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Trace- and minor-element mineralogy of the microgranite at Ghurayyah, Kingdom of Saudi Arabia

by

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1/ U.S. Geological Survey, Denver, CO

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ABSTRACT

A study was made of those minerals containing rare-earth oxides, niobium, zirconium, and uranium. The mineralized microgranite is a circular stock about 900 m in diameter. Rare-earth minerals are widely scattered and those identified are xenotime and doverite. In addition, rare-earth oxides were found in senaite and thorite. Senaite, which is principally a titanium-, iron-, lead-, and zinc-bearing mineral, is extremely rare; Ghurayyah is only the fourth locality in the world where it has been found. Thorite, composed mainly of thorium, is a fairly common mineral in pegmatite and microgranite at Ghurayyah, especially in shear zones, but zircon is the most common accessory mineral in the stock. Niobium minerals are not abundant, but both pyrochlore and columbite-tantalite were identified. No uranium or tin minerals were found in any of the mineral separates. Autoradiographs show the distribution and size of the radioactive minerals.

Electron-microprobe studies were made of zircon, thorite, doverite, and senaite. Zircon is principally a silicate of zirconium, but it contains minor hafnium, yttrium, thorium and uranium. Thorite has a high iron-oxide content, a small Y_2O_3 content, and about 0.5 percent of UO_2. The thorium to uranium ratio in the mineral is 119 to 1. Doverite is made up principally of rare-earth elements, the most important of which is yttrium. The senaite from Ghurayyah is similar to that of the St. Peter Dome area, Colorado, and both have a high zinc content. The Ghurayyah senaite also contains a small amount of niobium.

Potential ore minerals occur as small grains along fractures or along grain boundaries of the larger felsic minerals. The size of the ore minerals is about 0.001 to 0.20 mm in diameter.

INTRODUCTION

The Ghurayyah microgranite forms a stock about 900 m in diameter with a circular cross-section and nearly vertical contacts (Drysdall, 1979). The stock, located about 85 km south-southwest of Tabuk (fig. 1), lies in a valley at the junction of Wadi Sadr and Wadi Assahlulah where the two wadis divide the pluton into three outcrop areas. The rock is primarily a light-gray weathering porphyritic leucocratic granite. The phenocrysts are principally euhedral microcline and quartz set in a finer-grained matrix of albite, microcline, and quartz with small amounts of riebeckite.

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The present mineralogical study of the microgranite was undertaken to examine possible ore-bearing minerals from a somewhat different perspective that has been previously used, and also to study them in greater detail. Previous detailed work on the microgranite was carried out in 1976 by Lalande (1977) of Watts, Griffis, and McOuat of Toronto, Canada, at which time sampling was done on a grid basis. Many more samples were studied during Lalande's work than the 12 samples reported on in the present study. Of the 12 samples, 6 consist of 3 samples each of two large composite samples sent to us by A. R. Drysdall. The remaining six samples were collected in November 1983 by Staatz and Drysdall. Most of these samples consist of veins, shear zones, or small pegmatites, which are either abnormally radioactive, or contain an unusual-appearing mineral (table 1.) The purpose of the letter sampling was to locate and identify any uncommon or rare minerals that had not been encountered during previous sampling by Lalande (1977).

