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The rare earth elements geochemistry of Lingshan tungsten-tin-bearing granites and their applications to petrogenesis of the granites

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Abstract: The Lingshan granite complex mainly consists of 4 rock types: (1) coarse porphyritic hornblende-biotite granite (140 Ma); (2) medium-coarse grained biotite granite (127 Ma); (3) medium-fine grained albitized zinnwaldite-bearing granite (100–126 Ma); (4) granite porphyry. In this paper, the petrological characteristics, petrochemical composition and rare earth elements (REE) contents of the various rock types and the REE contents of 5 rock-forming minerals are given. With the aid of petrochemical compositions and REE data the authors have discussed the genesis of the granites. It is postulated that a melt of the granite complex had been derived from Proterozoic phyllite-tuffite by partial melting and that crystal differentiation might have played an important role in the formation of Granite 2 and Granite 3.

REGIONAL GEOLOGY

The Lingshan granites are located in Jiangxi province, Southern China. Geotectonically it's location falls on the southwestern rim of the transitional zone—Qiantang Sag between the Yantze meta-platform and the Caledonian fold zone of Southern China. A deep fracture zone, the northeast Jiangxi fracture, passes through the northern district close to the Lingshan granites.

The regional basement strata are epi-metamorphic volcano-sedimentary rock series, belonging to the Late Proterozoic group. These are composed of sedimentary argillo-arenaceous clastic rocks and volcanic clastic rocks intercalated with lava. Under regional metamorphism, they gave rise to a set of epi-metamorphic rock series with a thickness of about 18,000 m, in which tuffaceous phyllite-tuffite have a wide distribution.

The Palaeozoic group consists mainly of a set of volcanic formation and Para-flysch formation, 10,000 m in thickness. The upper Palaeozoic and Mesozoic strata are weakly developed in the area. In these strata only a few volcanic rocks and red sandstone-shale formations can be seen in the southern part of the area. The neighbouring country rocks of the Lingshan granites are Sinian sillicified phyllite, sericitized phyllite and silicified slate, Cambrian calcareous shale and impure limestone, as well as a few Triassic sandstones and shales (Fig. 1).

The Mesozoic tectonic movements were mainly due to faulting. Along the faults there occur a large number of volcanic rocks and intrusions. These range in chemical composition from ultrabasic, acidic to alkaline. The acidic and intermediate rocks in particular have been widely distributed over the area. In these rocks one of the most

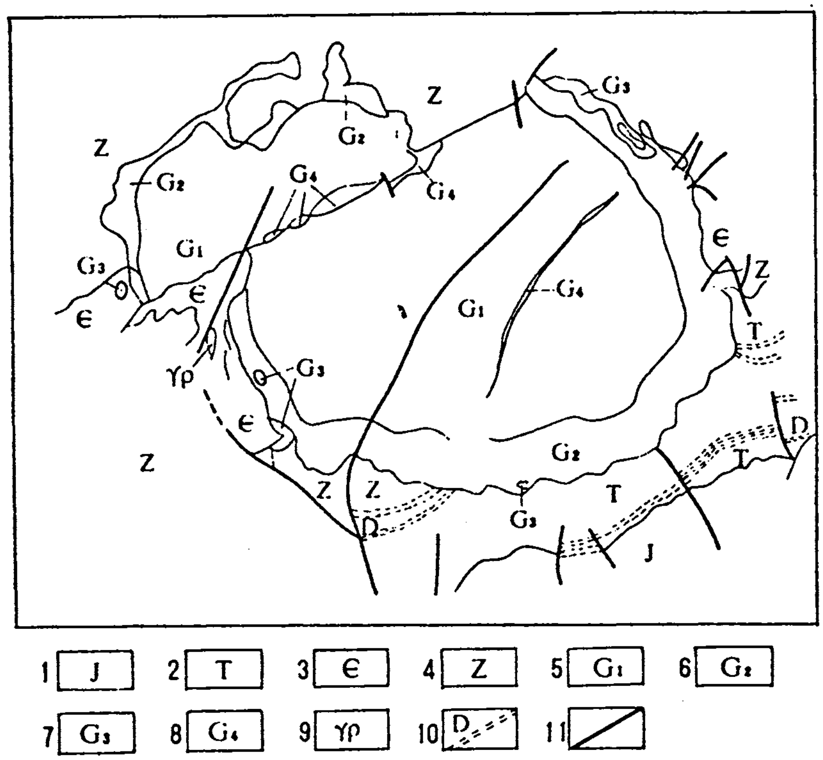

Fig. 1. Generalized geological map of Lingshan granite complex
1—Jurassic; 2—Triassic; 3—Cambrian; 4—Sinian; 5—coarse porphyritic hornblende-biotite granite; 6—medium-coarse grained biotite granite; 7—medium—fine grained albitized granite; 8—granite porphyry; 9—pegmatite; 10—fracture zone; 11—fault.

