

The mineralogy and geochemistry of uranium, thorium, and rare-earth elements in two radioactive granites of the Vosges, France

MAURICE PAGEL

Centre de Recherches sur la Géologie de l'Uranium, BP 23, 54501 Vandœuvre-lès-Nancy Cedex, France
 Centre de Recherches Pétrographiques et Géochimiques, BP 20, 54501 Vandœuvre-lès-Nancy Cedex, France

ABSTRACT. Two contrasting types of Hercynian U-rich granites can be distinguished by their accessory minerals: (1) subalkaline potassic granites (amphibole-biotite ± pyroxene) characterized by apatite-zircon-thorite-sphene-allanite and rare ThO₂-rich uraninite, in order of appearance in the magma, and (2) leucocratic granites (biotite and muscovite) which contain monazite-zircon-apatite-xenotime-ThO₂-poor uraninite and Ti oxides. Intermediate accessory mineral associations may also exist.

The mineralogy, crystallization history, and geochemistry of two high K-U-Th granites from the Vosges, France, is described. Their assemblage of U- and Th-bearing accessory minerals is listed, in order of appearance in the magma, in Group 1 (above). Trace elements (U, Th, Zr, Hf) and preliminary data on REE are discussed. In a layered sequence of the Crêtes granite, thorite, with up to 15% UO₂, is shown to be important during differentiation. There is a decrease of the Th/U ratio corresponding to a slight decrease of the Th content whereas there is an increase of the U content at the end of differentiation. The Crêtes and Ballons granites have REE patterns characterized by LREE enrichment with a La/Yb ratio of about 28 (Crêtes granite) and a slight negative Eu anomaly. These relationships are typical of subalkaline potassic granites of the Hercynian. The trace element associations are similar to those of the shoshonite association with high U, Th, LREE and Ba, Rb, and Sr contents. A hypothetical model for uranium mineralization associated with such granites is discussed in the light of these data.

THE geochemistry of U and Th during magmatic differentiation has been studied in many granites from different areas and it has been shown that the U and Th contents of granitic rocks generally increase during differentiation although in some

cases they decrease (Ragland *et al.*, 1967). The Th/U ratio can either increase (Whitfield *et al.*, 1959; Rogers and Ragland, 1961) or decrease (Larsen and Gottfried, 1960) depending on redox conditions, the volatile content, or alteration by endogene or supergene solutions (Falkum and Rose-Hansen, 1978).

Uranium in U-rich granites occurs mainly in accessory minerals, the commonest of which (excluding the peralkaline granites) are uraninite, thorite, monazite, xenotime, allanite, zircon, apatite, sphene, and Fe-Ti oxides. The use of autoradiography or fission-track methods with microprobe analysis enables the significance of such accessory minerals to be evaluated precisely. Recent mineralogical studies of U- and Th-bearing minerals in Hercynian granites (e.g. Ranchin, 1971; Le, 1975; Cuney, 1978; Pagel, 1979b) suggest that accessory mineral associations could differ significantly depending on the primary petrography and geochemistry of the granites and subsequent deuteric processes.

Since U, Th, and the REE are located mainly in the same accessory minerals, a study of these minerals should be useful in interpreting the REE pattern of granitic rocks and the relationships between granitoid suites. While some accessory minerals such as zircon, sphene, apatite, and allanite have been considered previously, others such as thorite, monazite, and xenotime have rarely been investigated. This work shows the importance of the accessory mineral association in the geochemistry of U, Th, and REE in granitic melts.

Two granites of the Vosges, France (fig. 1), were selected for study because they have particularly high contents of U and Th (Pagel, 1979a) and contain thorite as a major U-bearing accessory mineral. The petrological, geochemical, and structural studies of Gagny (1968), N'Sifa (1978), and Blanchard *et al.* (1978) on the Crêtes massif and Pagel and Leterrier (1980) on the Ballons massif were used as a basis for the investigation.

Despite their high U content, no economic concentrations of U are known. Ranchin (1971) and more recently Cuney (1978), Leroy (1978), and Pagel (1979b) note that uraninite is always present in granites where economic U mineralization occurs. A genetic model is developed which considers the deuteric formation of uraninite to be important in concentrating U in an easily leachable form prior to mineralization (Cuney, 1978).

GEOLOGICAL SETTING

The Hercynian Crêtes and Ballons massifs are located in the central and southern Vosges respectively. The Ballons granite forms an east-west elongated massif (fig. 1) intruded into Visean volcano-sedimentary formations and on the northern and southern contacts it cuts intrusions ranging in composition from gabbro to quartz-monzonite. The granite is bounded to the west by a later biotite granite. Two small leucocratic biotite granite stocks are located in the granite and aplites, microgranites, lamprophyres, and pegmatites also occur. Actinolite-pyroxene-biotite microgranites are abundant in the north of the Ballons massif and form isolated masses in the volcano-sedimentary rocks. The Crêtes granite is intrusive into gneisses on its north-east border and elsewhere into different types of granites.

ORIGIN OF SAMPLES AND PETROGRAPHIC DESCRIPTIONS

A summary of the petrography of the two granites is presented and their major element chemistry is given in Table I.

Crêtes granite

Samples of five granite types (Gagny, 1968) were selected to represent the least differentiated facies (GP and MIN 27) together with two 'intermediate' granites (MIN 9 and BN) and one sample of 'blue granite' (MIN 18) which is the most differentiated.

Modal analyses are expressed in wt %. The Crêtes granite contains relict pyroxene (< 1%) of augitic composition forming a core to amphibole. The amphibole (15 to 11%) is a Mg-actinolite

which coexists with biotite (25 to 20%) rich in MgO (13.9 to 15.7%) and TiO₂ (3.8 to 4.1%). Plagioclase, with an average composition of An₃₀ (10 to 21%), has a more basic core and the K-Na feldspar (43 to 24%) is well zoned and corresponds to orthoclase. Late microcline and quartz (11 to 23%) are the other major minerals.

The layered sequence is described by N'Sifa (1978) and Blanchard *et al.* (1978). The minerals in each of the granite types are similar although quartz and K-feldspar increase upwards in the sequence and amphibole, pyroxene, and biotite decrease.