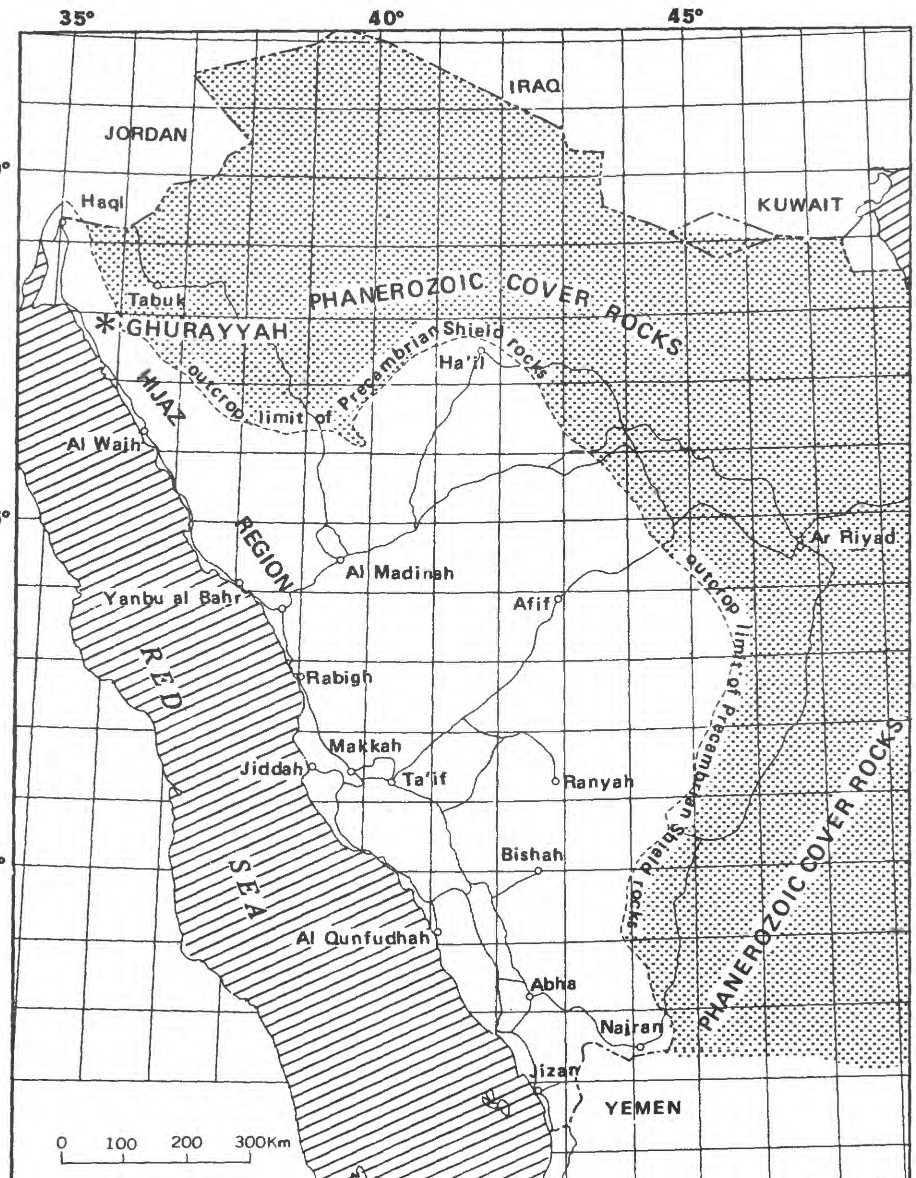

Figure 1.--*Location of Ghurayyah*

Our study of the potential ore-forming minerals includes not only the identification of those primary minerals in each sample, but also the location of secondary sources of various elements. For example, rare earths are the principal elements in such minerals as doverite and monazite; but because their atomic radii are similar to that of thorium, they may also replace thorium, and make up a significant part of a mineral such as thorite. Similarly, although niobium is a primary constituent of columbite-tantalite and pyrochlore, it may also replace titanium and occur in significant amounts in minerals such as rutile and ilmenite. The distribution and location of various radioactive minerals is illustrated by autoradiographs, and the elemental content of selected ore minerals was determined with the electron microprobe.

The work on which this report was based was performed in accordance with a cooperative agreement between the U.S. Geological Survey and the Ministry of Petroleum and Mineral Resources.

Table 1.--Location and type of samples collected at Ghurayyah by Staatz and Drysdall.

Sample no.	Location	Remarks
G-1	South of Wadi Sadr; north of and about two thirds of way up to the crest of the mountain from the wadi	A 7.5 cm thick shear zone. Radioactivity more than twice that of surrounding granite
G-2	South of Wadi Sadr; near mountain top	Granite containing large, euhedral feldspar crystals
G-3	South of Wadi Sadr at mountain top	A 4-cm thick quartz vein
G-4	South of Wadi Sadr; about half way up to the crest of the mountain from the wadi	A 1-cm thick vein. Radioactivity more than 10 times that of the adjacent granite
G-6	North of Wadi Sadr; east of Wadi Assahlulah near mountain top	Small pegmatite that is .9 to 1.2 m thick. Radioactivity is somewhat higher than the adjacent granite
G-7	North of Wadi Sadr and east of Wadi Assahlulah at mountain top	Small pegmatite about 5 cm thick. Radioactivity similar to that of the adjacent granite