interesting intrusions is the Dexin granodiorite porphyry, which is about 20 km from the Lingshan granites. It's chemical and mineralogical composition is similar to that of the enclaves in the Lingshan granites. This is the site of the famous ore deposit in China—the Dexin porphyry copper.

GEOLOGY OF THE GRANITES

The Lingshan intrusions, with an outcrop of about 200 km^2, occur as a ring granite complex which consists of stocks, bosses and apophyses. The last two always appear on the periphery of the stocks. The rock bodies were intruded into the Palaeozoic phyllite and limestone formation and have a sharp contact. The isotopic ages of mica of the granites determined by K-Ar method are 90–140 Ma.

The granite complex consists mainly of 4 rock types (Fig. 1) of various ages:

1. Granite 1—coarse porphyritic hornblende-biotite granite (140 Ma)
2. Granite 2—medium-coarse grained biotite granite (127 Ma)

3. Granite 3—medium-fine grained albitized zinnwaldite-bearing granite (100–126 Ma)

4. Granite 4—granite porphyry (90 Ma.).

The tungsten-tin mineralization in the area always appears on the exocontact zone of the granite complex. The tungsten-tin minerals are mainly cassiterite and wolframite and occur mainly in greisens and quartz veins. Gangue minerals in veins are quartz, zinnwaldite, topaz, flourite and hematite, etc. A few tungsten-tin minerals are also found in the altered granites.

The tungsten-tin mineralization is genetically related to the albitized zinnwaldite granite, but these granites are also genetically related to Granites 1 and 2.

Granite 1 with a Sr^{87}/Sr^{86} initial ratio of 0.7054 has a coarse-grained and porphyritic texture. It is light-grey in colour and the phenocrysts are mainly orthoclase, plagioclase (An 23–32) and quartz. The ground mass consists chiefly of plagioclase, microcline, quartz, biotite and hornblende. Contents of different minerals in this rock are: orthoclase 20–30%; microcline 10–20%; oligoclase 25–35%; quartz 20–25%; biotite 4–7% and hornblende 2–4%. Accessory minerals are mainly magnetite, ilmenite, sphene, allanite, apatite, zircon, thorite, etc.

Granite 2 with a pink to brown colour, possesses an even grained and massive structure. The rock contains microcline 40–60%; oligoclase (An 20–30) 10–30%; quartz 20–30% and biotite 4–6%. This granite is characterized by the absence of hornblende. The accessory minerals are characterized by the absence of sphene and allanite, but are rich in monazite, magnetite, zircon, fluorite, anatase, etc.

In the two above-mentioned granites there are a lot of dark grey enclaves. They are characterized by spherical or oval shapes with diameters ranging from 5 to 100 cm. The mineralogical compositions of these enclaves are similar to that of the Granite 1, but they contain more melanocratic minerals. Based on the mineralogical and petrological characteristics, it seems that the enclaves are residues of older crustal rocks which suffered partial melting.

Granite 3 is an albitized zinnwaldite granite. It has a fine-medium grained texture, light-grey colour and appears near the contact zone, especially on the exocontact zone. The area of these granites is about 0.1 km^2. In these rock bodies, albitization is developed in varying degrees. The rock-forming minerals are microcline 41–60%; albite (Ab 1–3) 5–10%; oligoclase 10–20%; zinnwaldite 5–7% and quartz 25–35%. Accessory minerals are magnetite, zircon, nioborutile, cassiterite, wolframite, columbite, topaz, fluorite etc.

Granite 4 is a granite porphyry which occurs as dykes.

