorites.

## FLUID INCLUSIONS STUDIES

The studied fluorites are enriched in various types of fluid inclusions. Taking into account several features, the inclusions are grouped into three basic types. Type (I) primary two phase (L+V) aqueous inclusions ranges from 20 to 70  $\mu\text{m}$  in size containing up to 30% vapour of the volume. They are distributed as individual isolated inclusions or distributed along short lines within the crystals as pseudo-secondary inclusions [Roedder (1984)]. They are often irregular, triangular, cubic, sphere and negative crystal forms (Fig. 4a,b & d). Type (II) secondary two phases (L+V) aqueous inclusions. These inclusions are the most abundant type in fluorite. They are arranged along healed fractures display oval, sphere or elongate shapes and up to 20  $\mu\text{m}$  in size Fig. (4c). Type (III) small number of monophasic liquid and monophasic vapour inclusions associated with type (I) two phases (L+V) aqueous inclusions, have oval shape and up to 20  $\mu\text{m}$  in size Fig. (4b).

Microthermometric measurements were made on the primary two phases inclusions. The temperature of initial melting ( $T_e$ ) observed at  $-47^\circ\text{C}$  to  $-49^\circ\text{C}$ , reflect the occurrence of  $\text{NaCl} + \text{CaCl}_2 \pm \text{KCl} \pm \text{MgCl}_2$  as dissolved salts in the aqueous solutions [Shepherd *et al.*, (1985)] while the last melting of ice noted at temperature ( $T_{\text{mice}}$ ) between  $-2.5^\circ\text{C}$  and  $-5.8^\circ\text{C}$ , corresponding to low salinity from 5 to 9 wt. % NaCl eq. with a maximum peak at 7 wt. % NaCl eq. (Fig. 5.a). The inclusions homogenized to liquid phase and homogenization temperatures range from  $100^\circ\text{C}$  to  $230^\circ\text{C}$  with majority at  $110^\circ\text{C}$  in Homr Akarem fluorite Fig. (5.b). In Homret Mikpid fluorite, the temperature of initial melting ( $T_e$ ) observed at  $-37^\circ\text{C}$  to  $-40^\circ\text{C}$ , indicates the presence of some other salts as K, Ca, Mg and Fe dissolved as chlorides in the aqueous salt system [Borisenko (1977)], while the final ice melting temperature ( $T_{\text{mice}}$ ) in the range from  $-3^\circ\text{C}$  to  $-4.3^\circ\text{C}$ , show low salinity from 5 to 7 wt % NaCl eq. with a maximum peak at 5 wt. % NaCl eq. Fig. (5.c). The total homogenization temperatures range between  $90^\circ\text{C}$  and  $190^\circ\text{C}$  with maximum peak at  $130^\circ\text{C}$  Fig. (5.d).

The coexistence of monophasic liquid and vapour inclusions with two phase aqueous inclusions may be due to the boiling process. This process plays an important role in the deposition of fluorite [Hill *et al.*, (2000)]. In the case of boiling, the homogenization temperatures can be taken as trapping temperatures [Strong *et al.*, (1984)].