MINERAL-SEPARATION STUDIES

The minerals in 11 bulk samples were separated and identified in the following manner: the samples were ground and screened, and the +20-mesh material was reground to pass through a 20-mesh screen. The +100-20-mesh fraction was saved, and the -100-mesh material was discarded. The retained fraction was then washed to remove dust particles that cling to the mineral grains and make identification difficult, and then was divided into heavy and light fractions by use of methylene iodide in a separatory funnel. The light fraction made up more than 95 percent of all samples. The heavy fraction was then spread out in a layer one grain thick and the magnetic fraction separated with a hand magnet. The magnetic fraction in all samples was very small and in all except one sample consisted principally of scrap iron from the grinders. In sample 297407, bag C, however, hematite intergrown with magnetite made up most of the magnetic fraction. The remainder of the heavy fraction was then divided into four parts of varied magnetic susceptibility by use of a Frantz Isodynamic Separator. Each of the six fractions for each sample were then examined under a binocular microscope and the minerals recorded. Any mineral not easily recognized was picked out and identified by X-ray diffraction pattern.

Some minerals are fine-grained, and many grains in the various fractions consist of several different minerals. In such cases, the composite grains were picked and X-rayed, and individual minerals were identified. If a particular mineral makes up less than 10 percent of a composite grain, the distinctive peaks on the X-ray diffractogram that identify the mineral may be hidden among peaks of more abundant mineral grains. Minerals occurring in small amounts may also fail to be identified because they are brittle and break up into fines, or they may be masked by iron oxides.

Granite, pegmatite, and sheared granite were the rock types examined. Minerals identified in 11 samples are listed in table 2. Quartz and pink microcline make up the greater part of the samples and white plagioclase is also abundant. Riebeckite, although noted in the field and in thin sections, is not abundant in these samples. Alteration of riebeckite to chlorite and(or) hematite was noted in most of the bags from composite sample 297407. Thorite is a moderately ubiquitous mineral and is the source of much of the radioactivity found in the microgranite. Thorite was found not only in highly radioactive shear zones and veins (samples G-1 and G-4, table 2), but also in some of the granite (samples G-2 and 297407, bags B and E, table 2). Rare-earth bearing minerals found in three samples are xenotime (YPO_4), doverite [$(Y,Ce)Ca(CO_3)_2F$], and senaite [$Pb(Ti,Fe,Mn)_{21}O_{38}$]. Xenotime and doverite contain yttrium-group rare earths, and senaite, although not listed in the above formula, generally contains 2 to 8 percent of yttrium-group, rare-earth oxides (Foord, Sharp and Adams, 1984). Xenotime appears to be the most common of the three rare-earth minerals.

Senaite is an extremely rare mineral, and Ghurayyah is only the fourth place in the world where it has been found. The mineral was first described from Minas Gerais, Brazil, in 1898 by Hussak and Prior. It has subsequently been reported in Macedonia, and in the Pikes Peak region, Colorado, U.S.A. (Foord, Sharpe, and Adams, 1984). At the latter locality, as at Ghurayyah, it is found in a small pegmatite associated with riebeckite-bearing granite, and it is also found associated with xenotime and thorite. Senaite is isostructural with davidite [$(La,Ce)\ (Y,U,Fe^{+2})\ (Ti,Fe^{+3})_{20}(O,OH)_{38}$], and hence, the X-ray diffraction patterns are almost identical. Both are placed in the crichtonite group of minerals. The chemistry, however, is widely different. Senaite contains major amounts of PbO, ZnO, and FeO compared to only trace amounts in davidite. Davidite, on the other hand, is rich in Ce_2O_3, and senaite contains only minor amounts of these two oxides.

Table 2.--Minerals identified in heavy-mineral separates from Ghurayyah

[*Identified by X-ray]