PETROCHEMICAL COMPOSITION AND REE CONTENTS OF THE GRANITES

The petrochemical compositions of the four types of granites, Proterozoic phyllite-tuffite and the Dexin granodiorite porphyry are listed in Table 1. Samples were

TABLE 1

CHEMICAL COMPOSITION (%) OF SEVEN ROCK TYPES

Rock name	Phyllite-tuffite		Granodiorite porphyry		Granite enclave			Hornblende—biotite granite							Biotite granite			Albitized granite						Granite porphyry
Rock symbol.	P		G_D		G_E			G_1							G_2			G_3						G_4
Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Chemical composition (%)																								
SiO_2	64.16	65.40	63.40	63.22	66.90	66.33	62.46	69.52	69.05	67.75	59.89	71.87	69.22	68.42	73.02	74.98	73.33	75.98	72.84	75.66	73.88	73.33	73.51	70.77
TiO_2	0.72	0.69	0.46	0.45	0.80	0.84	0.93	0.54	0.55	0.61	0.48	0.40	0.55	0.55	0.22	0.44	0.16	0.04	0.07	0.21	0.05	0.06	0.04	0.46
Al_2O	16.28	14.46	15.78	15.07	14.03	14.38	14.94	13.85	13.96	13.83	14.01	13.43	13.87	13.78	12.96	10.56	12.64	12.85	14.38	12.41	14.30	13.19	13.32	13.47
Fe_3O_3	1.95	1.61	2.32	2.55	1.20	1.22	2.83	1.13	1.17	1.11	2.89	3.27	1.66	1.23	0.76	1.08	0.65	0.29	0.33	0.55	0.16	0.90	1.30	1.40
FeO	4.30	4.80	2.34	2.89	3.56	3.92	3.57	2.50	2.35	3.35	0.37	0.24	2.81	2.99	1.43	2.22	1.49	0.74	1.09	1.38	0.78	0.36	0.93	1.89
CaO	1.04	1.51	3.71	3.83	1.91	2.44	2.55	1.80	2.12	1.90	0.23	—	1.75	1.59	0.73	1.11	0.48	0.16	0.16	0.29	0.10	0.68	0.48	1.11
MgO	2.10	2.05	2.32	2.55	1.18	1.23	1.20	0.36	0.67	0.81	0.96	1.01	0.49	0.74	0.15	0.01	0.48	0.05	0.10	0.29	0.07	0.16	0.48	0.55
MnO	0.14	0.14	0.03	0.05	0.09	0.09	0.11	0.05	0.06	0.08	0.04	0.08	0.06	0.08	0.03	0.04	0.04	0.01	0.02	0.02	0.01	0.04	0.08	0.05
K_2O	3.32	2.64	3.13	3.38	4.20	3.95	6.32	4.98	5.08	5.35	5.72	5.44	5.05	5.00	5.15	4.73	5.13	3.85	5.30	3.50	4.85	3.70	3.60	5.32
Na_2O	2.20	2.45	3.65	3.78	4.35	4.25	3.60	3.95	3.73	3.70	3.68	3.03	3.70	3.60	4.45	3.50	3.84	4.83	4.83	4.40	4.80	5.18	5.00	3.33
P_2O_5	0.17	0.20	0.04	0.25	0.22	0.21	0.33	0.16	0.14	0.18	0.10	0.10	0.15	0.18	0.04	0.05	0.06	0.04	0.02	0.05	0.05	0.04	—	0.13
H_2O^+	3.00	3.02	1.98	1.12	0.82	—	0.72	0.24	—	0.55	0.67	1.63	0.69	0.76	0.22	0.28	0.57	0.12	0.46	0.44	0.44	0.39	0.39	1.08
H_2O^-	—	—	—	—	0.24	—	0.12	0.22	—	0.14	0.45	0.25	—		0.20	0.12	0.21	0.24	0.24	0.14	0.08	0.61	0.38	—
CO_2	—	—	—	0.21	0.07	—	0.27	0.05	—	0.23	—	—	—	—	0.06	0.14	—	0.04	0.13	0.01	0.07	—	—	—
F	—	—	0.04	—	0.18	0.35	0.13	0.20	0.25	0.18	0.28	—	—	—	0.12	0.27	0.28	0.08	0.14	0.12	0.07	0.24	0.36	0.06
Total	99.38	99.03	99.31	99.35	99.77	98.88	100.08	99.56	99.54	99.77	99.25	100.85	100.00	98.92	99.55	99.51	99.26	99.38	100.11	99.55	99.73	98.86	99.76	99.63