Ballons granite

The Ballons granite (Pagel and Leterrier, 1980) is also characterized by early pyroxene in the cores of hornblende crystals (3 to 8%) which are chemically zoned. The biotite (3 to 9%) is less Mg-rich than the Crêtes granite. The alkali feldspar is orthoclase (30 to 40%) with an average of 20% albite. Plagioclase is less abundant (25 to 30%) and has an average composition of An₃₅ with a more basic core (An₄₅). As in the Crêtes granite, quartz is not abundant (15 to 20%). Propylitic alteration is extensive in the massif with the development of zoisite, pistacite, chlorite, albite, hematite, sericite, quartz, Ca-Ti-Si minerals and sulphides (mainly pyrite).

ANALYTICAL METHODS AND PROCEDURE

The U- and Th-bearing accessory minerals were located in thin polished sections using photographic nuclear plates (Ilford K2) of 50 μm thickness, which record the α-particle tracks emitted by radioactive elements. The exposure time was three weeks. Data for U, Th, and REE concentrations in accessory minerals were obtained with an automated Camebax electron microprobe or with an electron microprobe coupled with an energy dispersive analyser. The standards used were synthetic UO₂ and ThO₂ and the glasses REE 1, REE 2, and REE 3 of Drake and Weill (1972). Chemical data were also obtained on mineral separates but many difficulties such as sample representativity, inclusions, zoning, and contamination during preparation are involved.

Chemical data on whole rock and mineral separates were obtained by: (1) Fluorimetric analyses for total, 'mobile' and 'fixed' uranium. The fluorescence intensity of an uranyl-salt is measured after a fluoperchloric attack and separation on chromatographic paper. The paper is burned and the residue is mixed by melting. The methods of analysing 'mobile' and 'fixed' uranium are

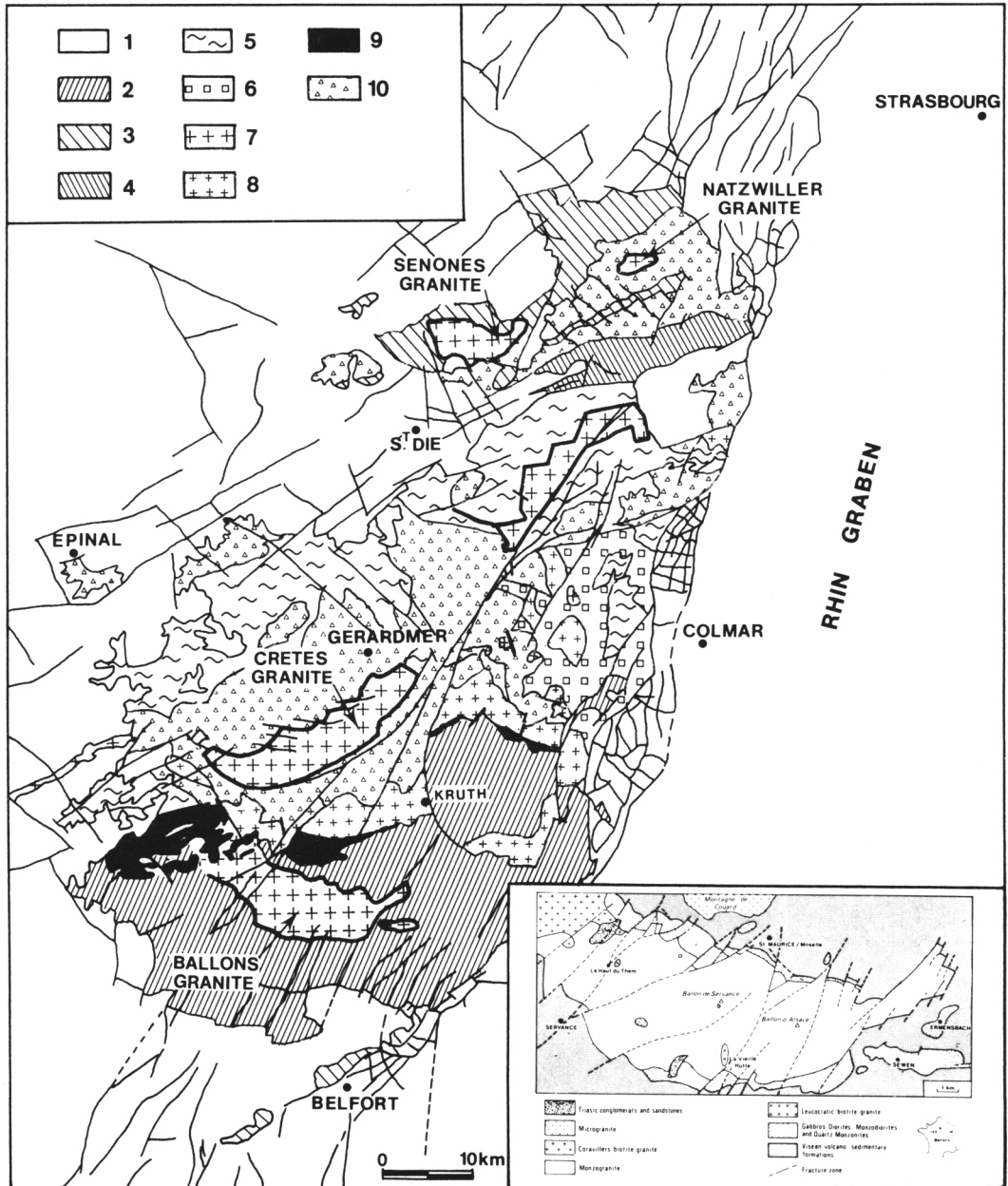


FIG. 1. Simplified structural and geological map of the Vosges massif based on Von Eller *et al.* (1972) and Fluck (1980). The inset shows more details of the Ballons massif (in Pagel and Leterrier, 1980). 1. Post-Stephanian sedimentary cover; 2. Viséan volcano-sedimentary formations; 3. Devonian volcano-sedimentary formations; 4. Schist formations (some are Precambrian); 5. Metamorphic basement (implied in the Caledonian and Hercynian orogenies); 6. Migmatites; 7. Subalkaline granites; 8. Granites related to the preceding ones (Fluck, 1980); 9. Microgranites; 10. Undifferentiated granites.