Sample no.	Mineralogy Large	Medium	Relative Amount Small	Rare
G-1	pink feldspar, quartz*	white feldspar sericite, hematite,* zircon,* thorite*	fluorite	calcite
G-2	pink feldspar, white plagioclase quartz	hematite, zircon*	sericite, titanite,* kaolinite,* thorite thorite	calcite
G-4	potassium feldspar,* feldspar,* quartz quartz	plagioclase,* hematite, thorite*	sericite limonite, zircon,* rutile* anatase,* doverite*	magnetite calcite
G-6	quartz,* pink feldspar chlorite*	muscovite,* thorite,* zircon*	senaite* xenotime*	magnetite, calcite
G-7	quartz pink feldspar	white feldspar, zircon,* zenotime,* thorite*	hematite, sericite, fluorite,	magnetite, calcite
297407 Bag A	quartz, pink feldspar	chlorite,* biotite,* zircon*	sericite,* plagioclase*	magnetite
297407 Bag B	plagioclase,* quartz	hematite,* zircon	sericite,* thorite*	calcite magnetite, fluorite
297407 Bag C	white feldspar, quartz	zircon*	hematite,* muscovite,* chlorite*	calcite magnetite, amphibole
297407 Bag D	quartz, pink feldspar	chlorite,* zircon*	hematite, columbite-tantalite*	magnetite
297407 Bag E	plagioclase,* quartz*	chlorite*	sericite,* hematite, zircon	magnetite, thorite
297407 Bag F	quartz,* pink feldspar, chlorite*	hematite,* zircon*	biotite,* plagioclase* thorite*	magnetite, calcite

Although high niobium values are reported for many samples (Drysdall, 1979), niobium minerals were not abundant in the samples we examined. We found columbite-tantalite in one sample of granite (297407, bag D) and pyrochlore in a small pegmatite (G-6). Zircon was found in all the samples, and small amounts of purple fluorite are widely scattered in the granite.

AUTORADIOGRAPHS

Autoradiographs can be used to determine the distribution and size of various radioactive minerals in rocks. Polished thin-sections are used with this technique. The sections, made without cover glasses, are placed on a film and the radiation emitted by radioactive minerals produces light spots on the developed film. The system we used is a radioluxograph, which uses a zinc-sulfide phosphor screen placed between the rock and the film (Dooley, 1958). The zinc sulfide screen acts as a photomultiplier and both enhances the brightness of the spots and shortens the time needed for an exposure. Five autoradiographs were made of the samples, four of which are shown in figure 2. Two types of samples are illustrated. *A* and *B* represent an abnormally radioactive shear zone and vein; they are 2 to 10 times more radioactive than the surrounding granite. The exposure time for these two samples was 21 hours. The principal radioactive mineral in both samples is thorite, which is most abundant in sample G-4. In places, thorite is sufficiently abundant that the images of adjacent or nearly adjacent grains commonly merge. Thorite occurs both as irregular patches, and as a distinct veinlet cutting across the rock. Thorite is not as abundant, occurs in smaller grains, and is more evenly distributed in sample G-1 compared to G-4. Autoradiographs *C* and *D* in figure 2 are of granite with nearly normal radioactivity. Exposure of these two samples for 21 hours was not long enough to differentiate the various radioactive mineral sources, so the autoradiographs were exposed for 66 hours. The brighter spots in both these samples probably represent thorite, which was also identified in the heavy-mineral separates. The amount of thorite in the two samples (297408, bags E and F) is much less and the grains are smaller than in samples G-1 and G-4. In addition to the brighter spots, there are many smaller and dimmer spots that probably represent a uranium- and(or) thorium-bearing mineral such as zircon, which is found in the heavy-mineral separates of both samples.

INDIVIDUAL-GRAIN STUDIES

Individual grains of several ore-forming minerals were investigated to determine their content of both major and minor elements. Many elements, especially those having similar atomic radii, substitute for one another in various minerals. Thus, the rare-earth elements commonly substitute for thorium in thorite, and hafnium substitutes for zirconium in zircon. To obtain data on the composition of individual minerals, selected grains from the mineral separates were polished and examined by one of three methods. The first is the scanning electron microscope (SEM) with an attached, energy-dispersive system (EDS) of X-ray fluorescence that can perform semiquantitative analyses. A second semiquantitative method is an EDS that attaches to the electron microprobe. We generally used either of these two semiquantitative instruments, depending on their availability, for preliminary examination of the minerals and also to select mineral grains for further work. The third method is quantitative and uses the electron microprobe.