TABLE 2

AVERAGE CHEMICAL COMPOSITION (%) OF THE FOUR TYPES OF GRANITES

	Rock symbol	G_E	G_1	G_2	G_3
	No. of samples	3	8	3	6
Chemical composition (%)	SiO_2	65.19	69.44	73.77	74.20
	TiO_2	0.86	0.52	0.26	0.08
	Al_2O_3	14.45	13.82	12.05	13.40
	Fe_2O_3	1.75	1.78	0.83	0.59
	FeO	3.68	2.09	1.71	0.88
	CaO	2.29	1.56	0.77	0.31
	MgO	1.20	0.72	0.28	0.19
	MnO	0.09	0.07	0.04	0.03
	K_2O	4.75	5.23	5.00	4.13
	Na_2O	4.67	3.63	3.86	4.84
	P_2O_5	0.25	0.15	0.08	0.04
	F	0.22	0.23	0.22	0.18
	CO_2	0.17	0.14	0.10	0.08
	H_2O^+	0.77	0.76	0.36	0.32

analysed by routine chemical analysis. The average chemical compositions of the 4 types of granites are shown in Table 2 while Figure 2 describes the systematic variations of SiO_2, K_2O, Na_2O, TiO_2, CaO, etc. It may be seen that from the enclaves through the early Granites 1, 2 to the late Granite 3, the contents of SiO_2 progressively increase and Al, Fe, Ca. and Mg gradually decrease. From Table 1 it may also be seen that the Dexin granodiorite porphyry approaches the enclave in composition.

The contents of rare earth elements (REE) of the 7 rock types in Table 1 are listed in Table 3. In this table, samples Nos. 5, 8, 12 and 16 were analysed by neutron activation and others by the inductively-coupled plasma method. Samples 5 and 6, 8 and 9, 12 and 13, 16 and 17 were analysed by both methods and hence a comparison could be made between these two methods. From Table 3 it can be seen that values of the same samples which were performed by different methods are very close to each other.

The chondrite REE normalized diagrams are shown in Figures 3 and 4. Table 4 shows rare earth element contents of 5 minerals in Granite 1, i.e. sphene, hornblende, biotite, oligoclase and alkali feldspar. The mineral/rock distribution coefficients for REE are shown in Figure 5. From this figure it may be seen that for sphene and hornblende, their REE ratios in mineral/rock are more than 1 while for feldspar and biotite, their REE ratios in mineral/rock are less than 1. This may be due to crystal differentiation in the granite. Table 5 shows a characteristic ratio of different rocks of Lingshan complex.