TABLE I (a and b). (a, left) Mean chemical analyses of granitic facies in the Ballons massif by automated emission spectroscopy (K. Govindaraju) and (b, below) chemical analyses on Crêtes samples (data from Gagny, 1968, and Blanchard et al., 1978).

Oxides (%) or elements (in ppm)	1		2		3		4		5		6	
	N=89	N=3	N=89	N=3	N=2	N=6	N=4	N=4	N=4	N=4	N=4	N=4
SiO ₂	66.07	73.50	74.06	68.24	65.93	76.33						
Al ₂ O ₃	14.52	12.17	13.19	15.05	14.40	11.77						
Fe ₂ O ₃	3.59	1.84	1.59	2.89	3.26	0.85						
MnO	0.07	0.02	0.03	0.05	0.05	0.01						
MgO	2.16	0.82	0.58	1.71	2.38	0.25						
CaO	2.78	0.59	0.80	1.57	2.27	0.44						
Na ₂ O	3.18	2.99	3.23	3.44	3.18	2.55						
K ₂ O	5.12	5.21	4.89	4.49	5.30	5.95						
TiO ₂	0.44	0.27	0.23	0.42	0.65	0.11						
l.i.	1.73	1.38	0.89	1.88	2.57	1.11						
Total	99.66	98.79	99.49	99.74	99.99	99.37						
Ba	1137	-	380	1004	1408	825						
Rb	333	-	446	227	328	395						
Sr	410	-	162	331	396	216						

Oxides (%) or elements (in ppm)	1		2		3		4		5		6	
	N=89	N=3	N=89	N=3	N=2	N=6	N=4	N=4	N=4	N=4	N=4	N=4
SiO ₂	61.68	11.79	6.14	0.11	5.89	3.86	2.14	5.03	1.04	1.23	98.91	
LAY A	67.45	12.34	2.68	0.08	2.67	2.20	2.38	6.39	0.71	1.51	98.41	
LAY B	60.87	11.73	6.10	0.16	5.79	4.32	2.30	4.93	1.04	1.26	98.50	
LAY C	64.48	13.07	4.18	0.15	4.23	3.21	2.61	5.34	0.70	1.05	99.02	
LAY D	63.11	12.86	5.06	0.09	5.13	3.41	2.49	5.06	0.83	1.13	99.17	
LAY E	67.18	13.72	2.94	0.05	3.11	1.76	2.39	6.99	0.46	0.85	99.45	
LAY F	62.70	12.81	5.40	0.11	5.32	3.44	2.43	5.01	0.90	1.18	99.30	
LAY G	66.61	13.27	3.29	0.06	3.26	2.59	2.59	5.96	0.46	0.95	99.04	
LAY H	65.44	13.05	3.95	0.11	4.29	2.44	2.55	5.59	0.65	0.98	99.05	
LAY I	75.80	12.74	0.31	0.04	0.20	0.35	2.98	6.35	0.09	0.36	99.22	
LAY J	60.50	13.60	5.48	0.09	5.63	3.31	2.27	6.67	0.92	1.16	99.83	
GP	60.40	14.10	5.99	0.10	6.24	3.66	2.12	6.53	1.06	0.94	101.14	
MIN 27	64.90	13.40	5.35	0.09	4.56	3.17	2.23	4.71	0.85	0.80	100.06	
MIN 18	61.50	14.05	5.25	0.09	4.66	3.12	2.33	6.39	0.89	0.78	99.06	
MIN 9	61.50	14.05	5.25	0.09	4.66	3.12	2.33	6.39	0.89	0.78	99.06	
BN	61.80	13.60	5.09	0.08	4.70	3.06	2.22	6.68	0.89	1.02	99.14	

1. Ballons monzogranite. Data from Pagel and Leterrier (1980)
 2. Vieille Hutte leucocratic granite. Data from Stussi (unpub)
 3. Haut du Them leucocratic granite.
 4. Corravillers granite. Data for an isolated area on the west border of the Ballons monzogranite.
 5. Crêtes microgranite.
 6. Aplité.
 l.i. = loss on ignition at 1000°C.
 N = number of analysed samples.

TABLE II. Partial electron-microprobe analysis of thorite in the Crêtes and Ballons granites

	Crêtes granite				Ballons granite		
	T ₁ -GC1	T ₂ -GC2	T ₁ -GC2	T ₂ -GC2	T ₁ -VB138	T ₂ -VB138	T ₃ -VB138
SiO ₂	17.45-16.88	17.53	17.76-17.66	17.74-17.66	16.39-15.53	15.74-17.13	15.57-15.99
ThO ₂	44.42-47.48	40.23	45.90-48.34	41.62-40.44	51.77-46.87	47.75-49.06	40.41-39.50
U ₃ O ₈	6.61- 2.95	9.93	11.79- 9.36	15.02-14.68	7.54-10.93	9.88- 7.04	2.72- 2.92
PbO	0.01- 0.02	0.10	0.85- 0.75	0.48- 1.96	0.35- 1.23	1.42- 0.33	9.28- 8.50
Ce ₂ O ₃	1.90- 2.13	1.48	2.98- 2.30	2.68- 3.75	0.52- 1.11	0.52- 0.42	1.23- 1.22
Fe ₂ O ₃	0.06- 0.06	0.65	0.48- 0.55	0.29- 0.06	1.35- 2.04	1.65- 1.68	6.52- 6.21
Total	70.25-69.52	69.92	79.76-78.96	77.83-78.55	77.92-77.71	76.96-75.66	75.83-74.34
Th/U	6.5 -15.7	3.9	3.8 - 5.0	2.7 - 2.7	6.7 - 4.2	4.7 - 6.8	14.5 -13.1

described by Coppens and Bernard, 1978; (2) γ spectrometry was performed with an Intertechnique SA 40 B instrument using the 2.62 MeV peak of Th; 200 g samples of < 200 mesh size were used to ensure homogeneity. The reproducibility was estimated to be $\pm 5\%$; (3) Instrumental neutron activation analyses for U, Th, Zr, Hf, and REE.