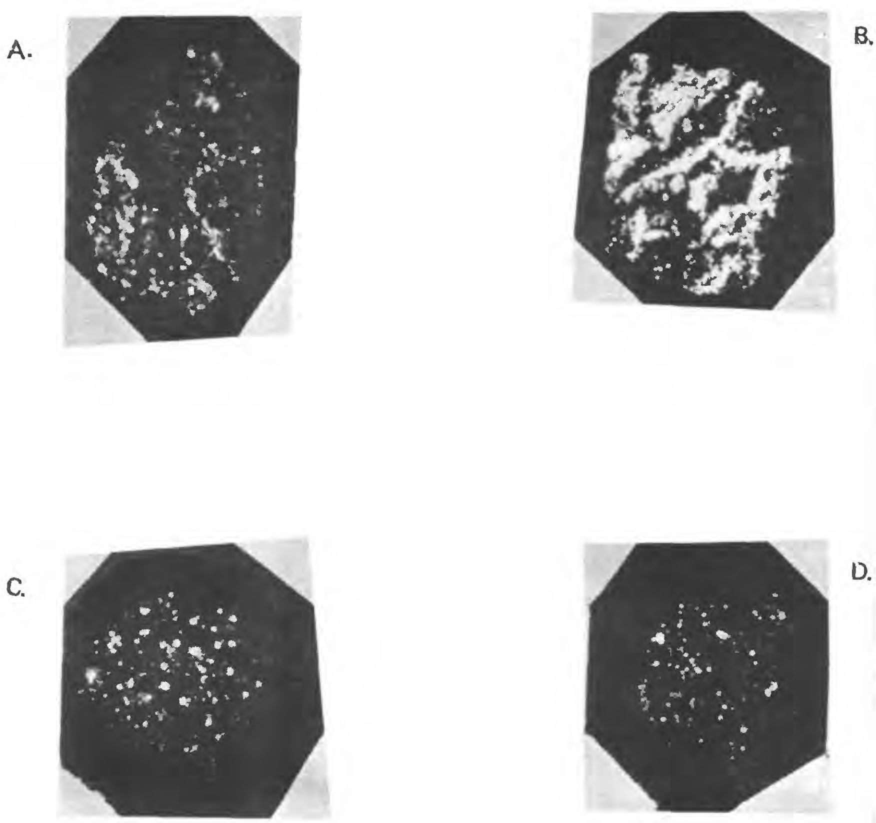

Figure 2.--*Autoradiographs of samples from Ghurayyah. Light spots indicate radioactive minerals. Exposure time for samples shown in* **A** *and* **B** *is 21 hours; that for samples shown in* **C** *and* **D** *is 66 hours.* **A**, *sample no. G-1 is from a shear zone;* **B**, *sample no. G-4 is from small vein;* **C**, *sample no. 297408, bag E is from granite; and* **D**, *sample no. 297408, bag F is from a granite.*

The most common accessory mineral of potential economic interest is zircon, which was found in heavy mineral separates of all samples. Zircon from 4 samples, using 2 to 6 grains per sample, was analyzed on the electron microprobe (table 3). Hafnium is the most important nonessential element in the zircon. The HfO_2 content of 17 analyses ranges from 1.24 to 4.96 percent. The zircons from 3 of the 4 samples have an average HfO_2 content of about 1.5 percent. The remaining sample, from a small pegmatite, averages more than 4 percent. The thorium and uranium content of zircon is highly erratic even in zircons from the same sample. The ThO_2 content varies from 0 to 0.46 percent and the UO_2 content from 0 to 0.25 percent. The ThO_2 and UO_2 contents are commonly much higher in other parts of the world. Rare earths, most of which are of the yttrium group, are also found in the zircons. The Y_2O_3 content in the four samples averages between 0.55 and 1.01 percent, but the most common cerium-group, rare-earth minerals are present in lesser amounts. The average Ce_2O_3 content in the four samples ranges from 0 to 0.13 percent, and the average La_2O_3 content ranges from 0 to 0.12 percent. Totals of all oxides analyzed in three samples are nearly 100 percent, indicating that determinations were made for all of the important elements, and that the analyses were reasonably accurate. Total oxides in sample G-7, however, is only about 80 percent, indicating the presence of elements not analyzed by the microprobe. In samples of metamict zircon from other areas, it was found that water was present, but it was not detected by the microprobe; it is believed that the zircon in sample G-7 is similarly hydrated.

Another important accessory mineral found in most of the heavy-mineral separates is thorite. It is most abundant in sample G-1 from the granite along a shear zone on the south side of Wadi Sadr. Eight grains from the sample were analyzed on the electron microprobe (table 4). The iron oxide content, which is calculated as Fe_2O_3, ranges from 7.96 to 26.92 percent, much higher than that of most thorites. About 0.5 percent UO_2 is found in these grains. This amount of UO_2 makes thorite one of the principal sources of uranium in the granite; nevertheless, the average thorium to uranium ratio in the thorite is 119 to 1. High thorium to uranium ratios are typical of rare earth and thorium deposits in alkalic igneous rocks. Amounts of Y_2O_3 in thorite grains is erratic and range from 0.4 to 5.10 percent. Small amounts of other rare-earth minerals may make up make up most of the unaccounted total.