GENETIC DISCUSSION OF LINGSHAN GRANITES

From Figures 3 and 4, it may be seen that the chondrite normalized patterns of

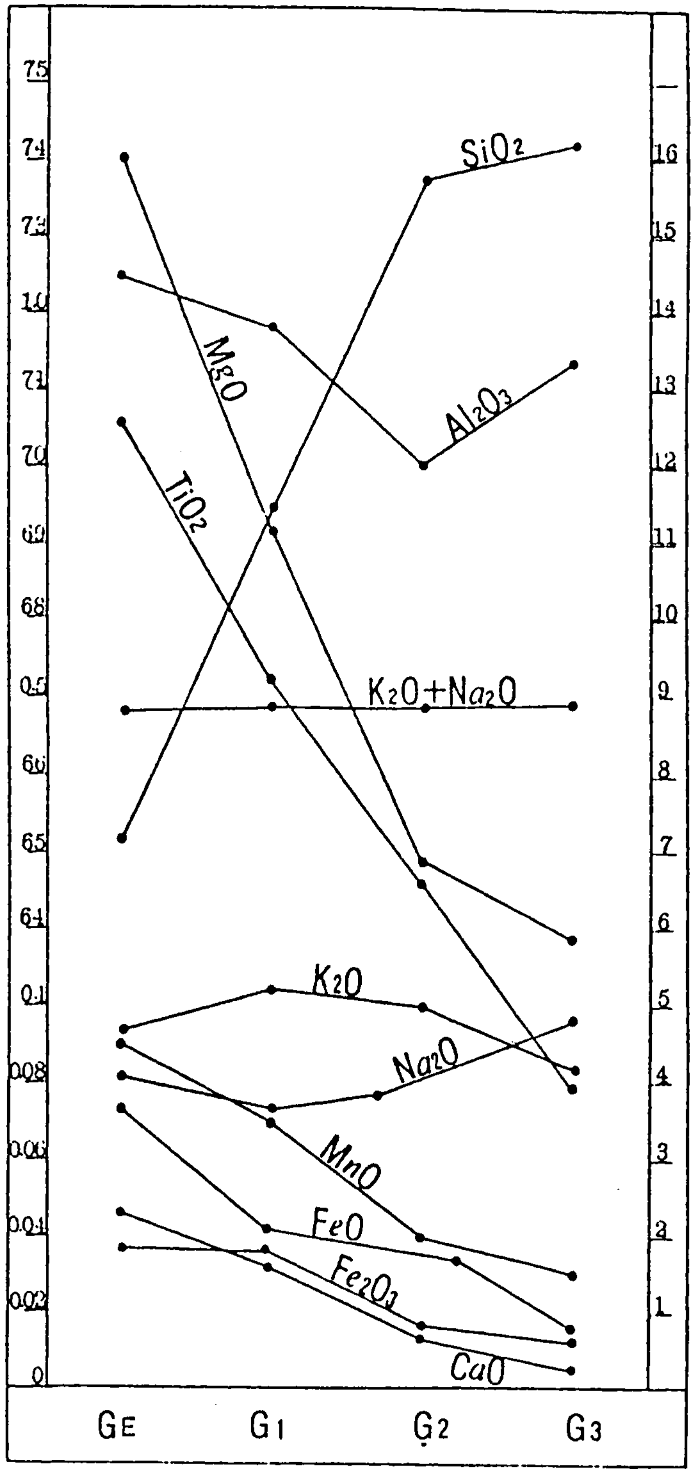

Fig. 2. Diagram showing systematic variation of petrochemical composition

TABLE 3

RARE EARTH ELEMENT CONTENTS OF THE SEVEN ROCK TYPES

Rock name		Phyllite-tuffite		Granodiorite porphyry		Granite enclave			Hornblende-biotite granite				Biotite granite		Albitized granite		Granite porphyry	
Rock symbol		P		G_D		G_E			G_1				G_2		G_3		G_4	
Sample No.		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
REE (PPM)	La	35.43	35.16	32.60	13.64	65.88	64.07	69.93	80.85	79.16	68.96	68.98	129.40	112.87	20.81	66.15	67.80	75.16
	Ce	75.78	76.90	62.07	21.98	121.00	128.52	149.36	145.00	141.78	139.58	147.16	225.00	214.43	42.00	43.54	127.00	136.32
	Py	8.15	8.51	6.27	3.48	—	15.06	16.25	—	15.05	14.12	14.64	—	20.39	4.15	2.10	—	14.48
	Nd	31.12	32.48	19.44	10.29	64.70	54.25	58.16	70.00	50.80	49.45	49.01	89.80	62.40	11.38	7.62	108.00	50.83
	Sm	6.97	7.66	4.16	1.81	9.07	10.45	10.10	9.56	10.18	9.05	10.05	11.98	11.63	2.29	0.57	7.51	8.53
	Eu	1.44	1.54	1.08	0.54	1.16	1.08	1.21	1.35	1.30	1.34	1.26	0.77	0.50	0.07	—	1.51	1.27
	Gd	5.86	7.01	3.42	1.21	9.80	8.91	8.61	13.40	9.12	7.89	8.53	15.90	9.88	1.72	0.78	15.10	7.36
	Dy	5.28	6.41	2.58	1.05	—	8.60	8.31	—	9.34	7.66	8.39	—	10.29	2.38	1.73	—	7.24
	Ey	3.14	3.91	—	0.68	—	5.64	4.69	—	—	4.62	—	—	—	1.80	2.42	—	4.29
	Yb	2.88	3.57	1.34	0.61	3.22	5.00	4.98	7.48	6.06	5.06	5.41	6.92	6.85	2.79	8.40	5.69	4.88
	Lu	0.38	0.56	0.41	0.08		1.07	0.72	0.95	0.94	0.51	1.01	0.85	0.66	0.72	1.88	—	0.81
	Y	26.51	32.96	13.07	5.04	—	46.53	46.23	—	52.16	43.25	45.40	—	63.67	7.38	4.42	—	42.58