100 to 150 mg samples were used for whole-rock analysis. Crêtes samples were irradiated with a neutron flux of $10^{14} \text{ n cm}^{-2} \text{ s}^{-1}$ in the Osiris reactor whereas the Ballons samples were irradiated in the Triton reactor (Fontenay aux Roses). The standard rocks used are GSN and BCR1. A correction for gradient flux was made for data on the Ballons samples. Details of the experimental procedure are given in Chayla *et al.* (1973) and Treuil *et al.* (1973). Values for normalizing REE concentrations to chondritic values were from Herrmann (1970)*.

URANIUM, THORIUM, AND REE IN MINERALS

The U- and Th-bearing minerals described are from the Crêtes and Ballons granites. Three groups which are important in magmatism and metallogenesis are distinguished on their U and Th contents. Group I consists of thorium and uranium silicates (thorite, ThSiO₄) or oxides (uraninite, UO₂). Group II consists of minerals in which U and Th replace other elements in the structure, especially monazite, allanite, zircon, sphene, and apatite (in decreasing order of substitutional possibilities). In Group III, U is associated with major rock-forming minerals.

* Editor's footnote: these differ from the values of Nakamura (1974) which are used for calculating normalized REE values in several recent British publications.

Group I: uranium and thorium silicate or oxide

Thorite is common in this type of granite with 5 to 10 crystals in each thin section. The thorites are always metamict with the apparent crystal size varying from 10 to 150 μm . Thorite formed early in the crystallization sequence and is generally included in, or in contact with, biotite and amphibole. In layered samples from the Crêtes granite (fig. 2) thorite is located preferentially in actinolite-biotite layers. Quantitative chemical data are presented in Table II; chemical heterogeneity of thorite is quite common. The sum of oxides shows a 20-30% deficit due to non-analysed elements (Ca, Ti, Zr, P, etc.) and hydration. During metamictization oxidation of Fe²⁺ and U⁴⁺ occurs. The U₃O₈ content is highly variable from 3 to 15% for the Crêtes granite and 0 to 10.9% for the Ballons granite. The Th/U ratio varies from 2.7 to 15.7 with a mean close to the average Th/U ratio for granites. The Ce₂O₃ content is high (1.5 to 3.7% for the Crêtes granite and 0.4 to 1.2% for the Ballons granite). Staatz *et al.* (1976) distinguished two groups of thorites on the basis of REE: (1) a LREE-enriched group with Ce or Nd dominant, and (2) a HREE-enriched group with Dy or Yb predominant. Crystals are often inhomogeneous with less U in the grain boundaries and fracture zones. Pb is higher in the grain boundaries whereas the Ce distribution is more homogeneous. These observations indicate that the chemical composition of thorite is highly variable depending on primary formation and secondary alteration.

Uraninite is scarce in the Crêtes and Ballons granites with only 1 or 2 crystals in 10 thin sections. Cubic crystals 20 to 40 μm across are intergranular. The presence of uraninite corresponds to a U content which is always higher than 14 ppm. The

ThO₂ content is high, 8 to 10% in uraninite of the Ballons granite (Pagel and Ruhlmann, 1979) and 10% in a uraninite from the Crêtes granite. The REE content is also high with a Ce₂O₃ content of 0.7%. The uraninite crystals are stable in surface samples probably due to the high thorium content (see Grandstaff, 1976) which is characteristic of subalkaline potassic granites rich in U. In contrast, leucocratic granites in France are characterized by uraninite crystals low in Th (Ranchin, 1971).

Group II: uranium, thorium substitution in accessory minerals

The REE content and pattern of accessory minerals of this group, in plutonic rocks, varies with magma composition and the crystallization temperatures and pressure of volatiles in the magma. The partition coefficient of U between magma and accessory minerals also depends on f_{O₂}, since Calas (1979) has demonstrated that U⁴⁺, U⁵⁺, and U⁶⁺ can coexist in a magma, and