Minor doverite [$(Y,Ce)Ca(CO_3)F$], the Y-analog of synchysite [$(Ce,La)CaCO_3F$], occurs in one sample. Partial analyses of 3 grains from the sample were made on the electron microprobe (table 5). We did not obtain analytical data for all the rare earths due to interference by the closely related elements. Semiquantitative data obtained from the SEM, however, indicate that in addition to the rare-earth oxides shown in table 5 there is approximately 3 percent Dy_2O_3 in each of the specimens. Other yttrium-group oxides are also probably present. CO_3 was not determined, because carbon cannot be measured on the electron microprobe using standard techniques.

Senaite, found in only one sample, was analyzed on the electron microprobe (table 6). Analyses of 5 separate grains of this mineral and their average are shown. The amounts of the various analyzed elements are similar to those found in senaite that contains zinc and Y-group elements from St. Peters Dome in the U.S.A., as presented by Foord, Sharp, and Adams (1984, p. 101). The total of all the elements analyzed in the Ghurayyah senaite is about 93 percent; most of the remainder is probably Y-group rare earths. A semiquantitative examination of the sample using the EDS system on the microprobe indicates that the mineral contains approximately 2 percent Yb_2O_3 and progressively lesser amounts of Er_2O_3 and Dy_2O_3. Smaller amounts of other Y-group rare earths are probably also present. On the other hand, neither of the principal Ce-group, rare-earth oxides (Ce_2O_3 and La_2O_3) were found in the senaite. Rare earth oxides in minerals throughout the deposit at Ghurayyah tend to belong to the Y-group.

Table 3.--Electron microprobe analyses of zircon from Ghurayyah.

[values in percent]

Sample no.	Specimen no.	ZrO_2	SiO_2	HfO_2	ThO_2	UO_2	Y_2O_3	Ce_2O_3	La_2O_3	CaO	Nb_2O_5	Total
G-2	a	63.19	31.37	1.31	.00	.00	.92	.00	.00	.00	.00	96.79
	b	62.11	31.14	1.40	.18	.13	1.19	.04	.00	.00	.00	96.19
	c	63.41	31.21	1.50	.03	.05	.93	.02	.00	.00	.00	97.17
	Average	62.90	31.24	1.40	.07	.06	1.01	.02	.00	.00	.00	96.72
G-7	a	50.54	26.77	3.59	.28	.00	.80	.00	.00	.16	.00	82.13
	b	48.35	25.92	4.96	.46	.13	1.15	.00	.00	.11	.00	81.07
	Average	49.45	26.35	4.18	.37	.07	.98	.00	.00	.14	.00	81.60
297407	a	63.71	32.38	1.67	.00	.00	.31	.11	.00	.04	.00	98.22
bag A	b	62.29	32.34	1.62	.29	.25	1.17	.00	.12	.00	.00	98.08
	c	61.29	32.04	1.34	.01	.23	1.05	.00	.00	.00	.00	95.96
	d	60.87	32.14	1.24	.03	.12	.94	.05	.00	.07	.00	95.46
	e	60.60	32.18	1.50	.18	.07	1.36	.00	.02	.00	.00	95.91
	f	61.76	31.97	1.47	.04	.04	.88	.01	.00	.00	.00	96.17
	Average	61.75	32.18	1.47	.09	.12	.95	.03	.02	.02	.00	96.63
297407	a	62.34	32.35	1.51	.17	.00	.81	.00	.12	.00	.00	97.30
bag D	b	60.65	32.17	1.32	.00	.00	1.01	.02	.00	.04	.00	95.21
	c	62.61	33.04	1.68	.00	.17	.00	.00	.00	.03	.00	97.53
	d	60.73	32.36	1.52	.30	.14	.91	.13	.08	.00	.00	96.17
	e	60.78	32.82	1.62	.00	.00	.54	.00	.00	.00	.00	95.76
	f	61.20	32.38	1.47	.00	.07	.02	.00	.00	.00	.00	95.14
	Average	61.39	32.52	1.52	.08	.06	.55	.03	.03	.01	.00	96.19

Table 4.--Electron-microprobe analysis of thorite grains from sample G-1, Ghurayyah.