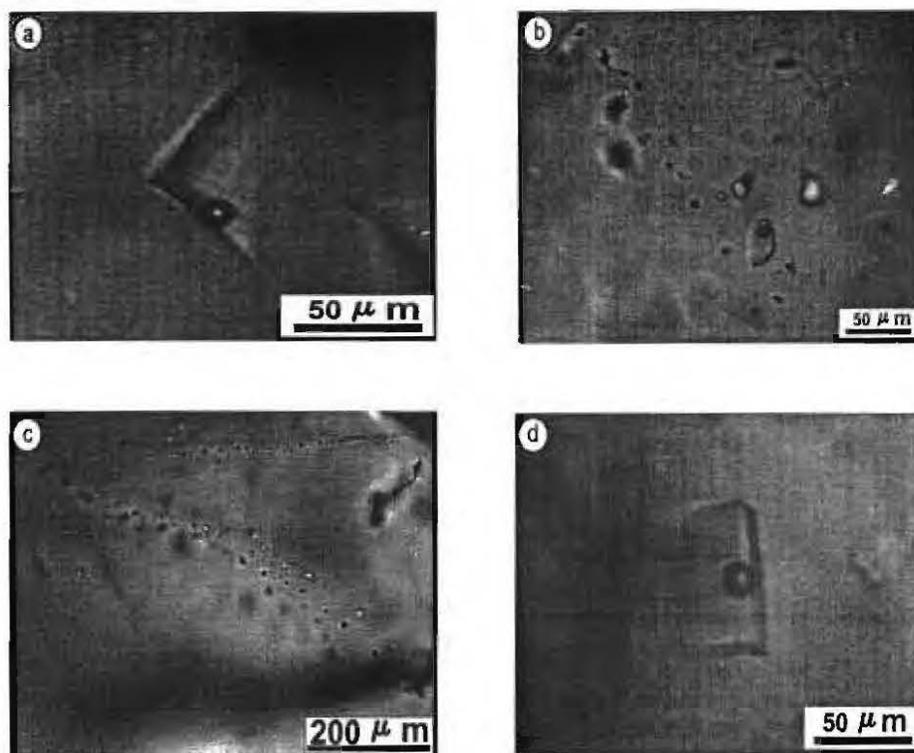


Fig. (4): a) Negative crystal primary two phases (L+V) inclusions,  
b) Monophase liquid and vapour inclusions associated with the trails of pseudo-secondary inclusions,  
c) Trails of secondary two phases (L+V) inclusions in Homr Akarem fluorite and  
d) Negative crystal primary (L+V) fluid inclusions in Homret Mikpid fluorite.

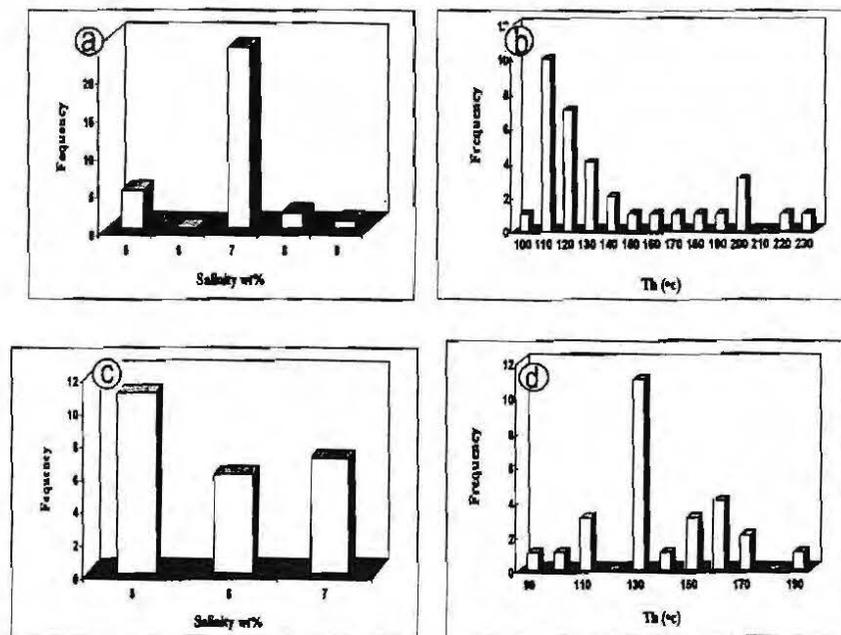


Fig. (5): Histograms (a & c) show the salinity distribution and (b & d) show total homogenization temperatures ( $T_h$ ) of two-phases (L+V) aqueous inclusions in Homr Akarem and Homret Mikpid fluorites, respectively.

#### Pressure estimation and interpretation of fluid inclusion results:

Isochores were calculated for the studied fluorites from FLINCOR computer program of [Brown (1989)], using equation of state after (Zhang and Frantz, 1987). The trapping conditions of Homr Akarem estimated at temperatures between 100°C and 230°C, and pressures between 120 and 300 bars. For Homret Mikpid the trapping temperatures were between 100°C and 190°C while pressures were between 240 and 360 bars Fig.(6 a and b).