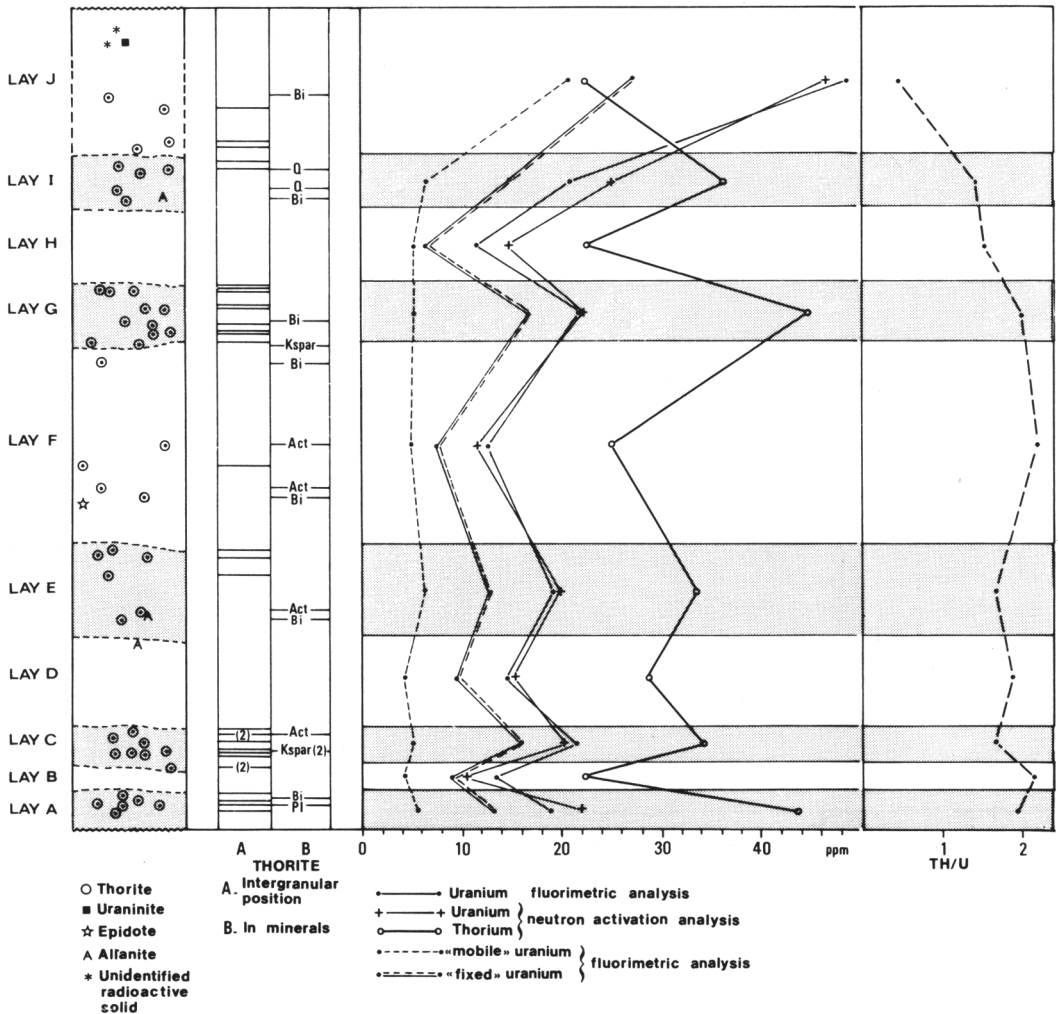


FIG. 2. Mineralogical localization of U-Th-rich accessory minerals in a layered sample of the Crêtes granite and variation of U, Th, and Th/U as a function of the sequence. Note that the 'mobile' U is nearly constant except in the last pegmatitic layer (LAY J). Bi = biotite; Act = actinolite; Q = quartz; Kspar = potassium feldspar; Pl = plagioclase. The length from the bottom of LAY A to the top of LAY J is 295 mm.

that the ratio between the three uranium species depends on f_{O_2} .

Sphene. Crystals are 0.5 to 1.0 mm in size and four main types are identified: (1) automorphic, in quartz or potassium feldspar, which can have inclusions of apatite, amphibole, or thorite. The thorite develops a pleochroic halo and radial fractures in sphene; (2) xenomorphic, between major minerals; (3) automorphic cores surrounded by xenomorphic sphenes especially in potassium feldspars; (4) as alteration products of biotites particularly in the Ballons granite.

Blanchard *et al.* (1978) found that automorphic crystals of sphene are more abundant in the quartz-feldspar layers and are formed in the granite after crystallization of the ferromagnesian minerals, actinolite and biotite. Data on sphene from the Central Sierra Nevada batholith (Dodge and Mays, 1972) show that *LREE* are enriched with a flat pattern from Eu to Lu. Sphene from the Ballons granite has high concentrations of *REE*, with values of 4900 ppm La or 2800 ppm La respectively. α -track counts indicate that the U content of sphene is 50 to 200 ppm.

Allanite. Crystals are scarce in the Ballons and Crêtes granites. They are not present in every thin section and generally only 1 grain is observed. Their size varies from 0.5 to 1.5 mm. They are brownish to maroon and zoned. Allanite may include plagioclase, quartz, hornblende, and sphene or may be included in orthoclase. Two microprobe determinations in a sample of the Ballons granite show that allanite is richer in ThO_2 (0.4 to 0.7%) than in UO_2 (up to 0.3%) and contains up to 10.4% Ce_2O_3 .

Zircon. Two populations of zircons are observed, differentiated by their size (Gagny, 1968) and habit (Pupin, 1976), in both the Ballons and the Crêtes granites. In the Ballons granite, microprobe determinations on two zircons show that the core has a UO_2 content between 0.03 and 0.5% whereas the rim may be considerably enriched with values up to 3.5% UO_2 . The outer part of zircon is also enriched in FeO, Ce_2O_3 (mean content of 1% on six analyses), MnO, CaO, Al_2O_3 , ThO_2 , HfO_2 upon the analysed oxides.

Apatite. Apatite crystals are more abundant in the Crêtes than in the Ballons granite as reflected by mean P_2O_5 content of 0.67% for the Crêtes granite and 0.27% for the Ballons granite. The apatite crystals are frequently included in biotite and amphibole and also located around them. In the Crêtes granite, more than 150 apatite crystals occur in millimetre size biotite in a thin section. According to Jurain (1962), the U content of apatite in the Ballons granite is 50 to 100 ppm, which is

characteristic of granitic rocks; the Th/U ratio is about 1.

Monazite and *xenotime* are observed only in quartz-monzonite.

Group III: uranium and thorium in the rock-forming minerals

The U content of the rock-forming minerals determined on separated fractions from the Ballons granite (which are affected by contamination with accessory minerals) is: plagioclase (1.5 ppm), orthoclase (1.4 to 3.7 ppm), hornblende (4.4 to 8.0 ppm), and biotite (more or less chloritized) (4.7 to 43 ppm). The U content of hornblende is lower than the range of 12 to 52 ppm given by Jurain (1962).

URANIUM AND THORIUM GEOCHEMISTRY

The U and Th contents increase gradually from the gabbro-diorite to the quartz-monzonite and the southern facies are richer in U and Th than the northern ones (Pagel, 1979a). The average Th/U ratio for the two series is nearly 5.

The Ballons monzogranite has an arithmetic average value for U of 12.8 ppm (88 samples) and a mean Th value of 50 ppm (44 samples). These U and Th contents are much lower than the southern quartz-monzonites and confirm the discontinuity observed in the major element geochemistry (Pagel and Leterrier, 1980).

Stussi (1970) has shown that in the southern Vosges, rhyolites have high U and Th contents related mainly to the accessory minerals thorite, zircon, and allanite. The absence of sphene in volcanic rocks could be due to the higher CO_2 content of the volatile phase. The geochemical similarity, based on major elements, between volcanic and plutonic rocks in the southern Vosges is confirmed (Stussi, 1970). The U content is lower for the leucocratic biotite granites than in granite with a similar Th value. The U, and Th/U values for the Corravillers biotite granite (fig. 1, Table III) are different and indicate a separate magmatic source.

All the dykes (lamprophyres or microgranites) in the Ballons massif are characterized by high U and Th but with a Th/U value of 3.8, a value higher than the Th/U of 2.1 to 2.5 obtained for the Crêtes granite (Tables IV and V).