[values in percent]

Individual grains	ThO_2	UO_2	Fe_2O_3	Y_2O_3	CaO	PbO	SiO_2	P_2O_5	Total
a	57.05	0.51	21.05	5.10	1.19	2.15	10.88	0.00	97.94
b	59.42	.56	26.92	.40	.53	.10	9.94	.18	98.05
c	64.51	.39	15.39	1.66	.78	.28	12.30	.09	95.40
d	67.10	.44	16.46	.82	.78	.93	10.61	.00	97.14
e	65.82	.54	18.97	.65	.81	1.51	9.89	.11	98.30
f	74.75	.78	.796	.71	.96	.34	10.39	.23	96.12
g	72.31	.69	10.01	.65	.55	.57	10.91	.29	95.78
h	61.88	.50	15.19	4.57	.64	1.92	8.17	.00	92.87
Average	65.36	.55	16.49	1.82	.78	.98	10.39	.11	96.48

Table 5.--Partial electron-microprobe of doverite from sample G-4, Ghurayyah.

[values in percent]

Specimen no.	Y_2O_3	Ce_2O_3	La_2O_3	Pr_2O_3	Nd_2O_3	CaO	MgO	MnO	Cl	F	P_2O_5
a	43.07	4.85	3.22	.17	2.19	18.13	.00	.01	.06	4.17	.00
b	49.51	2.73	2.66	.00	1.20	20.49	.00	.00	.07	3.55	.00
c	44.85	4.68	3.34	.22	1.30	19.96	.00	.01	.00	4.04	.00

Table 6.--Partial electron microprobe analyses of senaite from sample G-6, Ghurayyah.

[values in percent]

Element / Specimen no.	a	b	c	d	e	Average
FeO[1]	12.47	13.50	13.62	14.45	11.30	13.07
Na_2O	1.24	1.20	1.25	1.36	1.02	1.21
PbO	6.54	6.47	5.91	5.41	7.40	6.35
ZnO	7.32	6.57	6.70	6.77	7.33	6.94
MnO	2.18	1.73	2.01	1.89	2.84	2.13
Y_2O_3	.53	.56	.60	.52	.41	.52
Nb_2O_5	1.86	1.23	1.82	1.43	1.90	1.65
ThO_2	.10	.10	.00	.02	.00	.04
UO_2	.00	.00	.00	.00	.00	.00
TiO_2	61.00	60.37	59.25	60.57	63.05	60.85
SiO_2	.00	.04	.02	.06	.00	.02
F	.04	.07	.01	.00	.00	.02
O=F	.02	.03	.00	.00	.00	.01
Total	93.28	91.84	91.43	92.57	95.25	92.79

[1]Fe all calculated as FeO

GRAIN-SIZE STUDIES

The Ghurayyah microgranite is a porphyritic rock and contains phenocrysts of blocky microcline and stubby, bipyramidal quartz crystals. In parts of the stock, these minerals form nearly perfect crystals that are as long as 1 cm. In most of the stock, however, microcline is found in much smaller crystals. Mineral grains were measured in thin section with a micrometer ocular. The microcline grains range in size from about 0.60 by 0.60 mm to 0.3 by 3.5 mm. Quartz grains tend to be equant in form, and many fall in the range of 0.35 by 0.35 mm to 3.5 by 6.0 mm. No aegirine or riebeckite was found in the thin sections examined, but secondary sericite is present. This mineral tends to form clots of tiny grains. The size of the grains ranges from about 0.001 by 0.01 to 0.10 by 0.20 mm. Thorite is one of the most common accessory minerals in the the microgranite. It occurs as tiny grains along fractures and varies in size from about 0.008 by 0.008 mm to 0.11 by 0.13 mm. Although grains of doverite, davidite, and zircon were not noted in our thin sections, a comparison of these minerals in the heavy-mineral separates with thorite indicates that these minerals are approximately the same size.

DATA STORAGE

Petrographic descriptions, sample locations, thin sections, and results of chemical analyses are stored in Data-File USGS-DF-04-4 (Staatz and Brownfield, 1984) in the Jeddah office of the U. S. Geological Survey Saudi Arabian Mission.

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