TABLE 4

RARE EARTH ELEMENT CONTENTS OF FIVE MINERALS IN GRANITE I

REE	REE (P.P.M.)											
Mineral	La	Ce	Py	Nd	Sm	Eu	Gx	Dy	Ey	Yb	Cu	Y
Sphene	968.15	4263.84	705.50	2971.80	735.64	29.25	699.50	740.92	482.73	520.81	81.81	4056.68
Hornblende	923.21	1631.58	157.36	472.25	78.10	2.21	63.55	56.61	41.10	31.32	5.65	293.87
Biotite	14.38	30.14	4.69	13.96	2.94	0.24	2.85	2.41	1.97	1.35	0.55	13.12
Plagioclase	20.16	25.63	1.97	6.21	0.85	1.84	0.77	0.69	0.34	0.52	0.24	5.00
K-feldspar	11.69	11.04	1.09	2.65	0.46	2.07	0.42	0.34	0.32	0.23	0.27	1.93

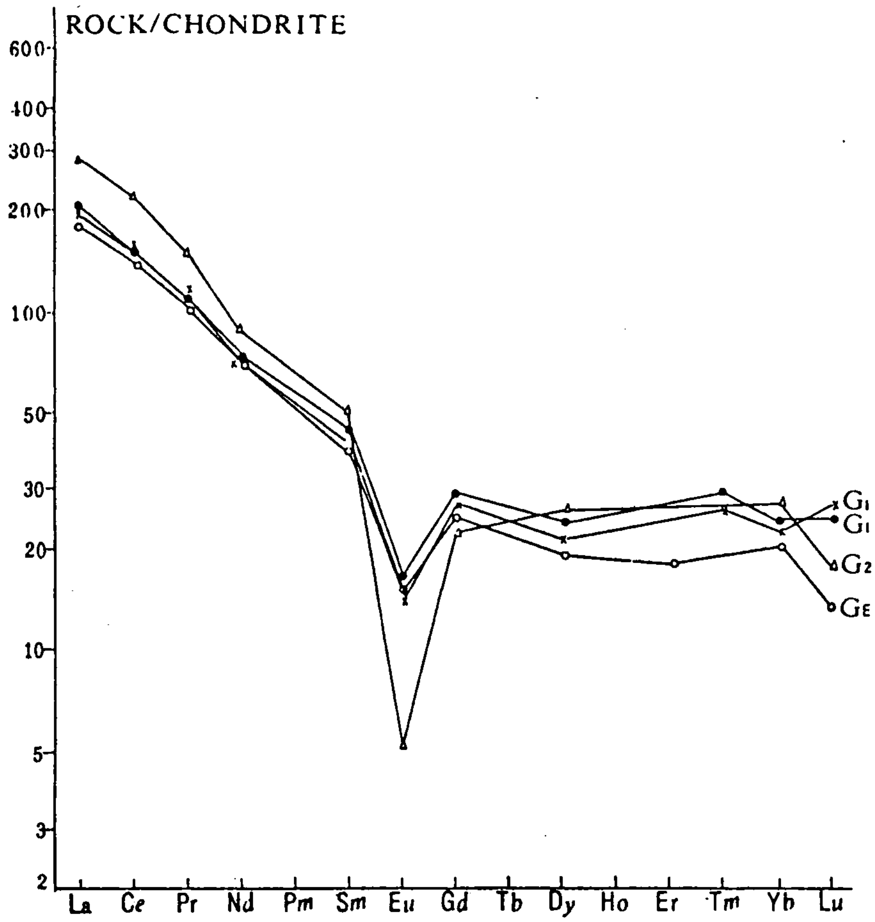

Fig. 3. Chondrite normalized REE diagrams of G_E. G1. G2.

TABLE 5

CHARACTERISTIC RATIOS OF REE FOR GRANITIC ROCKS OF THE LINGSHAN COMPLEX

Symbol Ratio	G_E	G_1	G_2	G_3
K/Rb	170.6	166.6	155.3	70.8
Rb/Sr	3.0	3.8	4.0	34.6
Li/Mg	0.01	0.02	0.04	0.18
Sr/Ba	0.21	0.14	0.10	0.16
Zr/Hf	17.8	10.6	9.4	14.2
La/Yb	14.0	13.9	18.4	7.46