A detailed study on a layered sample from the Crêtes granite (fig. 2, Table IV) shows that U and Th are much higher in the actinolite-biotite layers than in the quartz-feldspar layers except for the LAY J where the U content is very high. From LAY A to LAY F the Th/U ratios are higher in the actinolite-biotite layers than in the quartz-feldspar

TABLE III. U and Th data on the granitic facies of the Ballons massif

Facies	U _{min.}	U _{max.}	Ave.	Th _{min.}	Th _{max.}	Ave.	Th/U _{mean}
Ballons monzogranite	4.2	27.8	12.8 (88)	33.9	61.4	49.5 (44)	3.9
Vieille Hutte leucocratic granite	7.2	11.1	9.0 (4)	43.0	51.5	47.4 (4)	5.3
Corravillers granite	5.1	9.1	7.1 (4)	19.4	27.0	23.6 (3)	3.3
Aplite	27	40	32 (3)	23	29	27 (3)	0.8
Micro quartz-monzonites	{ 17.8	{ 19.5	{ 18.6 (2)	{ 92.7	{ 93.2	{ 92.9 (2)	{ 5.0
	{ 21.2	{ 36.8	{ 29.0 (2)	{ 128.4	{ 134.1	{ 131.2 (2)	{ 4.5
Crêtes microgranite	10.2	15.7	12.5 (7)	46.6	50.9	49.3 (3)	3.8
Lamprophyres	{ 21.6	{ 36.6	{ 29.1 (2)	{ 64.4	{ 116.8	{ 90.6 (2)	{ 3.1
	{ 23.0	{ 32.0	{ 26.9 (4)	{ 35.0	{ 36.0	{ 35.5 (2)	{ 1.3
Epiyenite	25.6	28.2	26.9 (2)	66.0	68.7	67.3 (2)	2.5

Uranium was analysed by fluorimetry and thorium by γ -spectrometry. The number of measurements is indicated in parentheses.

layers and thereafter decrease gradually in the late stages. The 'mobile' U is nearly constant along the sample except in LAY J (Table III).

The aplitic facies in the Ballons massif are more enriched in U than the aplitic facies in the Crêtes granite. Some measurements on samples described petrographically by N'Sifa (1978) show that the U content is highly variable (3.4 to 13.8 ppm) and that the aplites, situated in flat joints, show the greatest enrichment. The lowest U contents are found in transverse and linear joints.

REE, Zr, Hf CONTENTS AND VARIATIONS IN THE CRÊTES GRANITE AND BALLONS GRANITE AND ASSOCIATED PLUTONIC ROCKS

The REE content for the Crêtes granite varies from 210 to 255 ppm (Table V), close to the average REE content of granite (Herrmann, 1970). The chondrite-normalized pattern (fig. 3) indicate that the LREE are more enriched than the HREE, with a La/Yb ratio *c.* 28 compared with the value of 12.8 of Herrmann, 1970 (Pagel *et al.*, in preparation), and there is a slight negative Eu anomaly.

Zr and Hf contents are higher in ferromagnesian-rich rocks with a correlation between Zr and Hf controlled by zircon. This is also seen in the Crêtes and Ballons granites.

Partial data obtained on the Ballons granite (Table VI) indicate that: (1) The La, Eu, and Tb contents of the Ballons granite are lower than in the Crêtes granite; (2) there is a substantial decrease of the Eu and Tb contents from the margin to the core as defined by Pagel and Letierrier (1980). There is also an apparent evolution of La excluding sample VB82 and of Zr and Hf.

TABLE IV. Fluorimetric analysis on different facies of the Crêtes granite

	Samples	U _{total} (μ g/g)	U _f (μ g/g)	U _M (μ g/g)	U _f /U _{total} %
Granite layers	LAY A	19.0	13.0	5.5	68
	LAY B	13.3	8.9	4.2	67
	LAY C	21.4	15.8	5.1	74
	LAY D	14.3	9.7	4.2	68
	LAY E	19.2	12.7	6.2	66
	LAY F	12.7	7.6	4.9	60
	LAY G	22.0	16.7	5.1	76
	LAY H	11.7	6.4	5.2	55
	LAY I	20.6	14.5	6.3	70
	LAY J	48.6	27.9	20.8	57
Granite type	MIN 27	14.0	4.1	6.9	37
	GP NOIR	16.7	7.4	7.0	51
	MIN 9	16.0	5.9	8.8	40
	MIN 18	15.5	5.5	9.2	37
	BN	18.0	7.4	8.6	46
Aplite	AP 1	3.4	2.4	0.8	71
	AP 2	8.1	5.6	2.5	69
	AP 3	5.6	3.7	1.8	66
	AP 4	13.7	5.8	8.1	42
	AP 5	4.9	3.3	1.5	67
	AP 6	11.7	6.9	4.4	59
Enclave	EN 1	16.8	12.3	4.0	73
	EN 2	8.3	4.2	3.7	51
	EN 3	9.4	4.9	4.3	52

Analyst: B. Hassko (Centre de Recherches sur la Géologie de l'Uranium).

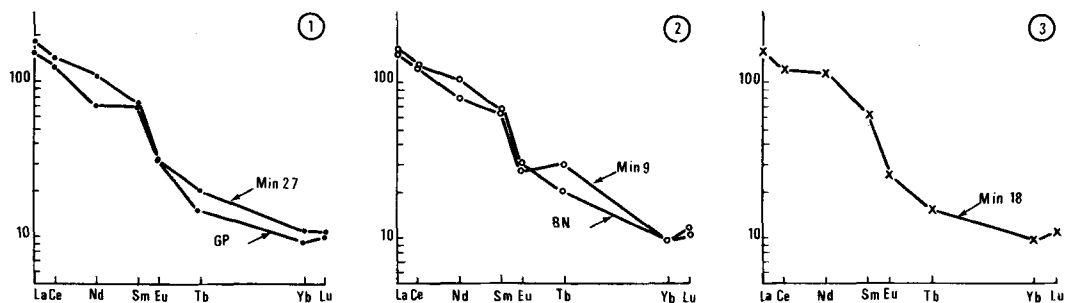


FIG. 3. Chondrite-normalized REE pattern for samples of the Crêtes granite. 1. 'Black variety' granites; 2. Intermediate granites; and 3. 'Blue' granite.

DISCUSSION

Importance of the U- and Th-bearing accessory mineral associations in granitic rocks

The geochemistry of certain trace elements in granites depends on the accessory minerals present. In the Ballons and the Crêtes granites, the accessory mineral association is characterized by the coexistence of thorite-sphene-allanite-scarce Th-rich uraninite with ubiquitous zircon and apatite.