The close spatial relationship between fluorite veins and the granitic rocks, the structural control of the veins, the abundance of fluorite as accessory mineral in the granite, the REE normalized patterns and the formation conditions of fluorite imply the genetic relationship between the granitic magma and the hydrothermal fluids from which fluorite was crystallized.

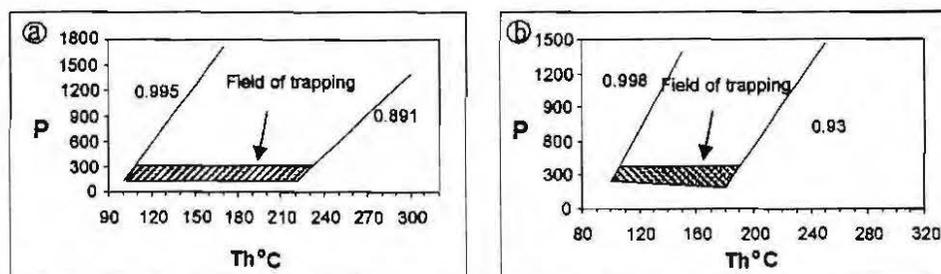


Fig. (6): Pressure - temperature diagrams show the condition of fluid inclusions trapping in the studied fluorite.

### CONCLUSIONS

Homr Akarem and Homret Mikpid rare metal granites are dissected by a number of fluorite veins. These veins are trending NE-SW and NW-SE in conformity with the general trend of faults dissecting the granitic bodies. Geochemically, the studied fluorites are enriched in Y, Pb, REEs and depleted in Sr contents with very low contents of Rb, Ba, Zr and Nb. The similarity in REE patterns between fluorite veins and host granites supports the genetic relation between them. The hydrothermal fluids which formed the fluorite veins were probably derived from the granitic melts. Fluid inclusions study indicates that these fluorite veins deposited from low salinity (5-7 wt. % NaCl eq.) and low temperatures (100°C-230°C) aqueous fluids due to boiling process. The pressures of trapping estimated between 120 and 300 bars for Homr Akarem, and 240 to 360 bars for Homert Mikpid fluorite.

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الملخص العربي

دراسة جيوكيمياء ومكتشفات السوائل لتمعنات الفلورايت في جرانيتات حمر عكارم وحمرة مكبد، جنوب

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وجد من الدراسة أن جرانيتات حمر عكارم وحمرة مكبد مقطوعة بعدد من عروق الفلورايت التي لها سمك مختلف والمحكومة تركيبيا حيث أنها تأخذ اتجاهات شمال شرق - جنوب غرب وشمال غرب - جنوب شرق. وقد أثبتت للدراسة الجيوكيميائية للفلورايت أنه يحتوي على تركيزات عالية نسبيا من الايتريوم والرصاص ومحتوى منخفض من الامترونيوم والروبيديوم والباريوم والزيركونيوم والنيوبيوم.

وقد اتضح من التمثيل البياني للعناصر الأرضية النادرة للفلورايت أنه غنى في العناصر الأرضية النادرة الثقيلة بالنسبة للعناصر الأرضية النادرة الخفيفة ويتميز بوجود شذوذ سلبي في الأيوبيوم. تشابه التمثيل البياني للفلورايت والجرانيتات الحاوية له يدل على علاقة منشأ بينهما.

وقد تبين من القياسات الميكروحرارية أن الفلورايت ترسب نتيجة لتفليان سوائل منخفضة الملوحة (5-7% NaCl). وقد تم تقدير أقل ظروف لتكوين الفلورايت عند درجات حرارة تتراوح بين 100°م إلى 230°م وضغط يتراوح بين 120 إلى 300 بار بالنسبة حمر عكارم، أما بالنسبة حمرة مكبد فعند درجات حرارة تتراوح من 100°م إلى 190°م وضغط يتراوح من 240 إلى 360 بار.