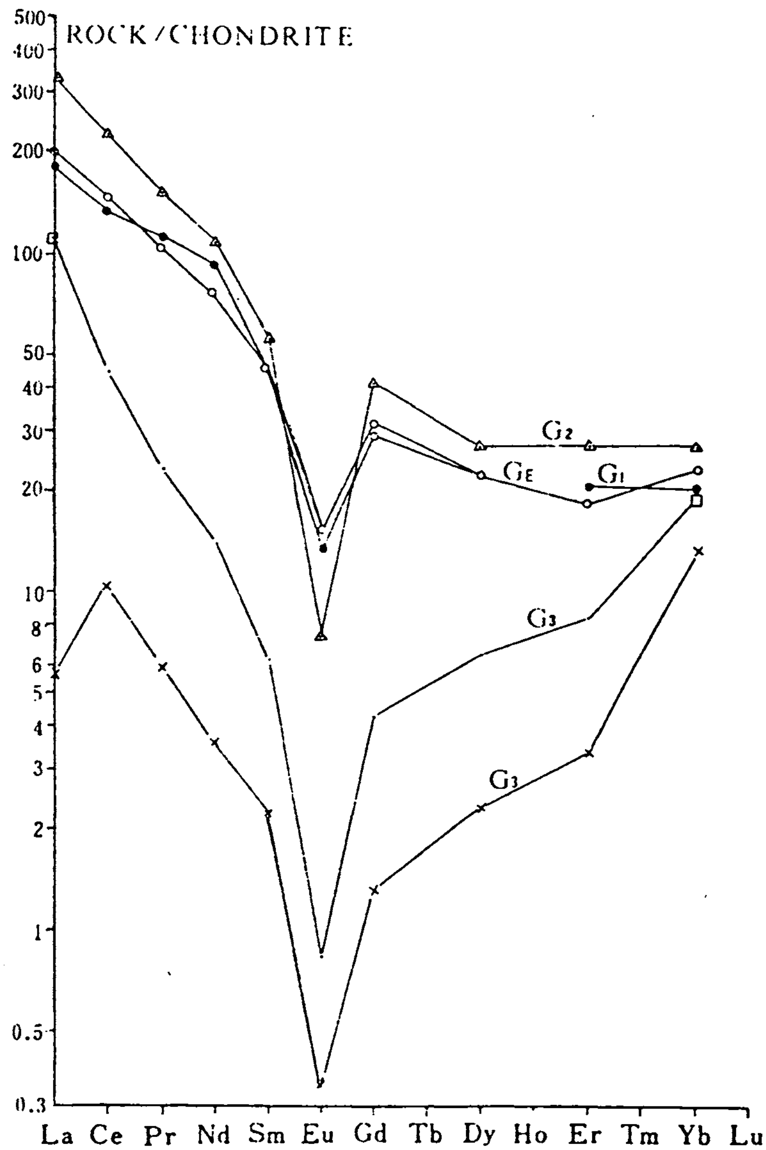

Fig. 4. Chondrite normalized REE diagrams of G_E. G1. G2. G3.