A compilation of mineralogical studies (Even, 1966; Coppens and Bolfa, 1963; Le, 1975) of similar subalkaline granites in France, including granites of Senones (northern Vosges), Ploumanac'h (northern Brittany), and Mayet de Montagne (north-east Central Massif), indicates that this association is a general feature of this type of granite and can be contrasted with the monazite-dominant, Th-poor uraninite \pm xenotime, \pm Ti oxide, apatite, and zircon of the Viseu-Guarda area in Portugal (Pagel, 1979b) or Limousin, France (Ranchin, 1971).

Textural relationships between apatite and zircon differ in the two associations. In the former,

apatite has few zircon inclusions although apatite inclusions are common in zircon whereas in the latter zircon inclusions in apatite occur frequently.

A parallel can be drawn with the magnetite-sphene pair in I-type and the ilmenite-monazite pair in S-type granites (Chappell and White, 1974; Ishihara, 1977; Ivanova and Butuzova, 1968). But between these extremes there is a continuity, as Le (1975) and Cuney (1978) have described the association monazite-xenotime-sphene-Th medium to very rich-uraninite with thorite-allanite-zircon and apatite in the Forez area (France).

The crystallization sequence of accessory minerals was determined mainly by textural observations and geochemistry. Apatite is generally considered to be a liquidus mineral as confirmed by its association with pyroxene. Moreover, all the minerals from the granite contain apatite inclusions; apatite crystals are relatively free of mineral inclusions, and zircon crystals frequently contain apatite. For peraluminous magmas, less than 100 ppm Zr is necessary for zircon supersaturation (Watson, 1979). With the high values of Zr, 530 ppm in the Crêtes granite and 160 ppm in the

TABLE V. U, Th, Zr, Hf, and REE (ppm) in different rock-type of the Crêtes granite. Neutron activation analysis

Ref.	U	Th	Zr	Hf	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Σ REE	La/Yb
GP	18.9	46.6	672	12.1	50.1	101	41	13.2	2.15	0.76	1.77	0.34	210.32	28.3
MIN 27	15.6	38.5	559	13.0	57.6	113	65	13.9	2.3	1	2.1	0.38	255.28	27.4
MIN 9	20.1	40.9	463	9.8	51.0	99.6	47	11.9	1.93	1.5	1.8	0.36	215.09	28.3
BN	21.0	44.0	467	10.2	52.9	104	61	12.6	1	1	1.8	0.39	235.79	29.4
MIN 18	17.4	39.3	489	9.5	50.1	94.6	68	11.5	1.8	0.75	1.8	0.38	228.93	27.8

Ballons granite, zircon is thus a near-liquidus phase as confirmed by the abundance of zircon inclusions in ferromagnesian minerals. Detailed morphological work such as that of Pupin (1976) on the Ballons granite, however, shows that there are different zircon populations and times of crystallization.

The association of thorite with actinolite-biotite layers in the Crêtes sample (fig. 2), and its occurrence as inclusions in amphibole and sphene but not in pyroxenes, suggest that thorite crystallization probably overlapped biotite and amphibole formation. Crystallization of sphene after ferromagnesian minerals but before K-feldspar and quartz is indicated texturally and confirmed by geochemistry (Blanchard *et al.*, 1978). Different generations are also seen, however, and sphene could result from deuteric alteration of ferromagnesian minerals. Uraninite formed late as indicated by its intergranular position in the Ballons granite and its occurrence in the pegmatitic facies in the layered sequence from the Crêtes granite. The ThO₂ content of the uraninite appears to depend on the ThO₂ content of the magma.

ROLE OF THE MAJOR AND ACCESSORY MINERALS IN THE GEOCHEMISTRY OF U, Th, AND REE IN GRANITIC MELTS WITH PARTICULAR REFERENCE TO THORITE

Only a maximum of 20% U is associated with major minerals (Table VII) and the few data available on Th show similar results. Hornblende contains more Th than biotite.

The early crystallization of thorite which can incorporate U (up to 15%) and REE (Ce up to 3.2%) reflects the geochemistry of these elements. The Th/U ratios of thorite vary from 2.7 to 14.5, probably the most representative value is between 2.7 and 5.0. This ratio is greater than the granite

ratio (≈ 2), so that thorite separation would lead to slight enrichment of U with differentiation. This is shown in fig. 2 where the late stages of LAY F to LAY J are enriched in U relative to Th. Assuming that 80% of Th is associated with thorite, which contains an average of about 10% U, about 60% of the U would be associated with thorite.

Thorite has little effect on the geochemistry of REE compared with sphene or allanite. In LAY B, for example, where the total REE content is 387 ppm and the Th content is 22 ppm, sphene played a major role in controlling the REE geochemistry.

Problems associated with interpreting REE in granitic rocks arise from the variable crystallization behaviour of accessory minerals in granites and mineral zoning. Mendenbach (1976) has shown that REE, Hf, Th, U, Y, Ca, and P contents are zoned in zircons from many granitic rocks, and in highly radioactive granites it is difficult to obtain precise data on minerals because of tiny inclusions of U-Th-REE-bearing accessory minerals.

In the zoned Ballons granite REE content decreases as differentiation increases (or as SiO₂ increases), consistent with the observation of Emmermann *et al.* (1975) for the Schwarzwald granites (Germany) and of Cocherie (1978) for the Calvi and Budduso granites (Corsica, France). This results from the crystallization of REE-bearing accessory minerals which causes the bulk partition coefficient, between solid phases and melt, to exceed one.

METALLOGENESIS

Economic U mineralization associated with granites is generally related to U-enrichment of the granites (see, for example, Moreau, 1977) and the most intriguing aspect of the amphibole-biotite \pm pyroxene granites with high U contents similar to mineralized granites and Th/U ratios of 2.5 to

TABLE VI. U, Th, Zr, Hf, and some REE (La, Eu, Tb) in the Ballons monzogranite (in ppm)

Sample ref.	U	Th	Th/U	Zr	Hf	Zr/Hf	La	Eu	Tb
VB 66	22	43	1.95	230	5	46	37	1.2	0.53
VB 138	17	42	2.5	155	3.8	41	33	1.2	0.48
VB 82	13	42	3.2	210	4.1	51	32	1	0.43
VB 60	21	40	1.9	133	3.8	35	31	0.9	0.36

Neutron activation analysis Pierre Süe Laboratory, Saclay. C.E.A. Division analysis.