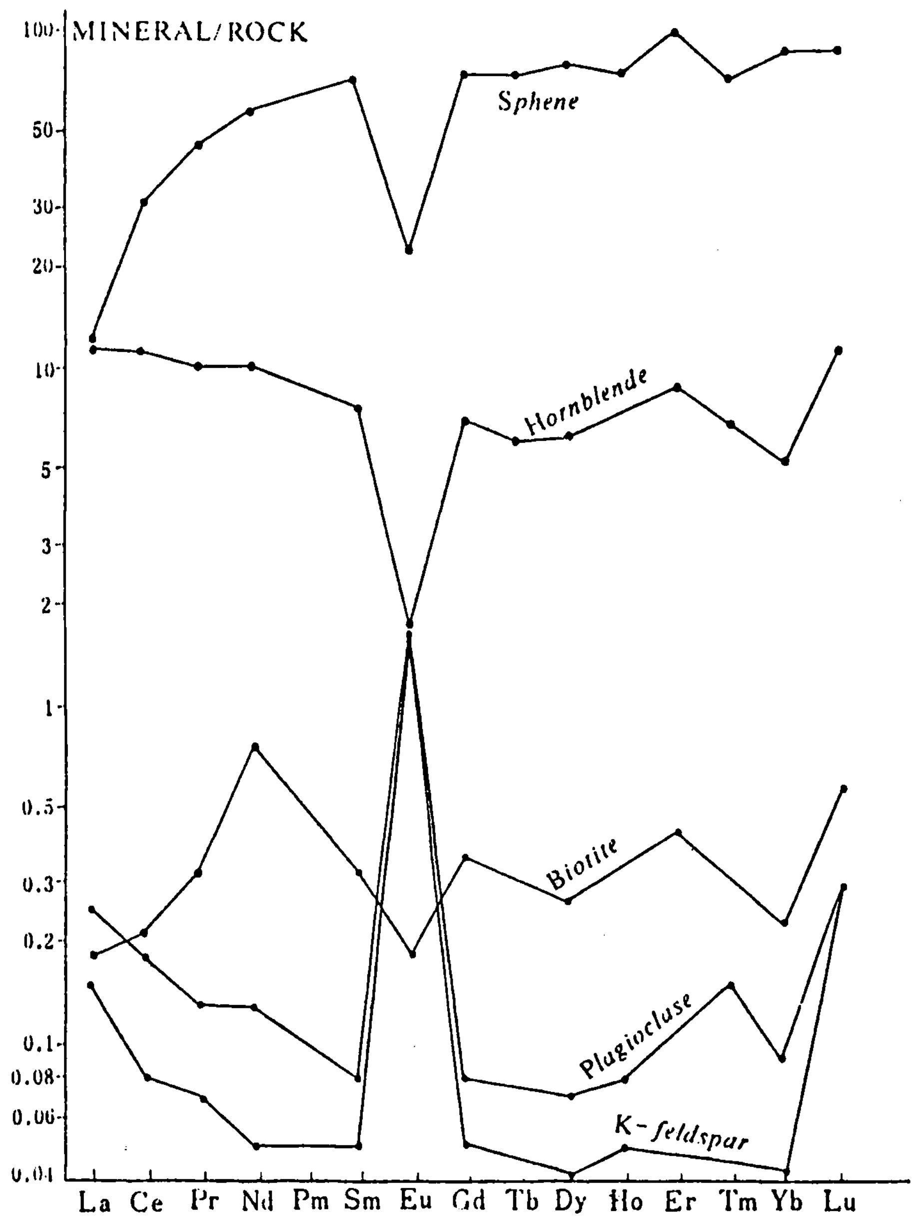

Fig. 5. Mineral/rock vs. REE pattern of the minerals.

the rocks are similar. They have an obvious negative Eu anomaly but REE abundances gradually decrease from one type to the other while the negative Eu anomaly is on the increase. From the systematic variation of Al, K, Si, Fe (Fig. 2), and the ratio of Nb/Ta, Zr/Hf, K/Rb, (Table 5), it may be suggested that there exists a certain relationship of consanguineous evolution among these granites. From Figure 5 it is also postulated that there exists a relationship of crystallization differentiation between Granite 1 and Granite 2. This may be proven by considering crystallizing sequences of different minerals in the granites, that is in order of sphene—hornblende—biotite—plagioclase—k-feldspar—quartz. Therefore, crystal differentiation might have also played an important role in the formation of Granite 2 and Granite 3.

As to the formation of the whole Lingshan granite complex, there are only four possibilities as follows:

1. Through a migmatization or granitization of country rock—Sinian phyllite and slate;
2. By way of a partial melting of the Sinian phyllite and slate;
3. The result of the crystal differentiation of granodiorite in depth;
4. By way of a partial melting of Proterozoic phyllite-tuffite.

Based on geological, petrological and geochemical evidences, it seems likely that the fourth possibility is the most reasonable. This is also confirmed by the rare earth data. With the aid of J.G. Schilling and J.W. Winchester's equation: $C^1/C^0 = 1/D + F(1 - D)$ we calculated the distribution of REE in these granites. Here we considered contents of REE of the Proterozoic phyllite-tuffite as C^0 and considered a bulk distribution coefficient of the enclave in Granite 1 as D (distribution coefficient of minerals from Arth and Hanson (1975). Then we take F = 10, 20, 30, 35, 40, 50 ... 100% respectively and work out C^1. It is clear that the obtained values for C^1 are very approximate to the rare earth content of Granite 1. Considering a low ratio Sr^{87}/Sr^{86} for Granite 1, the most reasonable parent of Granite 1 would appear to be the Proterozoic phyllite-tuffite.

Therefore it may be concluded that the melts of the Lingshan granites, especially Granite 1, had been derived from the Proterozoic phyllite-tuffite by 30–40% partial melting and a corresponding residue would be as such a rock whose mineralogical and petrochemical composition are similar to that of the enclave in Granite 1. This conclusion is consistent with results of geological research in this area.

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