In the massif zonation (Pagel and Leterrier, 1980) the differentiation increases from VB 66 to VB 60.

4.0 is that no economic U concentrations have been described. In the southern Vosges, one prospect, consisting of the Kruth pitchblende vein, is known in a granite which is mineralogically similar to the Crêtes granite (Geffroy and Sarcia, 1954). Several features of such granites are important from a metallogenic point of view.

(1) In contrast to granites which contain U mineralization, uraninite contains about 10% ThO₂ and its abundance is low. Most authors (Barbier, 1968, 1974; Ranchin, 1971; Le, 1975; Cuney, 1978) propose dissolution of uraninite as a source of U, using either a per-descensum (Barbier, 1968, 1974) or a hydrothermal model (Ranchin, 1971; Cuney, 1978). Laboratory experiments (Grandstaff, 1976) show that ThO₂-bearing uraninite is more resistant to alteration processes than pure UO₂ and detrital uraninite, which contains high Th, is known from the Indus river (Simpson and Bowles, 1977).

(2) As much as 60% of the U in the granites is in thorite which is resistant to alteration. In the Ballons massif, however, as a result of surface alteration and fracturing, important U loss has been observed because the thorite crystals are totally metamict and hydrated due to their high U content. In these cases thorite is more affected by alteration processes and it can result in U depletion in the granite. Moreover, Mendenbach (1976) demonstrated that migration of U and Pb takes place during zircon hydration.

(3) There was widespread propylitization of the Ballons monzogranite, probably by water expelled from the melt and derived from the enclosing volcano-sedimentary rocks. This alteration is characterized by limited metasomatism, on the scale of a hand specimen. Detailed geochemical

studies (Pagel and Leterrier, 1980) show that the primary geochemistry of such elements as Ba, Sr, Rb are conserved. The fluids involved in propylitization, essentially aqueous solution without CO₂, are not acid and are unable to extract U from such accessory minerals as thorite, zircon, sphene, or allanite as proposed for the Bois Noirs granite (Cuney, 1978). However, these fluids destabilize biotite and hornblende and could have liberated quantities of U. These minerals are altered to calcic minerals such as sphene, zoisite, pistacite, or a variety of sphene called grothite (SiO₂ 31.2%, CaO 29.1%, TiO₂ 31.7%, FeO 2.6%) which could have incorporated the liberated U.

(4) Pegmatitic and aplitic facies are sometimes enriched in U as observed in the Crêtes and Ballons massif (Pagel and Ruhlmann, 1979), showing that U is concentrated in the fluid phase at the end of crystallization of these granites. The pegmatites are scarce and preferentially located around the granite associated with Mo-Cu anomalies.

Thus the mineralogy and geochemistry of these amphibole + biotite ± pyroxene granites are not favourable for economic U concentrations by endogene processes unless there is powerful acid leaching. This has occurred in the Kruth area (fig. 1) where amphibole granite is intensively chloritized and muscovitized at its contact with an intruding leucocratic muscovite-bearing granite. Such granites should not be overlooked as targets for U exploration if there is evidence of circulation of an acid fluid phase or if surface or hydrothermal leaching of granite after metamictization of uraniferous minerals, such as thorite, has occurred. Such processes could lead to small concentrations of U in the granite or more probably provide a source of U for sedimentary deposits.

TABLE VII. *Quantitative distribution of U in major minerals of the Ballons granite. Note that more than 80% of uranium is contained in accessory minerals (thorite, sphene, zircon, allanite, apatite)*

	Modal values (%)	U content in mineral (ppm)	Modal amount of U in minerals (ppm)	Per cent of U in rock for each mineral (%)
Biotite	4	12.0 (1)	0.46	3.5
Amphibole	11	6.5 (6)	0.71	5.4
Plagioclase	28	1.5 (1)	0.42	3.2
K-feldspar	38	2.0 (3)	0.76	5.8
Quartz	18	1.0*	0.18	1.4
Major minerals	99		2.53	19.3†

* Assumed.

† Relative to a total U content of 13 ppm.

CONCLUSIONS

In the Hercynian of Europe, uraniferous granites with a U content greater than 8 ppm can be grouped into (1) amphibole-biotite \pm clinopyroxene granites (termed subalkaline potassic granites) characterized by the coexistence of accessory minerals such as thorite-sphene-allanite and scarce ThO₂-rich uraninite and (2) the biotite-muscovite granites with coexistent monazite-ThO₂-poor uraninite and xenotime. These associations are extreme, and intermediate associations are known, for example, in biotite granites. A lack of experimental data on the accessory minerals precludes any detailed interpretation but the former association reflects higher temperatures, as indicated by clinopyroxene and Mg-rich biotite crystallization, and higher f_{O_2} , as indicated by the predominance of magnetite.

REE analyses for the subalkaline granites, Calvi granite in Corsica (Cocherie, 1978), Senones granite in Vosges (Bornhorst and Balagna, 1979) and data from this study, show that they have normalized chondrite REE patterns characterized by LREE enrichment with typical La/Yb ratios from 27 to 36 and small negative Eu anomalies. Interpretation of REE patterns and modelling of granite fractionation is difficult because (a) REE are strongly partitioned into accessory minerals. Partition coefficients are not always known and where available depend on the chemical composition of the granite. (b) there are different generations of the accessory minerals with different chemistries, and (c) the accessory minerals are frequently chemically zoned.

The subalkaline granitoid association, first described from Corsica by Orsini (1976), is characterized by high U, Th, LREE and Ba, Rb, and Sr contents comparable with those of the shoshonite association (Morrison, 1980). The granites are formed by anatexis of the deep crust as a result of steep geothermal gradients caused by influx of basaltic melts. Barriere (1977) on the Ploumanac'h granite and Fluck (1980) on the Crêtes granite consider alkali basalt to be a possible primary magma, but isotopic work is needed to evaluate the relative contribution of mantle-derived and deep crustal-derived material.

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